NANOSTRUCTURED METAL OXIDES SUPPORTED ON STAINLESS STEEL WIRE MESHES: VERSATILE MONOLITHIC CATALYSTS FOR ENVIRONMENTAL AND ENERGY APPLICATIONS

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Thi Tan Vu
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At the time when I just finished the thesis, I was sitting in front of the computer and looking back the whole three and a half years in INCAR, I can not find exact words to express how much I appreciate and cherish this wonderful opportunity to do my PhD thesis in INCAR.

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List of Abbreviations

AAS: Atomic Absorption Spectroscopy
BET: Brunauer-Emmett-Teller
CB: Conduction Band
CVD: Chemical Vapour Deposition
DME: Dimethyl Ether
DOC: Degree of Crystallinity
DRS: Diffuse Reflectance Spectroscopy
EAI: Equilibrium Adsorption Impregnation
EDX/EDS: Energy-Dispersive X-ray Spectroscopy
EELS: Electron Energy Loss Spectroscopy
FTO: Fluorine-doped Tin Oxide
GHHSV: Gas Hourly Space Velocity
HMTA: Hexamethylenetetramine
ITO: Indium Tin Oxide
LPD: Liquid Phase Deposition
MD: Methanol Decomposition
MSR: Methanol Steam Reforming
MB: Methylene Blue
MF: Methyl formate
PEI: Polyethyleneimine
**Nanostructured metal oxides supported on SSWM**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>PEG</td>
<td>Polyethylene Glycol</td>
</tr>
<tr>
<td>PD</td>
<td>Photodeposition</td>
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<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SSWM</td>
<td>Stainless Steel Wire Mesh</td>
</tr>
<tr>
<td>STAH</td>
<td>Sacrificial Template Accelerated Hydrolysis</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature-Programmed Reduction</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible Spectroscopy</td>
</tr>
<tr>
<td>WHSV</td>
<td>Weight Hourly Space Velocity</td>
</tr>
<tr>
<td>XPs</td>
<td>Polysiloxane</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Resumen

Los catalizadores monolíticos son de gran interés para su aplicación en procesos industriales, aplicaciones energéticas y en sistemas de protección ambiental. En general, la utilización de catalizadores soportados conlleva importantes ventajas, tales como bajas caídas de presión, buena estabilidad mecánica, facilidad de manipulación y, en función del material, buenas conductividades térmica y eléctrica. En esta Tesis Doctoral se presentan nuevas estrategias de síntesis para la fabricación de catalizadores constituidos por óxidos metálicos de elevada superficie soportados en mallas flexibles de acero inoxidable (SSWM, acrónimo del término en inglés stainless steel wire mesh).

En la primera parte de esta Tesis se examinan diversos métodos de síntesis para la producción de nanovarillas de ZnO no polar y de nanohojas de ZnO polar depositadas en mallas metálicas, estudiando su aplicación como fotocatalizadores para la fotodegradación de azul de metileno en soluciones acuosas bajo irradiación ultravioleta. La actividad cataítica de algunos de los catalizadores desarrollados es, en el inicio de la reacción, superior a la que se obtiene para el fotocatalizador de referencia (P25 TiO₂), aunque disminuye rápidamente debido a la fotocorrosión. Para proteger a los catalizadores de este efecto se ha desarrollado con éxito una técnica novedosa que consiste en el recubrimiento de la superficie del fotocatalizador con una fina capa de polisiloxano.

En la segunda parte se ha investigado el empleo de nanohojas de ZnO, de elevada superficie y altamente polares, soportadas en SSWM, como molde de sacrificio para la preparación de óxidos metálicos nanoestructurados. Mediante un proceso de hidrólisis acelerada con molde de sacrificio (en inglés sacrificial template accelerated hydrolysis o STAH) se obtuvo una amplia variedad de óxidos metálicos de elevada superficie (i.e., CuO, α-Fe₂O₃, TiO₂, CeO₂, Cd₃ZnₓO (x=0.01-0.20) y Ni₀.7Zn₀.3O) soportados sobre las mallas. La
estructura de estos óxidos metálicos es una réplica fidedigna de la estructura del ZnO de partida. La clave de esta estrategia de síntesis es el uso como molde de nanoestructuras de ZnO que presentan una superficie muy elevada, y constituidas principalmente por caras polares. Estas caras son químicamente muy activas y son responsables de la generación de estructuras de óxidos metálicos de elevada superficie (hasta 275 m² g⁻¹).

Los óxidos metálicos obtenidos han sido investigados en diferentes aplicaciones: a) proceso tipo Fenton heterogéneo para la degradación de azul de metileno en agua (α-Fe₂O₃), b) degradación fotocatalítica de azul de metileno en agua (CdₓZn₁₋ₓO y TiO₂) y c) producción de hidrógeno a partir de metanol (Ni₀.₇Zn₀.₃O). El catalizador α-Fe₂O₃ soportado en SSWM presenta una actividad catalítica elevada y una buena estabilidad para la degradación de azul de metileno mediante un proceso de tipo Fenton en presencia de peróxido de hidrógeno. En cuanto a la fotodegradación de este mismo colorante bajo irradiación ultravioleta con catalizadores de óxido de cinc, la incorporación de Cd a la estructura de ZnO soportado sobre las mallas permite evitar la fotocorrosión de los catalizadores, manteniendo una buena actividad catalítica. Bajo radiación visible, esta solución sólida de CdₓZn₁₋ₓO muestra una actividad ligeramente mayor que la del ZnO de partida. La fotodegradación de azul de metileno bajo radiación UV con los catalizadores de TiO₂ soportados es óptima cuando los catalizadores han sido calcinados en el intervalo 450-600°C. Estos catalizadores presentan actividad catalítica intrínseca muy superior a la mostrada por las partículas de P25 TiO₂. Finalmente, el catalizador Ni₀.₇Zn₀.₃O soportado sobre mallas ha demostrado ser especialmente activo en la producción de hidrógeno mediante la reacción de descomposición de metanol, en la que destaca como uno de los más activos de la literatura.

Con las técnicas desarrolladas en esta tesis es posible fabricar una amplia variedad de óxidos metálicos de elevada superficie soportados en un material monolítico y flexible, como es la malla de acero inoxidable, que puede ser utilizado fácilmente en reactores catalíticos estructurados con elevadas prestaciones, para aplicaciones energéticas y medioambientales.
Abstract

Monolithic catalysts have acquired a great importance in industrial processes, energy applications and environmental protection systems. The systems based on these supported catalysts offer several important advantages such as a low pressure drop, good mechanical stability, easy manipulability and good electrical and thermal conductivity, depending on the monolith material. In this PhD Thesis, novel synthesis strategies are presented for the fabrication of catalysts made up of high-surface area metal oxides supported on flexible stainless steel wire mesh (SSWM).

First, several synthesis methodologies for producing non-polar ZnO nanorods and polar ZnO nanosheets deposited onto SSWM substrates are examined. The use of these materials as photocatalysts has been investigated for the photodegradation of methylene blue in aqueous solution under ultraviolet irradiation. The catalytic activity of some of the tested catalysts is initially higher than that of a commercial TiO$_2$ photocatalyst (P25 TiO$_2$), but it rapidly declines due to photocorrosion. To protect the catalysts against this phenomenon, a new technique that consists in coating the surface of the photocatalyst with a thin layer of polysiloxane has been successfully developed.

Second, highly polar high surface area ZnO nanosheets supported on SSWM substrates are used as template for the preparation via sacrificial template accelerated hydrolysis (STAH) of a large variety of nanostructured metal oxides (i.e. CuO, $\alpha$-Fe$_2$O$_3$, TiO$_2$, CeO$_2$, Cd$_x$Zn$_{1-x}$O ($x=0.01-0.20$) and Ni$_{0.7}$Zn$_{0.3}$O) supported on SSWM substrates. The structure of the metal oxides produced is a faithful replica of that of ZnO. The key point of this synthesis strategy is the use, as template, of ZnO nanostructures that have a large surface, consisting mainly of polar facets. These facets are chemically very
active and they are responsible for the generation of high surface area metal oxide structures (up to 275 m² g⁻¹).

These high surface area metal oxides have been investigated in three applications: a) the Fenton-like process for the degradation of methylene blue in water (α-Fe₂O₃), b) the photodegradation of methylene blue in aqueous solution (CdₓZn₁₋ₓO and TiO₂) and c) the production of hydrogen from methanol (Ni₀.₇Zn₀.₃O). SSWM-supported α-Fe₂O₃ has been found to have an outstanding catalytic activity and a good stability in the Fenton-like process for degrading methylene blue in the presence of hydrogen peroxide. As for the photodegradation of methylene blue in water under UV irradiation with ZnO-based catalysts, cadmium has been incorporated into the ZnO structure to produce a SSWM-supported CdₓZn₁₋ₓO catalyst that is stable against photocorrosion, while it maintains a significant level of activity. Under visible irradiation this solid solution shows a slightly better behaviour than pure ZnO. For the photodegradation of methylene blue under UV irradiation with SSWM-supported TiO₂, the best results are obtained with the photocatalyst calcined in the 450-600°C temperature region, where it exhibits an intrinsic catalytic activity much higher than that of P25 TiO₂ particles. Finally a SSWM-supported Ni₀.₇Zn₀.₃O has been used for the production of hydrogen in the methanol decomposition reaction, behaving as one of the most active catalysts ever reported in the literature.

With the techniques developed in this thesis we are able to fabricate a large number of high surface area metal oxides supported on a monolithic and flexible material (i.e., a stainless steel wire mesh) that can be easily employed in structured catalytic reactors with a high performance in environmental and energy applications.
LAYOUT
The present PhD Thesis describes the synthesis and applications of nanostructured metal oxides deposited on stainless steel wire mesh (SSWM) substrates. The papers generated from this work and published (4 plus annex), accepted (1) or submitted (2) to different scientific journals constitute the core of this thesis, which is organized as illustrated in Figure 1.

**Figure 1. Organization scheme of the PhD Thesis**

In the **Introduction** section an overview of the synthesis, structure and applications of nanostructured zinc oxide is presented, with special focus on the methods that allow the ZnO crystals to be grown on different substrates. ZnO is the common thread throughout this manuscript since it is directly employed for photocatalytic applications (block I of Results and Discussion section) or used as a template for the synthesis of other supported metal oxides (block II). Special emphasis is placed on the description of the highly polar SSWM-supported ZnO nanostructures which are used as templates for the synthesis of other high-surface area supported metal oxides by means of **sacrificial template accelerated hydrolysis** (STAH). Apart from the synthetic methods, the Introduction section includes a brief description of some applications of supported ZnO and supported metal oxides in different areas.
such as photocatalysis, Fenton-like reactions and hydrogen production. After this section, the different Objectives of this thesis are specified.

The Results and Discussion section is divided in two blocks that contain the most relevant results and the principal conclusions extracted from the papers that are included in each block. Block I contains three publications that describe the synthesis and photocatalytic properties of ZnO nanostructures supported on SSWM substrates. An additional publication has also been incorporated into this block as an annex for a better comprehension of the methodology used for the analysis of the experimental data obtained during the catalytic tests. This publication was already presented as part of the experimental work of the Master’s degree “Synthesis and Chemical Reactivity” (Inorganic and Organic Chemistry Department, University of Oviedo, 2011). Block II contains four publications centred on the synthesis and applications of SSWM-supported high surface area metal oxides produced by using the sacrificial template accelerated hydrolysis (STAH) method. These works include the environmental and energy applications of the materials, such as the photodegradation of organic compounds, the Fenton-like decomposition of organic compounds and the production of hydrogen from biomethanol.

The main contributions derived from the present thesis are disclosed in the final Conclusions chapter.

A detailed description of the publications included in the present thesis is given in the Table 1.
### Table 1. Summary of the publications included in this thesis

<table>
<thead>
<tr>
<th>Article</th>
<th>Journal</th>
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<td>A1. Tailoring the synthesis of stainless steel wire mesh-supported ZnO</td>
<td>Materials Research Bulletin</td>
<td>2012</td>
<td>1.913</td>
<td>Materials science, multidisciplinary</td>
<td>71/241 (Q2)</td>
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<td>AII. Stainless steel wire mesh-supported ZnO for the catalytic photodegradation of methylene blue under ultraviolet irradiation</td>
<td>Journal of Hazardous Materials</td>
<td>2013</td>
<td>3.925</td>
<td>Engineering, civil</td>
<td>2/122 (Q1)</td>
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<td>AIII. Fabrication of wire mesh-supported ZnO photocatalysts protected against photocorrosion</td>
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<td>2013</td>
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<td>1/42 (Q1)</td>
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<td>Annex. A simple visible spectrum deconvolution technique to prevent the artefact induced by the hypsochromic shift from masking the concentration of MB in photodegradation experiments</td>
<td>Applied Catalysis A: General</td>
<td>2011</td>
<td>3.903</td>
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<td>2014</td>
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<td>AVI. High surface area SSWM-supported TiO$_2$ prepared by STAH. A monolithic photocatalyst superior to P25 TiO$_2$</td>
<td>Submitted</td>
<td>2014</td>
<td>-</td>
<td>-</td>
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<tr>
<td>AVII. Novel high surface area SSWM supported Ni$<em>{0.7}$Zn$</em>{0.3}$O solid solution prepared by RT sacrificial template accelerated hydrolysis. Application in the production of hydrogen from methanol</td>
<td>Applied Catalysis B: Environmental (accepted)</td>
<td>2014</td>
<td>5.825</td>
<td>Engineering, environmental</td>
<td>1/42 (Q1)</td>
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* Impact factor is given for the year of publication, if available, or 2012 for recent articles
INTRODUCTION
1. **Nanostructured metal oxides: synthesis and applications**

Nowadays, nanomaterials are used all over the world and deeply penetrate into the daily life of human beings. Nanomaterials have attracted tremendous interest due to their remarkable performance in electronic, optoelectronic, electrochemical and electromechanical nanodevices. Among the nanomaterials, metal oxide nanostructures are very interesting because of specific properties such as high-temperature superconductivity, ferroelectricity, ferromagnetism, piezoelectricity, semiconductivity and catalytic activity [1, 2]. During the last decade, the development of nanometric metal oxides has been the subject of much research work; thus, the number of articles published concerning metal oxide nanostructures has increased exponentially, as illustrated in Figure 2.

![Figure 2. Evolution of publications on nanoparticles of main transition metal oxides (Scopus database, April 2014. Search: (TITLE-ABS-KEY(nanoparticles) OR TITLE-ABS-KEY(nanostructures)) AND TITLE-ABS-KEY(oxide) AND (TITLE-ABS-KEY(zinc) OR TITLE-ABS-KEY(titanium) OR TITLE-ABS-KEY(cobalt) OR TITLE-ABS-KEY(iron) OR TITLE-ABS-KEY(copper) OR TITLE-ABS-KEY(cerium) OR TITLE-ABS-KEY(nickel) OR TITLE-ABS-KEY(manganese)))](image-url)
The terms nanometric or nanostructured are applied to materials containing physically or chemically distinguishable components, at least one of which has nanoscale dimensions, i.e., one or more dimensions with a size in the 1 to 100 nm range [3].

**Figure 3. Schematic diagram that illustrates some applications of metal oxide nanoparticles**

Metal oxides with nanometric dimensions have unique properties which are closely related to the size of the particles [4-6]. The particle size of metal oxides has a strong influence on the properties of the material in two different ways. Firstly, metal oxides with nanometric dimensions undergo a change in their spectroscopic features with respect to larger particles, due to a surface effect, that is detected by Raman [7] or XRD [8]. Secondly, oxide nanoparticles have abundant under-coordinated atoms (like corners or edges) or oxygen vacancies. These defects lead to atomic arrangements different from those in the bulk material as well as occupied electronic states located above the
valence band of the corresponding bulk material, as a result of which the chemical activity of the metal oxide nanoparticles is enhanced with respect to the corresponding micrometric powders [9]. These properties of nanostructured oxides open the door to their use in a variety of applications such as sorbents [10], sensors [11-13], ceramic materials [14], photo-devices [11], field-effect transistors [15], UV lasers [16], piezoelectric generators [17], solar cells [1, 18] and as catalysts [19]. Some of these applications are illustrated in Figure 3. In addition, some semiconductor metal oxides such as ZnO or TiO₂ have been used in paints, protective coatings for metals, rubber processing and textiles, because of their large availability and non-toxicity [20, 21]. For the purpose of the present work, the interest of metal oxide nanoparticles is as catalysts or photocatalysts in processes such as the reduction of environmental pollution [19, 22], i.e., wastewater treatment [23], and H₂ production [11, 24].

One of the most relevant properties of metal oxide nanoparticles is their high surface area. This property is essential for the use of these materials in electrochemical systems or as catalysts, taking into account that the rate of the electrochemical/catalytic processes is greatly dependent on the surface area accessible to the reactants and the number of exposed active centres. In this respect, the fabrication of high surface area metal oxide nanostructures is an important field in present day research. These materials are commonly produced as nanopowders (unsupported particles), with numerous synthesis procedures that can be found in the recent scientific literature [25-28]. A typical example of these procedures is the hard template method [27, 28] in which porous carbons [25, 29] and mesostructured silica [26, 30, 31] are employed as hard templates. However, the template methodology is complex because it requires several synthesis steps and the use of corrosive agents for the removal of the template.

Catalysis is one of the most important applications of powdered or granulated metal oxide nanostructures. However, the use of powders entails several technical drawbacks, two of which are the difficult separation of the
Nanostructured metal oxides supported on SSWM particles from the reaction medium and the high pressure drop generated when the catalyst is employed in a fixed bed. Supporting the metal oxide particles on substrates allows a good dispersion and the use of porous substrates avoids sintering and agglomeration. Selection of an appropriate support is important since, in addition to general advantages such as easy handling and low pressure drop, it may specifically exhibit a high thermal or electronic conductivity, thereby favouring the catalytic process [32]. In the literature, many works can be found that describe the synthesis of metal oxides on several types of structured substrates such as ITO (indium tin oxide) [33], pure Al foils [34], polyethylene fibres [35], cordierite monoliths [36, 37], etc. In some cases the use of these substrates entails several drawbacks, such as their high cost and limited supply (ITO), fragility and difficult manageability (ITO, polyethylene fibres), etc. The metallic supports such as wire meshes or foams with micrometric dimensions constitute a good alternative because they offer several important advantages such as a low-cost, high availability, easy manageability, flexibility, robustness, high thermal and electrical conductivity, etc. In particular, stainless steel wire meshes (SSWM) have been recently used with a great success for supporting high surface area cobalt oxides [38, 39].

In the recent literature, several synthesis procedures can be found to support metal oxide nanoparticles on structured substrates. Supported metal oxides are conventionally synthesized by means of chemical vapour deposition techniques [40-42]. However, the high cost of the equipment and the technical barrier that restricts coatings to a small area have limited their application. Chemical-solution deposition [43] or pulsed laser deposition (PLD) [44-46] have also been investigated as a means to generate thin films of oxides. The hydrothermal method has proved to be a useful, simple and powerful strategy to synthesize metal oxides [47]. This method relies on the chemical reactions and changes in the solubility of substances to grow nanocrystals in a sealed heated aqueous solution kept above ambient temperature and pressure.
Given the importance of supported metal oxide structures for a variety of applications such as those mentioned above, the development of novel synthesis strategies for the fabrication of these materials has become an issue of great importance. The new procedures must fulfil several requirements: a) an easy methodology involving only a few steps, b) the use of low-cost widely available reagents and non-sophisticated equipment, c) avoidance of corrosive chemical products, d) the need for mild conditions (i.e., low temperature and pressure) and e) adaptability of the methodology to the synthesis of a variety of metal oxides by means of a slight change in the synthesis conditions. Some of these methods, explored in this thesis, will be identified and described in sections 2.2 and 2.3.

2. Zinc oxide: a catalyst and a template for the synthesis of metal oxide catalysts

2.1. Zinc oxide structure

Among the nanostructured metal oxides, zinc oxide (ZnO) is one of the most important materials in the field of nanotechnology in present-day research [48, 49]. The renewed interest in this material has arisen due to the development of novel synthesis strategies for the fabrication of high-quality single crystals and epitaxial layers, that allow the manufacture of ZnO-based electronic and optoelectronic devices [50].

The most common structure of ZnO is hexagonal wurtzite (hexagonal phase, space group P6₃mc) [51]. It consists of alternating planes of tetrahedrally coordinated Zn²⁺ and O²⁻ ions, stacked along the c-axis, as illustrated in Figure 4.

Bulk electronic properties, optical properties, intrinsic electronic surface states, the ability to become non-stoichiometric and several other properties characteristic of ZnO are determined by the lattice structure and the type of bonding.
Another important characteristic of ZnO is its polar surfaces. The most common polar surface is the basal plane (0001) (Figure 5) [52]. One end of the basal polar plane terminates with partially positive Zn lattice sites (empty dangling bonds) and the other end terminates in partially negative oxygen lattice sites (filled dangling bonds), as illustrated in Figure 5a. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(000\bar{1}) surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as variance in surface energy. To maintain a stable structure the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO±(0001) surfaces are exceptions: they are atomically flat, stable and exhibit no reconstruction [52]. The other two most commonly observed facets for ZnO are (2\bar{1}10) and (01\bar{1}0), which are non-polar and have lower energy than the ±(0001) facets.

By controlling certain synthesis conditions it is possible to produce hexagonal platelets (Figure 5c) rather than hexagonal rods (Figure 5b) [12] when growth along the a-axis is promoted. This means that modification of the synthesis parameters could be applied to modify the aspect ratio of ZnO nanostructures and, therefore, the polarity of the resulting ZnO structures. Bearing in mind that the physicochemical properties of ZnO are very much...
dependent on the morphology of the nanostructure (i.e., rod or platelet), it is important to develop synthesis tools that are able to control the type of ZnO nanostructure, one of the main objectives of this thesis.

**Figure 5.** ZnO structures: a) Lattice model of ZnO showing the polar and non-polar planes and dangling bonds on (0001) polar faces. b) Hexagonal rod structure of ZnO [53]. c) Hexagonal platelet structure of ZnO

### 2.2. Methods for producing supported ZnO nanostructures

The growth of ZnO nanostructures on different types of substrates has been carried out by means of a wide range of techniques, such as etching [54],
Nanostructured metal oxides supported on SSWM electrodeposition [55], metal-organic chemical vapour deposition [56], physical vapour deposition [57], pulsed laser deposition [58] and electrospinning [59, 60]. These methods normally require complex multi-step procedures. On the other hand, the hydrothermal synthesis of ZnO nanostructures supported on substrates has several advantages, compared to the above mentioned methods, such as the use of simple equipment, catalyst-free growth, low cost, uniformity of production, environmental friendliness and safety [61]. By means of hydrothermal methodologies, structural and chemical properties such as crystal morphology, size and polarity can be easily adjusted by modifying the reaction temperature, reaction time, concentration of precursors or by using additives [62, 63].

The fabrication of non-polar ZnO nanostructures on substrates by hydrothermal growth has been intensively studied in recent years [52]. For example, Ko et al. [64] reported the high density selective growth of long branched “treelike” multigeneration hierarchical ZnO nanowires supported on a FTO (fluorine doped tin oxide) conductive glass substrate. The length of these ZnO nanowires is 2–10 μm and their diameter is in the 30–50 nm range. This structure is very effective in dye-sensitized solar cells. Feng et al. [65] prepared ZnO nanostructures deposited on ITO substrates by a PEG-assisted hydrothermal synthesis strategy. They showed that, by varying the amount of PEG and the PEG/Zn²⁺ molar ratio, different morphologies of ZnO structures can be obtained: microrods (3 μm in length and 1 μm in diameter) and microspheres (5 μm in diameter). Additionally, Chen et al. [66] synthesized highly uniform and parallel ZnO nanorods with sharp ends, and with a length of around 3 μm and a width of about 400 nm. The synthesis was conducted at low temperature and did not require any organic agent. Later, Xu et al. [67] reported a process for growing ZnO nanowire arrays on ITO substrates, that allows ZnO nanowires with a length of 30 μm to be obtained.

Regarding the fabrication of polar ZnO structures, copper plate-supported polar ZnO nanosheets with a flower-like morphology were synthesized by Shao et al. [68] and Bai et al. [69] through a hydrothermal
route using zinc chloride and ammonia as reactants. These flower-like structures, averaging around 30 μm in size, are composed of sheets around 150–250 nm thick. Kakiuchi et al. [70] reported the synthesis of ZnO nanosheets by the pyrolytic transformation of hydrothermally grown Zn₄CO₃(OH)₆·H₂O nanosheets. The nanosheets were initially formed as assemblies on glass substrates during hydrothermal growth in aqueous solutions of urea and a zinc precursor (chloride, sulfate, acetate or nitrate) at 80°C. The transformation of Zn₄CO₃(OH)₆·H₂O into ZnO took place without any change in the microstructure of the nanosheets. These are approximately 50 nm thick and have a BET surface area as high as 88.5 m²·g⁻¹. In none of these works was the yield of ZnO on the support reported.

There are many works in the literature that describe the hydrothermal synthesis of zinc oxide on different supports such as ITO [65, 66], copper plate [69], silica or polyester films [66], polyethylene fibres [35] and stainless steel wire mesh (SSWM) [71]. Of these supports, SSWM exhibits a number of significant advantages such as a good thermal and electronic conductivity, high flexibility, low cost and wide availability. Thus, monolithic configurations of the ZnO nanostructures can be produced to display different properties for use in catalytic micro-reactors.

The dimensions of non-polar ZnO nanorods or polar ZnO nanosheets are known to affect their optical properties. For instance, the optical transmittance of ZnO deposits is favoured by a diminution of their thickness [72]. The ultraviolet radiation shows better quantum yield (better penetration through the deposited ZnO) when the ZnO layer is thinner. Similarly, it is thought that the photocatalytic efficiency of supported ZnO materials for the degradation of pollutants could be increased by using ZnO photocatalysts of small particle size.

One of the objectives of this thesis is to explore the synthesis of SSWM-supported ZnO nanostructures displaying different morphologies and
yields to allow the appropriate material to be selected for different applications.

2.3. ZnO nanostructures as templates for the synthesis of high surface area metal oxides. The sacrificial template accelerated hydrolysis (STAH) method

In a recent work, Liu et al. [73] presented an elegant and simple method to produce supported metal oxide nanotubes based on the use of ZnO nanorods as a hard template. This method denoted as sacrificial template accelerated hydrolysis (STAH) is a procedure that allows the generation of the new metal oxide structure, while the ZnO scaffold is simultaneously removed. The process is very simple and requires only one step, once the ZnO template is available. This is an important advantage over classical hard template techniques, since it notably simplifies the synthesis procedure and, in addition, avoids the use of oxidation stages or the need for corrosive products to remove the template. Basically, the STAH approach [73] consists of the formation of metal oxide nanostructures through the hydrolysis of the metal ions in the vicinity of ZnO nanowires, which serve as scaffold and whose simultaneous etching by the protons produced accelerates the hydrolysis reaction. Under the name of STAH it was first used for the production of Fe$_2$O$_3$ nanotubes [73], although under the name of liquid phase deposition and in the presence of a reducing agent it was originally used for the synthesis of TiO$_2$ nanotubes [74]. Later, it was successfully applied to the preparation of ZnO/α-Fe$_2$O$_3$ nanosheets [75], SnO$_2$/α-Fe$_2$O$_3$ nanotubes [76] (although SnO$_2$ was simply deposited on the ZnO scaffold), platinum and palladium nanotubes for electrocatalysis and chemical sensing [77, 78], NiO-based electrodes [79, 80] and active electrocatalysts consisting of mixtures of noble metal (Pd, Pt and Ag) nanotubes prepared by a wrongly called hydrothermal variation of the STAH method (the synthesis was performed at ambient pressure) [81]. Recently, arrays of CeO$_2$ nanotubes were also synthesized by ZnO
dissolution/CeO₂ deposition from cerium nitrate solutions at 95°C [36]. Table 1 shows several examples of the metal oxide nanostructures synthesized by the STAH method. In all these examples ZnO nanowires were used as the sacrificial template and the resulting metal oxide nanostructures consisted of hollow nanowires. As indicated in Table 2, the ZnO structures were supported on a variety of substrates.

The mechanism of the STAH method is schematically illustrated in Figure 6 for the synthesis of the original α-Fe₂O₃ nanostructures. In a first step, the supported ZnO nanowires are immersed in an aqueous solution containing Fe³⁺ ions at room temperature. In this aqueous solution the hydrolysis of metal ions generates protons (H⁺) (Eq. 1). These protons attack the ZnO scaffold (Eq. 2) and the dissolution of the zinc oxide takes place (Figure 6). It is important to note that this attack occurs only on the ZnO polar faces (0001) [36] because of their intrinsic high reactivity. As a consequence, the ZnO polar faces are gradually dissolved.

\[
[\text{Fe(H}_2\text{O)}_6]^{3+} \rightarrow [\text{Fe(OH)}(\text{H}_2\text{O)}_5]^{2+} + \text{H}^+ \quad (1)
\]

\[
\text{ZnO} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O} \quad (2)
\]

\[
[\text{Fe(OH)}(\text{H}_2\text{O)}_5]^{2+} \rightarrow \text{Fe(OH)}_3 + 2\text{H}^+ + 3\text{H}_2\text{O} \quad (3)
\]

The consumption of H⁺ when the ZnO is etched accelerates the Fe³⁺ hydrolysis reaction. As a result, the iron hydroxide precipitates (Eq. 3) onto the non-polar faces of the ZnO nanowires (Figure 6). Finally, this process yields hollow hexagonal rods of metal hydroxide (Figure 6), whereas the ZnO nanorods are completely removed. A final calcination step is needed to obtain the metal oxides.

From the above discussion it follows that the polar faces of the ZnO are the key to the generation of hollow metal oxide structures. According to Feng et al. [36], as the polar (0001) face of the ZnO nanowire is positively charged, nucleation of metal hydroxides on the top surface of the ZnO nanowire will be hindered due to an electrostatic effect. In consequence, nucleation of metal hydroxide will occur only on the non-polar ZnO faces of the nanowire. This
implies that the (0001) polar faces will be selectively dissolved by the attack of the protons which will lead to the formation of the hollow rods (Figure 6).

Table 2. Supported metal oxide structures generated by using ZnO nanorods as templates following the STAH methodology

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Type of template nanostructure</th>
<th>Final product</th>
<th>SEM image of the final product</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>nanowires</td>
<td>α-Fe$_2$O$_3$</td>
<td><img src="image1.png" alt="SEM image" /></td>
<td>[73]</td>
</tr>
<tr>
<td>Si wafer</td>
<td>nanowires</td>
<td>Pd</td>
<td><img src="image2.png" alt="SEM image" /></td>
<td>[78]</td>
</tr>
<tr>
<td>Stainless steel plates</td>
<td>nanowires</td>
<td>NiO</td>
<td><img src="image3.png" alt="SEM image" /></td>
<td>[79]</td>
</tr>
<tr>
<td>ITO</td>
<td>nanowires</td>
<td>CeO$_2$</td>
<td><img src="image4.png" alt="SEM image" /></td>
<td>[36]</td>
</tr>
<tr>
<td>ITO</td>
<td>nanorods</td>
<td>TiO$_2$</td>
<td><img src="image5.png" alt="SEM image" /></td>
<td>[74]</td>
</tr>
</tbody>
</table>
The STAH synthesis strategy commonly uses as template ZnO nanostructures made up of hexagonal nanowires or nanorods whose geometrical characteristics (diameters of hundreds of nanometers) permit the assumption that the specific surface areas of the metal oxides obtained will be low. This is only an assumption because these values have not been reported in any of the revised papers, with the exception of the ZnO/α-Fe₂O₃ nanosheets described by Qin et al. [75], which have a specific surface area of 27 m² g⁻¹. Although not mentioned by the authors, the XRD pattern of the ZnO in their ZnO/α-Fe₂O₃ nanosheets has a (100)/(002) intensity ratio higher than 1 (Figure 3 in [75]), which indicates that the ZnO crystals have a greater proportion of polar surfaces [82] than the typical ZnO nanowires employed in other works (e.g. [73]). In the present thesis we will prove that this fact is essential for obtaining metal oxides with high values of specific surface area,
for which we will make use of a large surface area highly polar SSWM-supported ZnO template.

The yield of the metal oxides on the support surface after the synthesis is also generally omitted. Again, according to the geometry of the nanotubes (typically short length nanotubes perpendicular to the support surface), we believe that the metal oxide yield with respect to the substrate will be also low. In relation to the use of supported metal oxide particles as catalysts, as in this thesis, (i.e., in photocatalysis, for H₂ generation, in the Fenton-like reaction, etc.) or as substrates in energy storage systems (i.e., supercapacitors), it is crucial that the synthesized materials have not only a high surface area but also a high metal oxide yield, which is one of the main objectives of this PhD Thesis.

3. Potential applications of supported metallic oxide structures

3.1. Photocatalysis

Over the last two decades, the use of TiO₂ and ZnO as photocatalysts has been thoroughly investigated. Photocatalysis by semiconductors, such as those indicated above, is a well-established method for degrading organic contaminants in wastewaters. When a photon with energy greater than the band gap of the semiconductor is absorbed by the solid, an electron is excited from the valence band to the conduction band, resulting in an electron-hole pair. These excited state conduction band electrons and valence band holes have several possible fates: a) they can recombine and dissipate the energy as heat whilst still in the bulk matrix of the crystal; b) they can become trapped in defect traps; c) they can migrate to the surface, where they recombine; d) they may take part in redox reactions with electron donors or acceptors adsorbed onto the surface, which is the desirable pathway if degradation of organic contaminants is to occur [83]. In aqueous systems these adsorbed
species will correspond to water molecules, hydroxide ions and oxygen molecules.

\[ \text{Figure 7. Band gaps (eV) and redox potentials for several semiconductors referred to the normal hydrogen electrode (NHE). Adapted from Ania et al. [84]} \]

The chemical potentials of photogenerated electrons and holes depend on the position of the energy levels in the semiconductor. More specifically, the redox potential of a donor species adsorbed on the surface of the photocatalyst needs to be more negative (higher in energy) than the valence band position of the semiconductor in order to fill the electron vacancies. Similarly, acceptor molecules must have a redox potential that is more positive (lower in energy) than the conduction band. In view of this, one of the advantages of TiO2 and ZnO compared to other semiconductors is that their electronic structure is such that it allows both the reduction of protons and
the oxidation of water [85]. This can be appreciated in the redox potential diagram shown in Figure 7.

In order to achieve a high photocatalytic efficiency, a number of conditions are required. Firstly, the band gap of the semiconductor must be greater than the redox potential of the H₂O/OH• couple and, in addition, the material must be photo-stable. Secondly, it is important that the recombination of electron-hole pairs be minimized. In other words, they need to be kept apart to allow time for the redox reactions to occur. Separation can be achieved by trapping electrons or holes in defects [86] or by using electrical conductive supports [71].

The holes in the photocatalyst valence band can oxidize the adsorbed water or hydroxide ions, while electrons in the conduction band can reduce molecular oxygen to superoxide anions [87]. These processes are summarized in the following equations.

\[
\text{Semiconductor} + h\nu \rightarrow e^- + h^+ \tag{4}
\]

\[
h^+ + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{OH}^*_{\text{ads}} + \text{H}^+ \tag{5}
\]

\[
h^+ + \text{OH}^*_{\text{ads}} \rightarrow \text{OH}^*_{\text{ads}} \tag{6}
\]

\[
e^- + \text{O}_2 \rightarrow \text{O}_2\cdot^- \tag{7}
\]

\[
\text{O}_2\cdot^- + \text{H}^+ \rightarrow \text{HO}_2\cdot \tag{8}
\]

\[
\text{O}_2\cdot^- + \text{HO}_2\cdot + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \tag{9}
\]

The degradation of organic contaminants is commonly attributed to oxidation by hydroxyl radicals. This process is schematically described in Figure 8. This has led to the use of the term “Advanced Oxidation Processes”, although there is evidence that in some systems reductive pathways also operate [88].
Titanium dioxide (TiO₂) nanoparticles have been widely studied for photocatalytic applications over the last two decades [90, 91]. TiO₂ is relatively inexpensive, insoluble in water and non-toxic. It can provide photogenerated holes with a high oxidising power because of its wide band gap (3.2 eV) [92]. Most of the photocatalysts found in the literature are in the form of powders. Only a few supported photocatalytic systems have been reported, even though they have clear advantages from a practical point of view [93-95]. The most important advantage is that the separation of the supported photocatalysts from the reaction medium is simple, which minimizes the power requirements. In addition, they can be adapted to operate in flow-type continuous reactors [96, 97]. Fernández et al. [98] reported two methods of deposition of TiO₂ powders on different substrates (glass, quartz and stainless steel) and the deposited titania shows a similar photocatalytic activity to that of the powder form. Some authors [99, 100] developed a new type of supported photocatalyst that consists of mixtures of noble metal nanoparticles and commercially available TiO₂ nanoparticles (P25, Degussa-Evonik) deposited on quartz substrates. Later, Jung et al. [71] studied
the synthesis and photocatalytic activity of CuO-ZnO nanowires supported on stainless steel wire meshes (SSWM). In particular, they showed that CuO-ZnO structures supported on SSWM exhibit an enhanced photocatalytic activity with respect to catalysts using other supports, such as ITO. This result they attributed to the efficient charge separation of the electron-hole pair favoured by the SSWM support [71]. Other advantage of SSWM is its flexibility, which allows the mesh to be easily shaped to the desired configuration. In the present thesis one of the objectives is to produce TiO₂ nanoparticles supported on SSWM with a high photocatalytic activity. With this aim in mind, we shall take advantage of the versatility of the sacrificial template accelerated hydrolysis technique to produce the supported titania.

ZnO shares many properties with TiO₂ including a similar band gap (see Figure 7). There have even been several examples of ZnO displaying a higher photocatalytic activity than TiO₂ [101]. In addition, ZnO exhibits a better quantum efficiency because it can absorb a larger fraction of the solar spectrum than TiO₂ [102] and its price is even lower than that of TiO₂ [103]. Compared to TiO₂, ZnO can be easily supported on different types of substrates by means of low temperature synthesis methods [104]. As indicated in section 2.2, in this work we shall perform extensive investigation into the synthesis of SSWM-supported ZnO nanostructures with different morphologies, as an important objective of this thesis is to study the effect of different morphologies on the photocatalytic activity of the synthesized materials.

However, the use of ZnO as a photocatalyst is limited by the photocorrosion phenomenon. This process occurs because of the action of UV radiation. As a consequence, the catalyst is partially dissolved, which gives rise to a dramatic decrease in catalytic activity [105]. The mechanism of this process is represented by the following self-oxidation reactions [106-108]:

\[
\text{ZnO} + 2h^+ + n\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_{n}^{(2-n)^+} + \frac{1}{2} \text{O}_2 + n\text{H}^+ \tag{10}
\]

\[
\text{ZnO} + 2h^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2} \text{O}_2 \tag{11}
\]
where $h^+$ are the positive holes created by the action of UV radiation. Photocorrosion is the main obstacle to the use of ZnO as an effective photocatalyst. Therefore, significant efforts have been made to reduce the degradation of ZnO. In general, the procedures used to achieve this involve the deposition onto the ZnO surface of: a) silver nanoparticles [109-113]; b) polyaniline monolayers [114]; c) graphitic carbon [115]; d) Nafion films [116]; e) AlSi nanoclays [117] and f) C$_{60}$ fullerenes, which become hybridized with ZnO [106]. Although the above modifications improve the photocatalytic stability of ZnO, some problems still persist. For instance, Bessekhouad et al. [118] have reported that the photocatalytic activity of the doped materials is impaired by thermal instability and by an increase in the number of hole/electron recombination centres. Therefore, the development of novel methods that provide an effective protection of the ZnO photocatalyst against photocorrosion is required. This is another of the objectives to be pursued in this PhD Thesis, by different methodologies.

An attempt has to be made to increase catalytic activity under visible irradiation, since the solar spectrum contains a large fraction of visible light compared to UV radiation. Recently, the photocatalytic activity of ZnO in the visible region has been improved by various techniques, such as: a) modification of the ZnO surface by non-metal element doping [119]; b) transition metal doping [120, 121]; c) the combination of ZnO with another semiconductor [122], etc. Of these methods, the coupling of different semiconductor photocatalysts offers great promise as it increases the charge separation of the electron-hole pairs, resulting in an increase in photocatalytic decolourization efficiency [123]. Recently, ZnO has been combined successfully with TiO$_2$ [124], CdO [125], CdS [126] and WO$_3$ [127]. CdO is a good candidate for coupling with ZnO due to its band gap, $\sim$2.2 eV [125], so that Cd$_x$Zn$_{1-x}$O nanostructures are active in the visible range. In addition, under visible light the excited electrons from the conduction band (CB) of ZnO can be easily transferred to the CB of CdO since the $E_{\text{CB}}$ of CdO is lower than the $E_{\text{CB}}$ of ZnO. These transferral processes increase the excess of electrons in the conduction band of CdO, which leads to a shift in the Fermi level of CdO [128].
Nanostructured metal oxides supported on SSWM increasing its photocatalytic efficiency. To the best of our knowledge, CdO-ZnO has been always synthesized in powder form. The use of CdO-ZnO supported on a target substrate (such as SSWM) as a photocatalyst for dye degradation processes in UV or visible has never before been reported. We shall perform this task in the present thesis and shall attempt to demonstrate in parallel that coupling CdO and ZnO may be also an excellent method to avoid photocorrosion.

3.2. Fenton-like reaction for the degradation of methylene blue in aqueous solution

Some of the materials synthesized in this work can be applied to various advanced oxidation processes to degrade pollutants in water. As commented in the former section, these processes are characterized by the production of the hydroxyl radical (OH•) as primary oxidant. One of the most intensively studied advanced oxidation processes is the Fenton reaction which is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide. This process is based on the transfer of an electron between H₂O₂ and iron ions to produce reactive radicals. This reaction employs homogeneous iron-based catalysts [129]. When the catalyst is heterogeneous (solid catalysts) the reaction is denominated Fenton-like reaction [130]. This has been widely studied as an alternative treatment of wastewater. The degradation mechanism of organic pollutants by the Fenton process is as follows:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{OH}^• + \text{H}_2\text{O} \tag{12}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HOO}^• + \text{H}^+ \tag{13}
\]

Of the heterogeneous Fenton-like catalysts, α-Fe₂O₃ is the most common iron-containing solid catalyst. α-Fe₂O₃ is a crystalline polymorph of Fe₂O₃, which is chemically and thermally more stable than other Fe₂O₃ crystalline polymorphs. Furthermore, α-Fe₂O₃ powder can be easily synthesized by
various methods, among which calcination is widely used [131]. Recently, Fe₂O₃-containing mesoporous materials have attracted much attention because of their high surface area and high catalytic activity for the degradation of dyes in the Fenton-like reaction [132]. However, the use of α-Fe₂O₃ catalysts in powder form involves a series of technical challenges, the most important of which is, again, the separation of the nanosized particles from the reaction medium. By using a catalyst supported on a substrate this problem can be overcome. One of the objectives of the present study is the synthesis of high surface area SSWM-supported α-Fe₂O₃ catalysts and their application in the heterogeneous Fenton-like reaction.

3.3. Hydrogen production

In the 19th century, coal was the principal source of energy whereas in the 20th century petroleum was the dominant one. Now in the 21st century, dominated by the Kyoto agreement, renewable energy sources are expected to play a more important role in the energy market. One of the disadvantages of renewable energies is that they are intermittent so that a storage system must be found. Hydrogen, as an energy carrier, can be obtained from renewable energy sources and transformed into clean energy on demand, thus facilitating the integration of renewable energy sources into the energy market.

Hydrogen is the most abundant element in the universe and exists almost everywhere in our planet, although always combined with other elements, such as in water, natural gas and oil. Therefore hydrogen must be obtained from these sources. More than 100 million metric tons of hydrogen are annually produced in the world [133], mainly from natural gas reforming.

The amount of energy produced during hydrogen combustion is higher than that released by any other fuel on a mass basis. Additionally, hydrogen as a fuel does not produce CO₂ emissions. Thus, the use of hydrogen can help us to reduce air pollution, global warming and greenhouse emissions. A hydrogen
supply and demand model for a future hydrogen-based society is presented in Figure 9 [133].

![Diagram of Hydrogen Supply and Demand Model](image)

**Figure 9. Hydrogen Supply and Demand Model [133]**

As stated above hydrogen is an energy carrier and has to be produced from a variety of sources (water, biofuels, biomass, coal, natural gas, etc.). Consequently it will be as clean as the method employed to produce it. Of the different sources, biomass has many advantages: it is a renewable source, it can be grown anywhere and it produces lower net carbon emissions than fossil fuels. Biomethanol is a type of biofuel that is often overlooked in many reports dealing with biomass as a source of energy in favour of the more popular bioethanol, even though it offers important advantages. For example a lower temperature is needed to transform it into hydrogen and a smaller amount of coke is formed, since biomethanol has a high H/C ratio and no C-C bonds [134]. As it is a liquid at RT, it is easy to transport and store. From a technological point of view the origin of methanol (biomethanol or methanol...
Introduction

31

from fossil fuels) is not important, since the reactions involved in the production of hydrogen are the same. Hydrogen can be produced from methanol either by decomposition (MD) (Eq. 14) or by steam reforming (MSR) (Eq. 15).

\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad (14)
\]

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \quad (15)
\]

From Eqs. 14 and 15 it can be seen that MSR produces 50% more hydrogen than is obtained from MD, this difference being due to contribution from water. This fact, coupled with the absence of CO as a major reaction product, makes the MSR process more attractive than the methanol decomposition process. However, compared to methanol decomposition, MSR requires a substantially higher amount of heat to vaporize the reactants, conduct the reaction and compensate for the heat loss from the reactor and the effluent streams [38]. In the case of methanol decomposition, the heat for the reaction can be provided by burning the carbon monoxide released, either in a preferential oxidation step or after it has been separated from the hydrogen stream in a catalytic membrane reactor [135]. In any case, the production of hydrogen from methanol typically requires the presence of solid catalysts. Copper-based catalysts have received considerable attention for the production of H\(_2\) by MSR [136-138], as well as high surface area copper manganese spinel (CuMn\(_2\)O\(_4\)) [139]. Several works have focused on methanol decomposition by using, as catalysts, noble metals, copper or nickel supported on graphite, on active carbon or, in some cases, on diamond [140-143]. Some authors have investigated the use of metal oxides such as CeO\(_2\) [144], Fe\(_2\)O\(_3\) [145], Co\(_3\)O\(_4\) [146] for methanol decomposition. In all of these cases, the catalysts employed for producing hydrogen are in powder form. Although powder catalysts are highly effective, their handling entails problems such as the generation of high pressure drops in the reaction system. Supported catalysts therefore provide an attractive alternative. Recently Marbán et al. [38] presented a new structured catalytic system consisting of mesoporous doped Co\(_3\)O\(_4\) nanowires supported on a very fine stainless steel wire mesh
Nanostructured metal oxides supported on SSWM [38]. They used this catalyst for the decomposition of methanol (with CuO-coupling [38]) and ethanol steam reforming (with K-doping [147]). In this type of catalytic system, the metal wire mesh provides a large geometric surface area for holding the catalyst, while guaranteeing a negligible pressure drop and a good heat transfer throughout the reactor. The catalytic activity recorded for this type of catalyst was among the highest ever reported in the literature [38, 147]. In this thesis we shall explore other SSWM-supported materials, prepared via sacrificial template accelerated hydrolysis. In particular, we shall attempt to prepare for the first time a high surface area Ni_{0.7}Zn_{0.3}O solid solution that has never before been tested as a catalyst. A final objective of this thesis is to test this catalyst for the production of hydrogen from methanol.

4. Concluding remarks

Catalysts play an important role in environmental protection and energy production. The advantages of monolithic catalysts, such as that they produce a small pressure drop, have good mechanical stability and are easily separated from the reaction medium, make them superior to conventional powder catalysts. In this PhD Thesis, the development of novel synthesis methods to obtain high surface area metal oxides supported on stainless steel wire meshes (SSWM) will be investigated for the design of advanced monolithic materials to be used in heterogeneous catalysis. To achieve this goal, we shall first examine various hydrothermal methods for growing ZnO nanostructures on SSWM substrates with morphologies that can be tailored by controlling the synthesis parameters. This will make it possible to study the effect of the dimensions, yield and polarity of the fabricated ZnO nanostructures on their photocatalytic activity. It is well known that ZnO-based materials undergo almost total deactivation from photocorrosion in just a few reaction stages. Protection of the catalysts against this phenomenon will be one of the main aims of this thesis.
A second and novel synthetic approach for the fabrication of high surface area metal oxides supported on SSWM will also be developed. This consists of a sacrificial template accelerated hydrolysis (STAH) technique using a large surface area highly polar SSWM-supported ZnO template. With this technique we shall attempt to produce several high surface area metal oxides (α-Fe$_2$O$_3$, CuO, CeO$_2$, TiO$_2$, Cd$_x$Zn$_{1-x}$O, Ni$_{0.7}$Zn$_{0.3}$O) supported on SSWM that will then be tested for different applications including the Fenton-like degradation and photodegradation of dyes in water and the production of hydrogen from methanol.
OBJECTIVES
In accordance with the ideas advanced in the Introduction section, the *main objective* of this thesis is to develop novel synthesis strategies focused on the fabrication of stainless steel wire mesh-supported high-surface area metal oxide nanostructures which will be used as catalysts for the abatement of aqueous pollutants and the production of hydrogen. In order to achieve this general aim, the following *specific objectives* are proposed:

- To optimize the structural properties of ZnO nanoparticles supported on SSWM substrates by controlling the operational parameters (*i.e.*, synthesis temperature, synthesis time, and additives) of the hydrothermal processes selected as the synthetic routes.

- To synthesize and optimize the structural characteristics of high surface area metal oxides (*i.e.*, CuO, CeO$_2$, α-Fe$_2$O$_3$, TiO$_2$, Cd$_x$Zn$_{1-x}$O, Ni$_{0.7}$Zn$_{0.3}$O) supported on SSWM substrates which are generated by the use of polar ZnO nanostructures supported on SSWM as a sacrificial template.

- To evaluate the catalytic performance of several high surface area metal oxides supported on SSWM substrates in the following processes:
  
  - The photodegradation of pollutants in aqueous phase by using SSWM-supported nanostructures made up of TiO$_2$, ZnO or Cd$_x$Zn$_{1-x}$O as photocatalysts.
  
  - An advanced oxidation process for the continuous degradation of organic compounds by means of the Fenton-like process employing SSWM-supported α-Fe$_2$O$_3$ nanostructures as catalyst.
  
  - The production of hydrogen from methanol by using a novel catalyst consisting of Ni$_{0.7}$Zn$_{0.3}$O solid solution supported on SSWM substrates.

- To explore new strategies for protecting the supported ZnO nanostructures against the photocorrosion phenomenon that occurs when these photocatalysts are exposed to UV radiation.
RESULTS AND DISCUSSION
1. Block I: Synthesis and photocatalytic properties of stainless steel wire mesh-supported ZnO nanostructures

*Figure 10. Schematic illustration of the research activities described in Block I*
This block includes the works focused on the fabrication of stainless steel wire mesh (SSWM)-supported ZnO nanostructures and their application in the photodegradation of methylene blue in aqueous solution under UV irradiation.

Article I describes several hydrothermal methodologies for synthesizing SSWM-supported ZnO nanostructures. Article II presents the results on the application of these nanostructures in the photodegradation of methylene blue in aqueous solution. Article III shows the use of polysiloxane coatings for the protection of SSWM-supported ZnO photocatalysts against photocorrosion. For a clearer understanding, Figure 10 illustrates the relevant details of the work contained in this block.

1.1. Synthesis of SSWM-supported ZnO nanostructures

As reported in the Introduction section, numerous procedures for the synthesis of ZnO can be found in the literature [52]. Of the methods proposed, the hydrothermal synthesis of ZnO constitutes the most popular route as it requires moderate temperatures and low cost reagents. In the case of supported ZnO there are just few papers dealing with the application of hydrothermal methods that permit to obtain high yields of ZnO on the substrates. Briefly, the synthesis of ZnO by hydrothermal methods entails the following steps: a) the hydrolysis of the zinc precursor; b) the \textit{in situ} formation of the hydroxide complexes and c) the growth of ZnO on the surface of the substrate. In this work, we have used the hydrothermal approach to synthesize ZnO supported on SSWM adapting a number of different synthesis protocols obtained from literature for other supports, and we have analyzed the influence of several parameters on the final properties of the SSWM-supported ZnO materials, as summarised in Article I (\textit{Tailoring the synthesis of stainless steel wire mesh-supported ZnO}, Vu et al., Materials Research Bulletin, 47 (2012) 1577-1586). The operational conditions modified during the synthesis were the following: a) the pre-treatment of the substrate, b) the
Results and Discussion: Block I

concentration of the zinc precursor, c) the temperature and time of the synthesis; and d) the use of additives.

These conditions were varied in order to optimize the properties of the ZnO particles deposited on the substrate: i.e., morphology, crystallinity and the yield of ZnO deposited with respect to the substrate.

In the hydrothermal synthesis approach adopted, the substrate is commonly subjected to a seeding step, which involves the incorporation of nanocrystallites on the surface of the support prior to the hydrothermal process itself. In this way, the seeds will favour the growth of ZnO crystals according to a nucleation-growth mechanism, which would not be the case with a non-seeded substrate. We have observed that the seeding procedure leads to an improvement in the yield of ZnO on the mesh and to a more homogeneous distribution on the support surface. Indeed, the amount of ZnO deposited increases with the number of the seeding cycles leading to a highly compact forest of ZnO nanorods growing perpendicular to the substrate.

The synthesis temperature used for the growth of ZnO is one of the most important factors that affect the final morphology and yield of the SSWM-supported ZnO materials. In general, an increase in the synthesis temperature leads to an increase in the ZnO yield, although the optimum temperature depends on the method selected for the synthesis. Additionally, the increase in temperature produces changes in the morphology of the samples. For instance, when the temperature is increased from 25 to 50°C in the samples synthesised by the Chen method [66], the ZnO crystals become thicker and more rounded at the tip.

The effect of synthesis time on the yield and morphology of ZnO structures has also been analysed. A clear increase in ZnO yield is observed with the reaction time. However, in some cases, such as in the samples synthesised following the Chen method [66] for periods of time longer than 10 hours, the increase in yield is accompanied by an increase in the size of the
nanostructured metal oxides supported on SSWM

Hydrothermal synthesis usually involves the use of additives such as chemical complexing agents. These additives have at least one functional group, which enables these species to play several important roles such as promoting the formation of crystalline ZnO nuclei which can eventually grow into well-oriented parallel arrays of ZnO crystals or preventing homogeneous nucleation [67, 148]. In the present work, polyethylene glycol (PEG) and polyethyleneimine (PEI) are used as surfactant polymers. As indicated in literature [67, 148], we have observed that the use of PEG increases the ZnO yield, while PEI produces an improvement in the uniformity of ZnO nanostructures distributed over the surface.

In this work we were able to synthesize ZnO nanostructures supported on SSWM distributed homogeneously over the metallic wire mesh. By selecting the synthesis conditions we were able to vary the ZnO yield from 3 to 30 wt.%. The ZnO nanostructures obtained exhibit a prismatic morphology with a hexagonal cross-section, with lengths ranging from 700 nm to 6 µm and widths from 70 nm to 2.3 µm. The crystal size of ZnO as calculated by Scherrer’s equation is in the 30-45 nm range. Although all the protocols lead to the same prismatic morphology, the appearance of the samples varies depending on whether growth takes place preferentially in the direction of the a-axis or c-axis. This appearance can be related to the I_{101}/I_{002} ratio in the XRD spectra. Higher values of I_{101}/I_{002} are obtained when the hexagonal structures grow preferentially in the direction of the a-axis. This parameter varies over a wide range, 0.14-1.83, and can play an important role in photocatalytic applications [149, 150]. Taking into account the potential applications of ZnO, it would appear advisable to maximize the ZnO yield and geometric surface area, as well as to promote the formation of selected planes so that they are more active in photocatalytic reactions.

The results obtained in this work show that the properties of SSWM-supported ZnO can be controlled and optimized by selecting the appropriate
Results and Discussion: Block I

synthesis parameters. In this way, it is possible to produce ZnO nanostructures in high yields, and to generate uniform ZnO layers made up of hexagonal prisms and with a wide range of crystal properties.

1.2. Photocatalytic activity of SSWM-supported ZnO nanostructures

Photocatalysis is an attractive technology for the degradation of recalcitrant pollutants in water, as mentioned in the Introduction section. Although TiO$_2$ is by far the most employed photocatalyst, many other semiconductor metal oxides [90, 91], and specifically ZnO [101], have also been proposed. The vast majority of the photocatalysts studied are in powder form with all the difficulties in handling and recovering that implies. Consequently, supported photocatalysts are nowadays an important research area. In this work, several types of prismatic nanostructures of ZnO supported on SSWM have been tested for the photocatalytic degradation of methylene blue (MB) under ultraviolet (UV) irradiation. The main results have been published in Article II (Stainless steel wire mesh-supported ZnO for the catalytic photodegradation of methylene blue under ultraviolet irradiation, Vu et al., Journal of Hazardous Materials, 246-247 (2013) 126-134).

The degradation of MB during the photocatalytic reaction under UV irradiation was followed by UV-Vis absorption spectroscopy. The typical analysis procedures only consider the changes in the main peak of the absorption curve of MB, located at $\sim$664 nm. However, the presence of intermediate degradation compounds affects the intensity of this peak, masking the true MB concentration. In order to determine the true methylene blue concentration we developed a deconvolution technique that allows the contribution of the reaction intermediates (azure A, azure B and azure C) to the spectra to be taken into account, without the need for actually measuring them. This procedure is described in a paper included in the Annex (A simple visible spectrum deconvolution technique to prevent the artefact induced by
the hypsochromic shift from masking the concentration of methylene blue in photodegradation experiments, Marbán, Vu, Valdés-Solís, Applied Catalysis A: General, 402 (2011) 218-223).

The photocatalytic activity of the different SSWM-supported ZnO samples has been compared to that of commercial TiO₂ (P25 Evonik-Degussa). A comparison cannot be performed directly in terms of conversion, which is affected by the operation parameters. For this reason, it is important to determine the intrinsic catalytic activity of the different materials. The reaction rate can be expressed by the potential equation:

\[ - \frac{dC_{\text{MB}}}{dt} = kC_c C_{\text{MB}}^n \]  

(16)

In equation (16) \( C_{\text{MB}} \) is the concentration of MB at a given time \( t \); \( k \) is the reaction rate constant \( (\text{mg}_{\text{MB}}^{-1} \text{mg}_c^{-1} \text{L}^n \text{min}^{-1}) \); \( n \) is the apparent reaction order; \( C_c \) is the catalyst dosage at a given time that, in the case of supported catalysts, varies with time due to successive sample retrieval for analysis, as indicated in equation (17).

\[ C_c = \frac{w_c}{V_0 (1 - b \times t)} \]  

(17)

where \( V_0 \) is the initial liquid volume and \( b \) is a constant that can be obtained by linear regression.

For \( n=1 \), equation (16) is coincident with the well-known Langmuir-Hinshelwood equation for diluted solutions [151]. Equation (16) can be solved for \( n=1 \) or \( n \neq 1 \), and values of \( k \) and \( n \) can be obtained. However, the catalytic activities, expressed by the values of \( k \), cannot be compared unless the values of \( n \) are identical. To overcome this problem, we used the following parameter to evaluate the intrinsic catalytic activity of the samples:

\[ A_c = \frac{1}{t_{0.5} C_{c,0}} \]  

(18)
Results and Discussion: Block I

where t_{0.5} is the semiconversion time (min) and C_{C,0} is the catalyst dosage at t=0 (mg L^{-1}). In principle the A_C parameter is independent of the catalyst dosage [152], although it is affected by mass transfer limitations and the quantum yield. This parameter allows the intrinsic activity of different catalysts to be compared on a catalyst mass basis but, in a series of reaction stages performed with the same catalytic sample, it is necessary to consider how the catalyst losses affect the absolute catalytic activity. To establish this, it is convenient to employ the inverse of the semiconversion time for a fixed initial catalyst dosage (333 mg L^{-1}):

\[
\frac{1}{t_{0.5}} = A_C \times 333 \times \frac{C_{C,0}}{C_{C,0}'}
\]

where C_{C,0}' is the catalyst dosage at the beginning of the first reaction stage (UV time=0) and C_{C,0} is the catalyst dosage at the beginning of the reaction stage under analysis, in which the catalyst displays the intrinsic activity A_C.

By using these parameters, remarkable differences in catalytic activity among the catalysts described in Article I were obtained. The best results were obtained with the catalyst synthesised following the method reported by Ko and co-workers [64]. This catalyst exhibits an intrinsic catalytic activity higher than that of the commercial P25 TiO_2 particles, even though the quantum yield, which affects the intrinsic activity values, is significantly higher in the case of the particulate system than for the monolithic catalysts, as is indicated in Articles III and VI.

The results presented in Article II indicate that there is no correlation between the catalytic activity of ZnO and several structural characteristics such as the ZnO crystal size (d_{XRD}) or the geometric surface area of the SSWM-supported ZnO particles. A direct correlation between catalytic activity and the amount of polar surfaces, that might be expected for unsupported ZnO particles [82], has only been found for the samples with long ZnO prisms (L>1500 nm). On the other hand, there is a clear correlation between the catalytic activity (parameter A_C) and the dimensions of ZnO nanostructures,
especially the length of the prisms, which exhibits an inverse relation with catalytic activity. This result can be ascribed to the fact that the ultraviolet radiation is better distributed in a SSWM-supported ZnO sample with thinner ZnO nanostructures (i.e., there is a higher quantum yield) [72].

In several cases it has been observed that the reaction order (n) is clearly higher than 1, suggesting that catalyst deactivation has occurred during the reaction. This deactivation is attributed to the photocorrosion of zinc oxide, that produces some loss of catalyst mass, a phenomenon that has been thoroughly studied in this thesis, as described in Articles III and V.

1.3. Photostabilization of SSWM-supported ZnO nanostructures

In recent years, several studies, including Article II, have shown that ZnO can display a higher initial photocatalytic activity than TiO$_2$ [101] but this high activity quickly decreases with reaction time due to ZnO photocorrosion [105]. Several strategies can be found in the literature to avoid photocorrosion, some of which are mentioned in Article III (Fabrication of wire mesh-supported ZnO photocatalysts protected against photocorrosion, Vu et al. Applied Catalysis B: Environmental, 140-141 (2013) 189-198). In that work we present a novel procedure to protect SSWM-supported ZnO catalysts against photocorrosion, which is summarised below.

The catalyst employed in these experiments consists of SSWM-supported high surface area ZnO nanosheets with a large proportion of polar surfaces, as reflected by the high intensity ratio of the XRD peaks corresponding to faces (100) and (002) ($I_{100}/I_{002}=3$). This material was tested for the catalytic photodegradation of methylene blue (MB) under UV irradiation, during several reaction stages.

The catalyst exhibits a good photocatalytic activity. In the first reaction stage all the MB is degraded in less than one hour. Unfortunately the catalytic
Results and Discussion: Block I

Activity diminishes significantly after successive reaction cycles. This loss of activity is undoubtedly a consequence of the photocorrosion process, which causes extensive dissolution of ZnO (after seven cycles, the amount of ZnO dissolved is around 78 wt.%).

As reported in the literature, silver-doped ZnO should lead to an enhancement in catalytic activity and endow the catalyst with a better stability against photocorrosion [109-112]. We have adopted this strategy by depositing Ag nanoparticles on the surface of the catalyst by two different procedures: i) equilibrium impregnation and ii) photodeposition. The results obtained show that the doping of ZnO with small amounts of silver enhances its initial photocatalytic activity. However, it was found that the photocatalytic stability of Ag-doped ZnO is very similar to that of the undoped catalyst. A new strategy was therefore examined to enhance catalyst photostability, consisting of coating the catalyst with a thin layer of polysiloxane (XPs), adapted from the methodology developed by Dastjerdi et al. [153] for protecting antibacterial Ag-TiO₂ nanoparticles in textiles. This procedure reduces the surface area of the catalyst (from 80 to 28 m² g⁻¹) but does not affect the crystal structure of the ZnO. The XPs coating was performed with a dip-coating device designed and fabricated in our laboratory, which allows cycling operation. The XPs layer was homogeneous and almost transparent to incoming radiation.

The catalytic activity of XPs-protected SSWM-supported ZnO is initially lower than that of the unprotected catalyst, although it remains approximately constant in the following reaction stages. Consequently after 3 stages the catalytic activity of the XPs-protected catalyst becomes significantly higher than that of the uncoated catalyst. It has been established that the optimum concentration of XPs in the dip-coating solution is 1 wt.%; a concentration that completely prevents the loss of ZnO during the successive reaction stages.

We also coated the Ag-doped SSWM-supported ZnO catalysts with XPs solutions of different concentrations. A XPs concentration of 0.3 wt.% in the
A tentative mechanism for the photocatalytic reaction in the XPs-coated ZnO particles comprises the photoexcitation of the ZnO particles by the incoming UV radiation through the transparent XPs monolayer, the generation of electron–hole pairs on the ZnO electronic bands, the migration of the generated excitons through the XPs monolayer towards the external surface of the coated particles and the final photodegradation reactions on that surface. A too thick XPs layer (Si/Zn>>1) causes the excitons to recombine before they reach the external surface of the XPs coating (and hence a loss of catalytic activity) whereas a too thin layer (Si/Zn<1) is insufficient to protect the ZnO particles from the action of water (i.e., to prevent the photocorrosion reaction (10)).
Article I

Tailoring the synthesis of stainless steel wire mesh-supported ZnO

Tan T. Vu, Laura del Río, Teresa Valdés-Solís and Gregorio Marbán

## Tailoring the synthesis of stainless steel wire mesh-supported ZnO

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- Crystal structure

### Abstract

The aim of this work was to synthesize different nanostructures of zinc oxide supported on a stainless steel wire mesh, using hydrothermal processes in which several conditions were applied. The effect of the different synthesis parameters on the final properties of the samples (yield and geometrical dimensions) were analysed and discussed. The ZnO nanomaterials obtained exhibit a homogeneous distribution over the metallic wire mesh, with mass yields in the range of 3-30 wt.%, a prismatic morphology with a hexagonal cross-section, lengths between 700 nm and 6 µm and widths in the 70 nm-2.3 µm range. These nanomaterials are intended to be applied in photocatalytic reactions and as catalyst supports.

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## 1. Introduction

Zinc oxide is a commercial material of significant interest that is used in many different applications. It is frequently used in paints, protective coatings for metals, rubber processing, and sunscreens because it is abundant and nontoxic. ZnO is industrially used as a heterogeneous catalyst in several processes, from which the production of methanol from syngas is the most important in terms of volume [1]. ZnO films and nanostructures are also of interest due to their semiconducting and optical properties, which make them suitable for emerging electronic applications. The use of ZnO as a photocatalyst for the degradation of synthetic organic dye-water mixtures makes it a strong contender against TiO_2_ photocatalysts. Zinc oxide shares many of the properties of TiO_2_ including a similar bandgap and, due to the high demand for titanium in multiple applications, the price of ZnO is now lower than that
of TiO$_2$ [2]. Several authors claim that ZnO is even more active than TiO$_2$ and displays a higher quantum yield [3,4].

The use of these ZnO catalysts in powder form presents a series of technical challenges, one of which is the separation of the particles from the reaction medium. Supporting the catalysts allows the dispersion of the particles to be maintained and, in this way, sintering and agglomeration are avoided. Some supports also take part in the catalytic process, favouring either charge separation (high electric conductivity supports) or the adsorption of reactants (highly porous supports). One can find many works in the literature describing the direct synthesis of zinc oxide on different supports [5-10] such as ITO (indium tin oxide [8,9]), copper plates [10], silica, crystal or polyester films [9], polyethylene fibres [11], etc. By means of the synthesis methods described in the literature [12] it is possible to obtain a wide variety of crystal morphologies, using structure directing agents, such as hexamethylenetetramine, polyethylene glycol, polyethylene imine, etc. In general they are low temperature hydrothermal methods (below 100°C) sometimes followed by a calcination stage (350-450°C).

We recently developed a procedure to prepare cobalt oxide catalysts supported on metallic wire meshes which perform very well in different processes [13,14]. In the present work we have attempted to synthesize ZnO nanoparticles on stainless steel wire meshes by using methods as reported in the literature but with other supports [6-10]. These methods occasionally involve a previous seeding stage consisting of impregnation with zinc acetate. This stage makes it possible to obtain a homogeneous dispersion of ZnO crystals in the subsequent stages [7]. To our knowledge only one precedent can be found in the literature for the preparation of ZnO crystals on the surface of a stainless steel wire mesh [15]. This work in question was released during the preparation of the present study and dealt with the synthesis of CuO-ZnO nanowires on stainless steel meshes similar to those used here. This catalyst was tested for the catalytic photodegradation of Acid Orange 7 under ultraviolet irradiation. The results of the test showed that the CuO-ZnO structures supported on the stainless steel mesh exhibit an enhanced photocatalytic activity with respect to other supports. The authors associated this effect with a better mass transfer through the stainless steel mesh. The synthetic procedures employed in the present work have produced materials with a wide range of properties, rendering them of interest not only for photocatalytic applications but also as catalyst supports.
2. Experimental

2.1. Materials

All the chemical reagents were of analytical grade and were not subjected to any additional purification before use. All the aqueous solutions were prepared with deionised water. The support was a stainless steel wire mesh [30 μm wire diameter and 40 μm screen opening] provided by CISA. Prior to being coated with ZnO the mesh was washed with HNO₃ (4M) at 60°C for 4 hours and then with isopropyl alcohol in an ultrasonic bath for 10 minutes. The following reagents were used: hexahydrated zinc nitrate (98%; Sigma-Aldrich), zinc chloride (Prolabo), dihydrate zinc acetate (Prolabo), polyethylene imine (PEI; MW=800; Sigma-Aldrich), hexamethylene-tetramine (HMTA; >99.5%; Sigma-Aldrich), polyethylene glycol (PEG; MW=10,000; Sigma-Aldrich); aqueous ammonium hydroxide (20-30 vol.%; Sigma-Aldrich), ethanol (96%; Panreac) and potassium hydroxide (>85%; Probus).

2.2. Synthesis methods

The synthesis of ZnO was performed on supports consisting of rectangular pieces of wire mesh (5×3 cm²), previously washed with HNO₃ (4M) at 60°C for 4 hours and then with isopropyl alcohol in an ultrasonic bath for 10 minutes. None of the synthesis methods mentioned below have been ever applied to stainless steel wire meshes.

Seeding. In some cases, prior to the synthesis of the ZnO crystals on the mesh surface, ZnO seeds were allowed to form on the clean mesh to act as active centres for the growth of the ZnO crystals. Seeding was carried out by adapting a procedure used by Greene et al. [5,6]. A 5 mM solution of zinc acetate in ethanol was added dropwise onto the clean mesh for 10 seconds. Afterwards the mesh was rinsed with ethanol and nitrogen-blown until dryness. This procedure was repeated five times. Finally, the mesh coated with small zinc acetate crystallites was calcined in air at 350°C for 25 minutes. The complete process (impregnation + calcination) was carried out between one and three times (prefixes S0, S1, S2 and S3 in sample references for no seeding and one to three seeding stages, respectively). This method favours a homogeneous distribution of ZnO quantum dots (3-4 nm) over the support surface [7,8].
Ko method [7]. This method produces ZnO nanowires over the substrate surface. 50 mL of an aqueous solution of Zn(NO$_3$)$_2$·6H$_2$O (25 mM), HMTA (25 mM) and PEI (5 mM) was introduced into a Pyrex® bottle. Next the seed-covered mesh (S2) was vertically inserted into the bottle which was then closed and kept in an oven at 95°C for 7 hours. After reaction the mesh was thoroughly washed with deionised water and calcined in air at 350°C for 10 minutes.

Bai method [10]. This method provides samples with nanorose morphologies. The precursor solution was prepared by dissolution of 1.7 g of ZnCl$_2$ in 50 mL of deionised water and kept under magnetic stirring. Next a concentrated solution of ammonia (32 vol.%) was added dropwise until the precursor solution reached a pH of 10.35. The solution was then introduced into a polypropylene flask containing the mesh. The flask was closed and immersed in a water bath at 95°C for 5.5 hours. After the synthesis the flask was allowed to cool down to room temperature. The mesh was thoroughly washed with deionised water and immersed in an ultrasonic bath for 10 minutes in order to detach all the particles not firmly linked to the mesh surface. Finally the sample was vacuum dried at 60°C for 1 hour.

Shao method [16]. This method is a slight modification of Bai method. The only difference lies in the hydrothermal synthesis time. In this case, the flask containing the mesh was immersed in a water bath at 95°C for 2 hours and then cooled down to room temperature. After thoroughly washed with deionized water and cleaned in an ultrasonic bath for 10 minutes, the sample was vacuum dried at 60°C for 1 hour.

Xu method [6]. This method leads to the formation of parallel nanorods. The clean mesh was subjected to two seeding stages (S2) before the synthesis of ZnO. 50 mL of an aqueous solution of Zn(NO$_3$)$_2$·6H$_2$O (25 mM), HMTA (12.5 mM), PEI (5 mM) and ammonium hydroxide (0.35 M) was introduced into a Pyrex® bottle. Next the mesh was vertically inserted into the bottle which was then closed and kept in an oven at 87°C for 3 hours. After the reaction the mesh was thoroughly washed with deionised water and calcined in air at 450°C for 30 minutes.

Feng method [8]. The wire mesh was subjected to two seeding stages (S2) prior synthesis. 35 mL of water and 0.02 g of polyethylene glycol were introduced into a Pyrex® bottle. The mesh was then immersed in the solution. After one hour 15 mL of an aqueous solution of Zn(NO$_3$)$_2$·6H$_2$O (90 mM) and HTMA (90 mL) was added. The bottle was then closed and kept in an oven at 95°C for 4 hours. After the synthesis the
bottle was allowed to cool down to room temperature. The mesh was thoroughly washed with deionised water and vacuum dried at 60°C for 1 hour.

*Chen Method* [9]. According to the authors this method allows bushes of nanowires to form on the support surface. Two solutions were prepared: (#1) 3.7 g of KOH in 17 mL of water and (#2) 1.85 g of Zn(CH$_3$COO)$_2$·2H$_2$O in 16.6 mL of water. Solution #2 was added dropwise to the solution #1 under magnetic stirring. The resulting transparent solution was introduced into a Pyrex® bottle. The mesh was inserted into the bottle that was then closed and immersed in a water bath at 25°C for different lengths of time (0.5-24h). After the synthesis the mesh was thoroughly washed with deionised water and vacuum dried at 60°C for 1 hour.

Table 1 shows the group of variables that were used in this work to prepare the different catalysts.

**Table 1.** Variables employed in this work for the synthesis of stainless steel wire mesh-supported ZnO

<table>
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<th>Method</th>
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<th>Additives</th>
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<td>Zn(NO$_3$)$_2$</td>
<td>HMTA</td>
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<td>450°C 30min</td>
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<td>S2-Ko</td>
<td>Zn(NO$_3$)$_2$</td>
<td>HMTA</td>
<td>95°C 4h</td>
<td>350°C 10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PEI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feng [8]</td>
<td>S2-Feng</td>
<td>Zn(NO$_3$)$_2$</td>
<td>HMTA</td>
<td>95°C 4h</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>S0-Feng-8h</td>
<td></td>
<td>PEG</td>
<td>95°C 8h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S0-Feng-14h</td>
<td></td>
<td></td>
<td>95°C 14h</td>
<td></td>
</tr>
<tr>
<td>Chen [9]</td>
<td>S0-Chen-X</td>
<td>Zn(CH$_3$COO)$_2$</td>
<td>KOH</td>
<td>25°C Xh</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>S2-Chen-X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S0-Chen-50°C</td>
<td></td>
<td></td>
<td>50°C 10h</td>
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</tr>
<tr>
<td></td>
<td>S2-Chen-50°C</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bai [10]</td>
<td>S0-Bai</td>
<td>ZnCl$_2$</td>
<td>NH$_4$OH</td>
<td>95°C 5.5h</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>S2-Bai</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S2-Bai-C</td>
<td></td>
<td>NH$_4$OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PEI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shao [16]</td>
<td>S0-Shao</td>
<td>ZnCl$_2$</td>
<td>NH$_4$OH</td>
<td>95°C 2h</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>S2-Shao</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* # prefix refers to the number of seeding stages

**X** suffix refers to the synthesis time in hours (0.5 – 24)
2.3. Characterization

*Structural characterization.* The aspect and morphology of the catalysts were studied by means of scanning electron microscopy (SEM, Zeiss, DSM 942 model). Image analysis of the microphotographs was used to evaluate the ZnO crystal dimensions (W=width, L=length, S=average separation between adjacent prisms; nm). With these parameters and the ZnO yield on a mass basis (Y), the geometric surface area of ZnO (cm²/gZnO) was evaluated by means of the following equation:

\[
S_g = 3S_m \left( \frac{W \left( L + \frac{3}{8} W \right)}{(S + W)^2} \right) \left( 1 - \frac{Y}{100} \right)
\]

where \( S_m \) is the specific surface area of the clean mesh (135 cm²/g). To derive this equation it is assumed that the ZnO crystals are hexagonal prisms growing perpendicular to the substrate surface. Therefore, application of this methodology to the samples with flower-like arrangements of prisms introduced a high degree of uncertainty in the value of geometric surface area. This parameter, which in no case is equivalent to the specific surface area of the samples, should be only used to rank the materials with different geometric surface areas. The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA and using Cu-Kα radiation (\( \lambda = 0.15406 \) nm). The crystal size values were estimated from the XRD pattern by means of Scherrer’s equation (\( d_{XRD} \)).

3. Results and Discussion

The synthesis parameters of the different methods employed are the key to controlling the size, distribution and morphology of the ZnO crystals obtained on the stainless steel meshes. Taking into account the potential applications of ZnO (catalyst and photocatalyst), it would appear advisable to maximize the ZnO yield and geometric surface area, as well as promote the formation of active planes in the photocatalytic reaction, for instance, by increasing the ratio of the polar surface (0001) to the non polar surfaces [17]. Although the synthesis methods used in this work are sufficiently well described in the literature, it must be said that we introduced a number of modifications in some parameters (seeding, additives, synthesis time and temperature, etc.) in order to improve the final properties of the catalysts (yield, homogeneity degree, etc.).
3.1. Effect of seeding

The deposition of seeds on the surface of the support allows the crystals to be grown out of the seeds by nucleation \[18,19\]. This procedure leads to an improvement in the distribution and yield of crystals on the mesh. Fig. 1 shows the effect of the number of seeding stages on the yield of ZnO for the different synthesis methods employed. In general, the yield increases with the number of seeding stages. In the case of the materials with the lowest yields (Ko and Chen (ZnCl\(_2\)) methods) the highest amount of ZnO was obtained after two seeding stages. The yields obtained by the Chen method are clearly dependent on the type of precursor employed (zinc chloride or zinc acetate), as can be appreciated in Fig. 1.

![Figure 1](image-url)

**Figure 1.** Effect of seeding steps on ZnO yield for the different synthesis methods employed

This result is contrary to what was observed by Chen et al. \[9\], who reported that the growth of the ZnO crystals on the surface of ITO was independent of the zinc precursor. As can be seen from the SEM photographs in Figs. 2 to 6, the ZnO prisms obtained by growth of crystals on the unseeded mesh (S0 prefix) display a disordered arrangement, without any preferential growing directions, whereas the meshes
previously coated with seeds show, in general, highly compact crystals that have grown perpendicular to the substrate. The difference between using unseeded and seeded meshes can be clearly appreciated in Table 2, which shows the values of the ZnO yields, as well as the geometric and crystal properties of the samples. Thus, the values corresponding to the length, width and separation of the crystals for S0-Bai and S0-Shao are clearly higher than those for S2-Bai and S2-Shao, respectively, confirming the high degree of compaction of the seeded materials. In most cases these samples were prepared after two seeding stages.

3.2. Organic additives

Several works in the literature on ZnO synthesis report the use of organic additives such as cetyltrimethylammonium bromide (CTAB) [20], ethylenediamine [21], diaminopropane (DAP) [22], PEI [6,7], PEG [8], etc. These molecules can be selectively bonded to certain planes of the ZnO nuclei, in order to cause their passivation and promote their selective growth in the direction perpendicular to the non-passivated planes. In the present work we used PEG and PEI as surfactant polymers. In the original method by Feng et al. [8] PEG was used to produce different ZnO morphologies (microrods and microspheres). To achieve this, the authors immersed the substrate (ITO) in the precursor solution with all the components, including PEG. In our study we immersed the meshes (seeded or unseeded) in a simple PEG solution for one hour before synthesis. In this way we were able to obtain yields around 40% higher than those obtained without any previous PEG impregnation.

PEI is generally used to avoid the growth of crystals in the bulk solution so as to favour the formation of crystals on the substrate, where the ZnO nuclei are larger and cannot be completely passivated by the polymer [6,7]. In the present work PEI was added to the precursor solutions for the Bai, Xu and Ko methods. In the last two methods the addition of PEI forms part of the synthesis procedure described by the authors. We applied it to the Bai method to test its effect on the properties of the resulting samples. A decrease in the yield from 27 wt.% (S2-Bai) to 23 wt.% was observed. This difference is attributed to the formation of nanocrystals in solution which is favoured by the absence of PEI. In principle the addition of PEI yields more homogeneous samples, with no deposits except those directly linked to the mesh surface. However, it also involves the incorporation of a calcination stage (350°C, 20 min) to remove the organic compound (S2-Bai-C). The calcination stage did not
Synthesis of SSWM-supported ZnO

seem to affect the samples obtained by the Xu and Ko methods, but with the Bai method it produced a clear distortion of the ZnO prisms, as a consequence of their high degree of compaction on the mesh surface (Fig. 2).

Table 2. Values of the ZnO yield and geometric and crystal properties of the samples

<table>
<thead>
<tr>
<th>Reference</th>
<th>L (nm)</th>
<th>W (nm)</th>
<th>S (nm)</th>
<th>ZnO yield, Y (wt.%)</th>
<th>Sg (cm²/gZnO)</th>
<th>Crystal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2-Ko</td>
<td>700</td>
<td>70</td>
<td>200</td>
<td>4.2</td>
<td>266</td>
<td>dXRD, I100/I002, I101/I002</td>
</tr>
<tr>
<td>S0-Bai</td>
<td>6000</td>
<td>2300</td>
<td>3200</td>
<td>7.0</td>
<td>186</td>
<td></td>
</tr>
<tr>
<td>S2-Bai</td>
<td>2600</td>
<td>520</td>
<td>500</td>
<td>26.8</td>
<td>401</td>
<td></td>
</tr>
<tr>
<td>S2-Bai-C</td>
<td>3500</td>
<td>600</td>
<td>350</td>
<td>27.3</td>
<td>410</td>
<td></td>
</tr>
<tr>
<td>S2-Xu</td>
<td>5100</td>
<td>140</td>
<td>500</td>
<td>19.0</td>
<td>1216</td>
<td></td>
</tr>
<tr>
<td>S3-Xu</td>
<td>4100</td>
<td>150</td>
<td>630</td>
<td>21.0</td>
<td>511</td>
<td></td>
</tr>
<tr>
<td>S0-Feng-8h</td>
<td>1300</td>
<td>200</td>
<td>500</td>
<td>5.8</td>
<td>189</td>
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<tr>
<td>S0-Feng-14h</td>
<td>1900</td>
<td>200</td>
<td>650</td>
<td>12.1</td>
<td>192</td>
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<tr>
<td>S2-Feng</td>
<td>700</td>
<td>100</td>
<td>200</td>
<td>2.9</td>
<td>315</td>
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</tr>
<tr>
<td>S0-Shao</td>
<td>4100</td>
<td>1800</td>
<td>3200</td>
<td>7.1</td>
<td>121</td>
<td></td>
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<tr>
<td>S2-Shao</td>
<td>3600</td>
<td>430</td>
<td>100</td>
<td>28.4</td>
<td>1638</td>
<td></td>
</tr>
<tr>
<td>S0-Chen</td>
<td>1700</td>
<td>150</td>
<td>460</td>
<td>14.2</td>
<td>243</td>
<td></td>
</tr>
<tr>
<td>S0-Chen-50°C</td>
<td>1250</td>
<td>200</td>
<td>850</td>
<td>13.3</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>S2-Chen-10</td>
<td>1500</td>
<td>80</td>
<td>150</td>
<td>17.8</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>S2-Chen-24</td>
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<td>65</td>
<td>100</td>
<td>33.9</td>
<td>1159</td>
<td></td>
</tr>
<tr>
<td>S2-Chen-50°C</td>
<td>1700</td>
<td>80</td>
<td>200</td>
<td>19.2</td>
<td>573</td>
<td></td>
</tr>
</tbody>
</table>

3.3. Effect of synthesis temperature and time

The effect of synthesis temperature on the samples prepared by the methods of Ko, Bai and Chen was also analysed. When the standard temperature of 95°C was used in the Ko method, the ZnO yields were low but appreciable (2-4 wt.%). When the temperature was decreased to 65°C the yield dropped to 0.2 wt.%. In the Bai method, the yield decreased from ~27 wt.% at 95°C (S2-Bai) to ~0.2 wt.% at 50°C. In the Chen method, the standard temperature specified in the procedure is 25°C [9]. After 10 hours at this temperature we obtained ZnO yields of between 14 wt.% (unseeded) and 18 wt.% (two seeding stages).
Figure 2. SEM microphotographs of the ZnO-meshes synthesised by the Bai method illustrating the effect of seeding.

A temperature increase up to 50°C produced similar yields (13 wt.% and 19 wt.% for the S0 and S2 meshes, respectively), although the morphology of the resulting samples was slightly different, as can be seen in Fig. 3. In the case of the unseeded
samples, at both temperatures the zinc oxide deposits were arranged like nanoflowers, but an increase in synthesis temperature produced thicker prisms. In the samples subjected to two seeding stages the nanocrystals grew perpendicular to the mesh surface. Again at the higher temperature the crystals were thicker and more rounded at the tip, and some parts of the mesh remained uncovered after synthesis (Fig. 3). The effect of synthesis time on the yield and geometric characteristics of ZnO was also analysed in the case of the samples synthesized by the Chen and Feng methods, SEM images of which are shown in Figs. 3, 4 and 5. For the samples prepared by the Chen method there was a clear increase in ZnO yield with synthesis time, as can be observed in Fig. 6. However, after 10 hours the increase in yield is due to the formation of large microcrystals of a different morphology to that of the nanocrystals formed on the mesh surface (Fig. 4).

With respect to the samples prepared by the Feng method, the unseeded samples showed an increase in ZnO yield from ~6 to ~12 wt.% when the synthesis time was increased from 8h to 14h. This was reflected in a higher density of nanoflowers, although their geometrical properties remained similar (Fig. 5). Again, when the mesh was seeded the nanoprisms did not grow grouped together in nanoflower arrangements but individually on the mesh surface and showed a more homogeneous distribution (Fig. 5; S2-Feng).

3.4. Tailoring the ZnO deposits

As can be seen in Table 2, and as mentioned above, if the right synthesis method is chosen it is possible to vary the ZnO yield between ~3 and ~29 wt.%, group the prisms in nanoflower arrangements (unseeded samples) or in parallel arrays (seeded samples) and adjust the height and width of the prisms over a range of 700-6000 nm and 70-2300 nm, respectively. In this way the ZnO deposit can be tailored for the process for which it is intended (as a catalyst in photocatalytic processes, as a catalyst support for thermal catalytic process, etc.). The synthesis methods that produce the highest yields are the Bai method (Fig. 2), the Xu method (Fig. 7) and the Shao method (Fig. 8). The Shao method is identical to the Bai method, except that it requires a shorter synthesis time.
Figure 3. SEM microphotographs of the ZnO-meshes synthesised by the Chen method illustrating the effect of synthesis temperature.
This is why the samples produced by both methods are so similar, both in their appearance (Figs. 2 and 8) and in their geometrical parameters (Table 2). The Xu method applied to the seeded meshes produces a very ordered alignment of the prisms that grow perpendicular to the mesh surface (Fig. 7). On the other hand, the Feng and Ko methods show the lowest yields of all the prepared samples. Nevertheless they produce very homogeneous coverings (bottom image in Fig. 5 and top image in Fig. 7) with randomly oriented prisms which are very small (Table 2) and, in the case of the sample prepared by the Ko method, with a very narrow distribution of geometric parameters. By means of equation (1) a rough calculation of the geometrical surface area of the samples can be performed. The highest geometrical surface areas are obtained by the methods of Xu and Shao, as they are one order of magnitude higher than that of the clean mesh.

Figure 4. SEM microphotograph of a ZnO-mesh synthesised by the Chen method after a synthesis time of 24 h
Figure 5. SEM microphotographs of the ZnO-meshes synthesised by the Feng method illustrating the effect of synthesis time.
The crystalline parameters ($d_{XRD}$ and $I_{100}/I_{002}$ and $I_{101}/I_{002}$ ratios) were obtained from the X-ray diffractograms displayed in Fig. 9, in which the peaks signalled with the Miller indexes correspond to the hexagonal structure of ZnO (zincite, 01-071-6424 pattern) [16, 23, 24]. There is a clear difference in the peak positions for the samples prepared by the Bai and Shao methods with respect to those of the other materials. This is evidenced by a shift of $\sim 0.08^\circ$ in the (002) peak towards lower angles, which implies a slightly larger unit cell for the materials synthesized by these methods. The diffraction pattern for these samples is coincident with that of a sample synthesized by García Martínez et al. [25] using a method with basic zinc chloride in basic conditions, i.e., the same precursor and conditions as used in the Bai and Shao methods. According to García Martínez et al. [25] this type of synthesis confers certain specific microstructural properties on the resulting crystals which explains the altered XRD peak positions. On the other hand, after the calcination of the sample prepared by the Bai method (S2-Bai C) the spectrum of the sample reverts to the typical position of zincite (Fig. 9). This might indicate that the shift in the peaks in the
case of the uncalcined samples could be due to the incorporation of impurities into the crystal network of ZnO (e.g. chloride) which decompose during calcination.

**Figure 7.** SEM microphotographs of the ZnO-meshes synthesised by the Ko and Xu methods
Figure 8. SEM microphotographs of the ZnO-meshes synthesised by the Shao method.

Figure 9. XRD spectra of the ZnO-stainless steel meshes synthesised in this work.
The crystal size of the samples is relatively small (in the range 30-45 nm) with the samples showing no clear trends (Table 2). In some works described in the literature it has been proven that photocatalytic activity does not depend on ZnO crystal size, but is proportional to the ratio of the intensities of peak (110) to peak (002) (parameter \( I_{110}/I_{002} \) in Table 2) \([17]\). \( I_{110}/I_{002} \) is higher when the hexagonal structures grow preferentially in the direction of the c axis \([26,27]\). The results included in Table 2 show that this parameter varies over a wide range, 0.07-1.27, promising again a wide range of materials for different applications.

4. Conclusions

Zinc oxide nanostructures supported on stainless steel meshes were synthesized by different methods reported in the literature. Certain parameters of these methods were modified in this work so as to optimize the final properties of the resulting materials. The methods employed yield materials with homogeneous coverings of hexagonal prisms and a wide range of geometrical and crystal properties: distribution in nanoflower arrangements (unseeded meshes) or in parallel arrays (seeded meshes), a ZnO yield in the range of 3-30 wt.\%, a crystal size in the range of 30-45 nm, XRD intensity ratios \( I_{110}/I_{002} \) in the range of 0.07-1.27 and uniform prismatic dimensions with a wide range of values (length 700-6000 nm; width 70-2300 nm). The inclusion of seeding stages, organic additives and higher synthesis times produces higher ZnO yields and gives rise to a more ordered distribution of the nanoprisms over the mesh surface.

References

Synthesis of SSWM-supported ZnO


Article II

Stainless steel wire mesh-supported ZnO for the catalytic photodegradation of methylene blue under ultraviolet irradiation

Tan T. Vu, Laura del Río, Teresa Valdés-Solís and Gregorio Marbán

Stainless steel wire mesh-supported ZnO for the catalytic photodegradation of methylene blue under ultraviolet irradiation

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HIGHLIGHTS
► Novel support of ZnO nanoparticles for photodegradation of organic contaminants.
► Small size of ZnO particles is key for high activity.
► The best catalyst has superior activity to TiO2 P25.
► Catalyst deactivation can be recognised by the reaction order.

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ABSTRACT
The aim of this study was to assess the activity of catalysts formed by nanostructured zinc oxide supported on stainless steel wire mesh for the photocatalytic degradation of methylene blue under UV irradiation. Catalysts prepared by means of different low temperature synthesis methods, as described in a previous work (Vu et al., Mater. Res. Bull., 47 (2012) 1577-1586), were tested. A new activity parameter was introduced in order to compare the catalytic activity of the different catalysts. The best catalyst showed a catalytic activity higher than that of the reference material TiO2 P25 (Degussa-Evonik). This high activity is attributed to a higher quantum yield derived from the small particle length of the ZnO deposited on the wire mesh. The photocatalytic degradation kinetics of methylene blue fitted a potential model with n orders ranging from 0.5 to 6.9. Reaction orders over 1 were attributed to catalyst deactivation during the reaction resulting from the photocorrosion of ZnO

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1. Introduction

Around one million tons of synthetic organic dyes are produced every year for the textile, leather, paint, food, plastics and cosmetics industries. A sizeable fraction of this is lost during the industrial process in wastewaters which are usually discharged into rivers and seas. The decolouring and cleaning of these polluted effluents is essential for the environmental sustainability of the above-mentioned industries.

Heterogeneous photocatalysis is one of the most attractive technologies for the decomposition of organic substances in wastewaters [1]. There are several materials with appropriate properties for acting as photocatalysts, such as TiO₂, ZnO, CdS, iron oxides, WO₃, ZnS, etc. Of these TiO₂ is the most widely used catalyst because it is relatively cheap and supplies photogenerated holes with great oxidative potential [2]. Zinc oxide shares many of the properties of TiO₂, including a similar bandgap. Due to the high demand for titanium in multiple applications the price of ZnO is now lower than that of TiO₂ [3]. Several studies claim that ZnO is even more active than TiO₂ and provides a higher quantum yield [4,5].

The use of ZnO catalysts in powder form implies a series of technical challenges, one of which is the separation of the particles from the reaction medium. Using a support for the photocatalysts maintains the dispersion of the particles and prevents sintering and agglomeration. Some supports also play an active role in the catalytic process by favouring charge separation (high electric conductivity supports) or the adsorption of reactants (highly porous supports). There are many reports in the literature of the direct synthesis of zinc oxide on different supports [6-11] such as ITO (indium tin oxide [9,10]), copper plates [11], silica, crystal or polyester films [10], polyethylene fibres [12], etc. The synthesis methods described in the literature [13] produce a wide variety of crystal morphologies, depending on the type of structure directing agent used, e.g., hexamethylenetetramine, polyethylene glycol, polyethylene imine, etc. In general these are low temperature hydrothermal methods (below 100°C) sometimes followed by a calcination stage (350-450°C).

We recently used several of these procedures [7-11] to synthesize ZnO nanoparticles supported on stainless steel wire mesh [14]. Wire mesh supported materials have recently been used as monolithic catalysts for different reactions (e.g. the preferential oxidation of CO [15], methanol decomposition [16] and N₂O decomposition [17]). In the present study the materials produced were tested for the photodegradation of methylene blue solutions under ultraviolet irradiation. The
results were then compared with those achieved with commercial TiO$_2$ particles (Degussa Evonik P25).

2. Experimental

2.1. Catalyst

All of the chemical reagents were of analytical grade and were not subjected to additional purification. The aqueous solutions were prepared with deionised water. The support was a stainless steel wire mesh [with a wire diameter of 30 μm and a screen opening of 40 μm] provided by CISA.

Table 1. Variables used in this work for the synthesis of stainless steel wire mesh-supported ZnO

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference$^a$</th>
<th>Synthesis</th>
<th>Additives</th>
<th>Crystal growth</th>
<th>Air calcination</th>
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</thead>
<tbody>
<tr>
<td>Xu [7]</td>
<td>S2-Xu</td>
<td>Zn(NO$_3$)$_2$</td>
<td>HMTA</td>
<td>87°C 3h</td>
<td>450°C 30min</td>
</tr>
<tr>
<td></td>
<td>S3-Xu</td>
<td></td>
<td>NH$_4$OH</td>
<td></td>
<td>450°C 30 min</td>
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<tr>
<td>Ko [8]</td>
<td>S2-Ko</td>
<td>Zn(NO$_3$)$_2$</td>
<td>HMTA</td>
<td>95°C 7h</td>
<td>350°C 10 min</td>
</tr>
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<td></td>
<td></td>
<td>PEI</td>
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<tr>
<td>Feng [9]</td>
<td>S2-Feng</td>
<td>Zn(NO$_3$)$_2$</td>
<td>HMTA</td>
<td>95°C 4h</td>
<td>-</td>
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<td></td>
<td></td>
<td>PEI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chen [10]</td>
<td>S2-Chen-10</td>
<td>Zn(CH$_3$COO)$_2$</td>
<td>KOH</td>
<td>25°C 10h</td>
<td>-</td>
</tr>
<tr>
<td>Bai [11]</td>
<td>S0-Bai</td>
<td>ZnCl$_2$</td>
<td>NH$_4$OH</td>
<td>95°C 5.5h</td>
<td>350°C 20 min</td>
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<tr>
<td></td>
<td>S2-Bai</td>
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</tr>
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</tr>
</tbody>
</table>

$^a$ S# prefix refers to the number of seeding stages

Prior to being coated with ZnO, the mesh was washed with HNO$_3$ (4M) at 60°C for 4 hours and then with isopropyl alcohol in an ultrasonic bath for 10 minutes. The following reagents were employed: hexahydrated zinc nitrate (98%; Sigma Aldrich),
zinc chloride (Prolabo), dihydrated zinc acetate (Prolabo), polyethylene imine (PEI; MW=800; Sigma Aldrich), hexamethylenetetramine (HMTA; >99.5%; Sigma Aldrich), polyethylene glycol (PEG; MW=10,000; Sigma Aldrich); aqueous ammonium hydroxide (20-30 vol.%; Sigma Aldrich), ethanol (96%; Panreac) and potassium hydroxide (>85%; Probus). The different synthesis procedures used with these reagents [7-11,18] are described in detail in [14]. Table 1 contains a list of all of the catalysts prepared in this work together with the variables employed for each method of synthesis. The references used in this work are the same as those in [14].

The photocatalytic experiments were performed over aqueous solutions of monohydrated methylene blue (>96%; Riedel de Häen). Commercial TiO₂ particles (Degussa Evonik P25) were used for comparison purposes.

2.2. Catalyst characterization

The morphology of the catalysts was studied by means of scanning electron microscopy (SEM, FEI Quanta FEG 650 model). Image analysis of the microphotographs was applied in order to evaluate the ZnO crystal dimensions (W=width, L=length, S=average separation between adjacent prisms; nm). With these parameters and the ZnO yield on a mass basis (Y, wt.%), the geometric surface area of ZnO (cm²/g) was evaluated by means of the following equation:

\[
S_g = \frac{35m}{S + W} \left( W \left( L + \frac{3}{8} W \right) \right) \frac{1 - \frac{Y}{100}}{\left( S + W \right)^2}
\]  

(1)

where \( S_m \) is the specific surface area of the clean mesh (135 cm²/g). To derive this equation it was assumed that the ZnO crystals are hexagonal prisms that grow perpendicular to the substrate surface. Therefore, the application of this method to the samples with a flower-like prism arrangement introduced a high degree of uncertainty with respect to the geometric surface area value. This parameter, which in no case is equivalent to the specific surface area of the samples, should only be used to rank materials with different geometric surface areas. The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA and using Cu Kα radiation (\( \lambda = 0.15406 \) nm). The crystal size values were estimated from the XRD pattern by means of Scherrer’s equation (\( d_{XRD} \)). The relative abundance of polar surfaces in the catalysts was evaluated from the ratio...
SSWM-supported ZnO photocatalyst

of the intensities of peak (101) to peak (002) \( I_{101}/I_{002} \) in the zincite XRD patterns. The values for all these structural characterisation parameters can be found in [14].

2.3. Photocatalytic tests

The photocatalytic methylene blue degradation experiments were carried out both on the supported catalysts (1×5 cm\(^2\) strips weighing ~100 mg) and on the commercial TiO\(_2\) particles (Degussa P25; 5-20 mg) in a 400 mL quartz beaker illuminated by two ring-type UV 22W lamps (Luzchem Ring-Illuminator) which predominantly emit radiation at 351 nm. The catalysts were immersed in a 60 mL aqueous solution of methylene blue, with an initial concentration of 10 mg/L. The reaction medium was magnetically stirred for 30 min under darkness to ensure adsorption/desorption equilibrium between the dye and the photocatalyst. Next the reactor was exposed to the UV lamps. Analytical samples were extracted for measurement after various reaction times, those with TiO\(_2\) particles being centrifuged to remove the particles before analysis. The visible absorption peaks of the analyzed samples were recorded in the 400-800 nm range by means of a UV-Vis spectrometer (Shimadzu UV-2401PC). The true methylene blue concentration was obtained from the visible absorption spectra by means of a recently published deconvolution technique [19] that takes into account the contribution of reaction intermediates to the spectra. In order to compare the photocatalytic activities of the materials the following considerations were applied:

(i) the catalyst dosage \( C_c = w_c/V \), where \( w_c \) is the weight of the catalyst and \( V \) is the volume of the liquid) remains constant during the reaction for the TiO\(_2\) particles, but increases slightly for the meshes, due to the regular removal of liquid samples for analysis. Thus, the actual catalyst dosage at any time \( t \) can be estimated from the following equation:

\[
C_c = \frac{w_c}{V_0(1-b\times t)}
\]  \hspace{1cm} (2)

where \( V_0 \) is the initial liquid volume and \( b \) is a constant that can be evaluated by linear regression;

(ii) the reaction rate can be expressed by the potential equation:
\[ \frac{dC_{MB}}{dt} = kC^n_{MB} \]  

(3)

where \( C_{MB} \) is the methylene blue concentration at any given time \( t \), \( k \) is the reaction constant \( (\text{mg}_{MB}^{-1}\cdot\text{mg}_{C}^{-1}\cdot\text{L}^{-1}\cdot\text{min}^{-1}) \) and \( n \) is the apparent reaction order. Factor \( C_C \) is introduced to account for the known dependence of the reaction rate on the catalyst concentration in the absence of screening effects [20-24]. Therefore, under chemical control the reaction constant \( k \) should be independent of the catalyst concentration.

**Table 2.** Equations for evaluating \( C_{MB} \) and the activity parameter \( A_C \) under different circumstances

<table>
<thead>
<tr>
<th>( C_C )</th>
<th>( A_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>constant; ( n=1 )</td>
<td>( \frac{k}{0.693} )</td>
</tr>
<tr>
<td>( C_{MB,0} \exp\left( -kC_{C,0}t \right) )</td>
<td>(4)</td>
</tr>
</tbody>
</table>

(9)

<table>
<thead>
<tr>
<th>( C_C )</th>
<th>( n \neq 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{MB,0} \exp\left[ -kC_{C,0}\left( 1+bt \right) \right] )</td>
<td>(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( C_C )</th>
<th>( n \neq 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{MB,0} \left[ \frac{c_{MB,0}^{1-n} - (1-n)kC_{C,0}t}{0.5^{1-n}} \right]^{1-n} )</td>
<td>(6)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( C_C )</th>
<th>( n \neq 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{MB,0} \left[ \frac{c_{MB,0}^{1-n} - (1-n)kC_{C,0}t}{0.5^{1-n}} \right]^{1-n} )</td>
<td>(7)</td>
</tr>
</tbody>
</table>

For \( n=1 \), equation (3) is coincident with the known Langmuir-Hinshelwood equation for diluted solutions [25]. The resolution of equation (3) under different circumstances gives equations (4) to (7) shown in Table 2. By fitting the concentration values from these equations with the experimental values of \( C_{MB} \) at different times, the values of \( k \) and \( n \) can be obtained. However, the comparison of catalytic activities cannot be performed with the values of \( k \) unless the values of \( n \) are identical. To
overcome this problem, we used the following parameter to evaluate the intrinsic activity of the catalysts:

\[
A_C = \frac{1}{t_{0.5} C_{c,0}}
\]  

(8)

where \(t_{0.5}\) is the semiconversion time (min). Depending on the values of \(C_c\) and \(n\), parameter \(A_C\) (mg \(\cdot\) L\(^{-1}\) \(\cdot\) min\(^{-1}\)) can be evaluated by any of the equations (9) to (12) listed in Table 2. On a ZnO or TiO\(_2\) mass basis, subscript \(C\) in equations (1) to (12) becomes \(Z\); on a catalyst mass basis, subscript \(C\) becomes \(MZ\) (mesh plus ZnO). Parameter \(A_C\) (\(A_Z\) or \(A_{MZ}\)) allows the activities of the catalysts to be compared at the same initial methylene blue concentration. In principle parameter \(A_C\) is independent of the catalyst concentration. This is evident for the cases where the catalyst concentration does not vary during the reaction (equations (9) and (11)).

3. Results and discussion

The deconvolution technique described elsewhere [19] was applied in this work to obtain the true methylene blue concentration during the photodegradation experiments carried out with TiO\(_2\) P25 and with the catalysts listed in Table 1. Figure 1 shows specific spectra corresponding to the samples extracted from the reaction media at different times using different stainless steel mesh-supported catalysts. The grey peaks (P7, P8 and P9) correspond to the intermediate compounds produced during the reaction, whereas the six black peaks correspond to methylene blue, of which P1 exhibits the highest absorbance at the mean wavelength [19]. All the fittings displayed are highly acceptable, as in the case of the other samples analysed in this work.

Figure 2 shows examples of the evolution of absorbance during the reaction for peaks in the visible region (P1: methylene blue, P7-P8-P9: intermediate compounds) corresponding to catalysts with different activities. As can be seen, the absorbances for peaks P7, P8 and P9 vary in a way one would expect for intermediate products, increasing at the beginning of the reaction and starting to decrease when the methylene blue concentration has fallen almost to zero. Especially noticeable is the significant contribution of the absorbances of the intermediate products to the total absorbance of the system, since this proves that it is necessary to use the deconvolution technique to evaluate the exact methylene blue concentration.
Figure 1. Absorption spectra in the visible region for samples taken at different reaction times for some of the catalysts tested in this work. The deconvolution peaks were obtained by the technique described in [19].

Table 3 shows the Gaussian parameters corresponding to the peaks of the intermediate products (P7, P8 and P9), averaged for all the photocatalytic experiments carried out with the mesh-supported catalysts and with the TiO₂ particles. Both the mean wavelengths (λ_i) and the standard deviations (σ_i) are very similar for both types of materials (the mesh-supported and TiO₂ catalysts) which suggests that the intermediate compounds formed in both cases are the same. These are azure A and azure B. Azure A is produced by the gradual demethylation of azure B, which in turn is produced by the demethylation of methylene blue [19].

In order to establish a basis for comparison, photodegradation experiments with commercial TiO₂ particles (P25 Degussa-Evonik) were previously performed. Figure 3 shows the variation of the methylene blue concentration with reaction time for different amount of TiO₂. The dashed lines represent the fitting of experimental points
to equation (4) (first order kinetics). With the kinetic constants obtained from the fitting, \( A_z \) activity values were evaluated by means of equation (9).

![Figure 2](image)

**Figure 2.** Examples of the evolution of absorbance during the reaction for different peaks of the visible region (P1: methylene blue, P7-P8-P9: intermediate compounds) corresponding to catalysts with different activities

**Table 3.** Gaussian parameters (mean wavelengths, \( \lambda_i \), and standard deviations, \( \sigma_i \)) obtained with the deconvolution technique for the peaks corresponding to intermediate products (P7, P8 and P9)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Catalyst</th>
<th>( \lambda_i ) (nm)</th>
<th>( \sigma_i ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P7</td>
<td>Mesh-supported ZnO</td>
<td>518.1 ± 4.8</td>
<td>40.3 ± 4.9</td>
</tr>
<tr>
<td></td>
<td>TiO(_2)</td>
<td>530.9</td>
<td>42.0 ± 2.9</td>
</tr>
<tr>
<td>P8</td>
<td>Mesh-supported ZnO</td>
<td>611.5 ± 2.0</td>
<td>34.9 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>TiO(_2)</td>
<td>611.2</td>
<td>38.8 ± 5.7</td>
</tr>
<tr>
<td>P9</td>
<td>Mesh-supported ZnO</td>
<td>651.8 ± 3.2</td>
<td>17.5 ± 4.9</td>
</tr>
<tr>
<td></td>
<td>TiO(_2)</td>
<td>648.4</td>
<td>19.1 ± 1.6</td>
</tr>
</tbody>
</table>
The inset in Figure 3 shows a plot of the values of $A_Z$ for the different catalyst weights. As can be observed, the intrinsic catalytic activity ($A_Z$) is independent of catalyst mass for values of mass equal to or below 10 mg. The decrease in catalytic activity for higher masses is typical of photocatalytic systems [20-24] and it is commonly attributed to a screening effect resulting from the catalyst particles being situated close to the irradiation source. However, this effect is usually observed for catalyst concentrations of more than 1 g/L [21,23] whereas in Figure 3 the decrease in $A_Z$ starts to occur at $\sim 0.25$ g/L. In our experiments no air was bubbled in the reaction vessel during the reaction, and therefore for higher TiO$_2$ masses the supply of oxygen from the atmosphere may become the controlling step, since this is known to occur with other processes, such as the photodegradation of phenol [26]. Therefore, in order to compare the activity of the catalysts prepared in this work with that of commercial TiO$_2$ the $A_Z$ value for the lowest TiO$_2$ mass ($5.8 \times 10^{-4}$ mg$^{-1}$-L·min$^{-1}$ as indicated in Figure 3) will be used. This value corresponds to the intrinsic (independent of mass) activity of TiO$_2$.

![Graph showing variation of methylene blue concentration with reaction time and catalyst weight](image-url)

**Figure 3.** Variation of the methylene blue concentration with reaction time for the experiments performed with reference catalyst P25 TiO$_2$. Inset: variation of the activity parameter, $A_Z$, with the catalyst weight.
Figure 4 shows the results of methylene blue photodegradation obtained for the different mesh-supported catalysts tested in this work. Remarkable differences in catalytic activity between the catalysts can be appreciated. The dashed lines in Figure 4 represent the fitting of the experimental data to equation (7). This equation was used because the classical first order reaction equation (5) provided unacceptable fittings in most cases, whereas the potential equation (7) gave good fitting results (Figure 4). The kinetic parameters obtained (k and n) are shown in Table 4.

![Graph showing methylene blue concentration vs. time for different catalysts](image)

**Figure 4.** Variation of the methylene blue concentration with reaction time for the different mesh-supported catalysts tested in this work. The dashed lines represent fittings to the potential equation (3).

In several cases the reaction order is clearly superior to 1, which could imply that catalytic deactivation has taken place during the reaction due to the photocorrosion of zinc oxide [27-29]. However, the existence of different values for the reaction order makes it impossible to compare the catalytic activities using the values of k. Therefore, in order to perform a strict comparison of catalytic activities we shall make use of the activity parameter, AC (either on a ZnO mass basis, Az, or on a total catalyst mass basis, AMZ) as defined by equation (8) and evaluated for the mesh-supported catalyst by equation (12) and for the TiO2 particles by equation (9). The values of Az and AMZ are presented in Table 4. For a better visualization of the data Figure 5 shows the values of Az and AMZ corresponding to the different catalysts. As can be observed,
the most active catalyst on a ZnO mass basis (AZ) is S2-Ko. This displays an even higher activity than TiO₂. The next most active is S2-Feng. The other catalysts all have a much lower catalytic activity. However, when considering the total mass of the catalyst (including the inert metallic mesh) none of the catalysts developed here have an activity comparable to that of TiO₂. This drawback is offset by the advantages derived from using a supported catalyst.

Table 4. Kinetic parameters for the methylene blue photodegradation obtained for the different catalysts analysed in this work

<table>
<thead>
<tr>
<th>Reference</th>
<th>k (n\textsuperscript{th} order) \textsuperscript{a} (mg\textsubscript{MB} \textsuperscript{-}1·mg\textsubscript{Z} \textsuperscript{-1}·L\textsuperscript{-1}·min\textsuperscript{-1})</th>
<th>n</th>
<th>A\textsubscript{Z} \textsuperscript{b} (mg\textsubscript{Z} \textsuperscript{-1}·L·min\textsuperscript{-1})</th>
<th>A\textsubscript{MZ} \textsuperscript{b} (mg\textsubscript{MZ} \textsuperscript{-1}·L·min\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2-Ko</td>
<td>6.1×10\textsuperscript{-5}</td>
<td>2.2</td>
<td>8.2×10\textsuperscript{-4}</td>
<td>3.5×10\textsuperscript{-5}</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.0×10\textsuperscript{-4}</td>
<td>1.0</td>
<td>5.8×10\textsuperscript{-4}</td>
<td>-</td>
</tr>
<tr>
<td>S2-Feng</td>
<td>5.6×10\textsuperscript{-5}</td>
<td>1.7</td>
<td>3.5×10\textsuperscript{-4}</td>
<td>1.0×10\textsuperscript{-5}</td>
</tr>
<tr>
<td>S0-Bai</td>
<td>1.9×10\textsuperscript{-6}</td>
<td>2.7</td>
<td>7.9×10\textsuperscript{-5}</td>
<td>5.5×10\textsuperscript{-6}</td>
</tr>
<tr>
<td>S2-Chen-10</td>
<td>2.5×10\textsuperscript{-5}</td>
<td>1.4</td>
<td>7.7×10\textsuperscript{-5}</td>
<td>1.4×10\textsuperscript{-5}</td>
</tr>
<tr>
<td>S0-Shao</td>
<td>2.8×10\textsuperscript{-8}</td>
<td>4.9</td>
<td>5.8×10\textsuperscript{-5}</td>
<td>4.1×10\textsuperscript{-6}</td>
</tr>
<tr>
<td>S2-Xu</td>
<td>4.5×10\textsuperscript{-5}</td>
<td>0.5</td>
<td>2.4×10\textsuperscript{-5}</td>
<td>4.5×10\textsuperscript{-6}</td>
</tr>
<tr>
<td>S2-Bai-C</td>
<td>1.3×10\textsuperscript{-5}</td>
<td>0.9</td>
<td>1.7×10\textsuperscript{-5}</td>
<td>4.6×10\textsuperscript{-6}</td>
</tr>
<tr>
<td>S3-Xu</td>
<td>2.8×10\textsuperscript{-5}</td>
<td>0.5</td>
<td>1.6×10\textsuperscript{-5}</td>
<td>3.5×10\textsuperscript{-6}</td>
</tr>
<tr>
<td>S2-Bai</td>
<td>2.7×10\textsuperscript{-12}</td>
<td>6.9</td>
<td>1.1×10\textsuperscript{-6}</td>
<td>3.1×10\textsuperscript{-7}</td>
</tr>
<tr>
<td>S2-Shao</td>
<td>4.1×10\textsuperscript{-9}</td>
<td>2.0</td>
<td>8.5×10\textsuperscript{-7}</td>
<td>2.4×10\textsuperscript{-7}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Z: ZnO or TiO₂  
\textsuperscript{b} MZ: Mesh+ZnO

Figure 5. A\textsubscript{Z} and A\textsubscript{MZ} values for the different catalysts tested in this work
SSWM-supported ZnO photocatalyst

The catalytic activity of mesh-supported catalysts depends a priori on several factors such as the presence of polar surfaces, the specific surface area of the active phase (number of active centres), the geometric properties, etc. Figure 6 shows the plots corresponding to the variation of AZ with the values of the different structural parameters of the catalysts.

Figure 6. Variation of AZ with I_{101}/I_{002}, d_{XRD}, L, W, S, Y and S_{g} for the mesh-supported catalysts tested in this work.
In spite of what other authors have suggested [30], the catalytic activity of the ZnO nanoparticles produced in this work bears, in principle, no apparent relation to the abundance of polar facets, expressed by the diffractometric relation I101/I002 (Figure 6). Neither the crystal size (dXRD) nor the specific geometric surface (Sg) seem to follow any noticeable trend with catalytic activity. However, a certain relationship can be observed between the AZ and ZnO yield values (i.e. the higher the load of ZnO in the catalyst, the lower the catalytic activity) and even more clearly between AZ and the nanoparticle dimensions, especially the length of the prisms, which shows an inverse relation with the catalytic activity. Possibly the ultraviolet radiation is more appropriately distributed (a better quantum yield) through the mesh-supported catalysts with a lower ZnO yield (because there is less ZnO mass to penetrate through) and, especially, in the samples with thinner ZnO deposits (smaller nanoparticles). Two examples of thick (S2-Ko) and thin (S2-Xu) deposits can be seen in the SEM images displayed in Figure 7.

![SEM microphotographs of the ZnO-meshes synthesised by the Ko and Bai method illustrating the effect of particle length on the photocatalytic activity](image-url)
It is known that the optical transmittance of zinc oxide deposits is favoured by a diminution of their thickness [31], as illustrated in the figure. The apparent relation between \( A_2 \) and the values of \( W \) and \( S \) (Figure 6) might be a consequence of the expected relation between these parameters and \( L \). Thus, if the catalysts with lower values of \( L \) are disregarded (\( L<1500 \) nm), then the expected relationship between catalytic activity and the abundance of polar surface \( \{110\}/\{100\} \) [30] becomes evident, as can be seen in the inset of Figure 6.

Three catalysts were selected for stability tests: the two most active catalysts on a total mass basis (S2-Ko and S2-Chen-10) and a catalyst with a reaction order close to one (S2-Bai-C). The tests consisted of following the catalytic activity during consecutive batch reaction stages. Figure 8 shows the variation of \( A_2 \) with \( t_{UV} \) for all the catalysts. This time value \( (t_{UV}) \) only includes the summation of the reaction times under ultraviolet irradiation. It does not take into consideration the adsorption stages under darkness. Each point in the plot stands for one reaction stage (120-150 min reaction). After each stage the catalyst was cleaned and dried for the next reaction stage. As can be observed, all three catalysts become deactivated to a lesser or greater degree after several reaction stages, the most stable being the least active catalyst (S2-Bai-C). The rate of deactivation can be modelled using a potential equation of the type:

\[
A_2 = A_{2,0} \times t_{UV}^{-d}
\]

(13)

in which \( A_{2,0} \) stands for the activity parameter at \( t_{UV}=0 \) and \( d \) is the deactivation parameter which is a direct function of the rate of deactivation. As can be observed in Figure 8, the value of parameter \( d \) increases with the initial activity of the catalyst. The main cause of the deactivation of ZnO is photocorrosion, which consists in the partial dissolution of Zn and the collapse of the ZnO crystal structure as a result of the action of UV irradiation. Photocorrosion occurs via the following reactions [28,29]:

\[
\text{ZnO} + 2h^+ + n\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_n^{(2-n)^+} + \frac{1}{2}\text{O}_2 + n\text{H}^+
\]

(14)

\[
\text{ZnO} + 2h^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2}\text{O}_2
\]

(15)

Several research groups have investigated how to reduce ZnO photocorrosion by means of procedures such as depositing silver [32-35], polyaniline monolayers [36], graphitic carbon [37], Nafion films [38] on the surface of the ZnO, or via hybridization of ZnO with C<sub>60</sub> [29]. As mentioned above, reaction orders of over 1 could be caused by the phenomenon of catalytic deactivation. This can be easily visualised in Figure 9.
This figure shows the theoretical variation of $C_{MB}/C_{MB,0}$ for experiments that yield the same initial reaction rate and different reaction orders. For a value of $n$ over 1, the reaction rate diminishes with time with respect to that obtained for $n=1$. Catalyst deactivation leads to the same result.

**Figure 8.** Variation of $A_Z$ with reaction time for consecutive batch experiments performed with three different catalysts (stability experiments). The solid lines represent fittings to equation (13)

**Figure 9.** Theoretical curves of variation of $C_{MB}/C_{MB,0}$ with reaction time for experiments yielding the same initial reaction rate and different reaction orders
Figure 10 confirms these findings. In this figure the values of ZnO losses after 12 hours of reaction and those of parameter d are plotted against the average value of reaction order for all the consecutive batch reactions performed with the catalysts. The losses of ZnO from photocorrosion, evaluated by the difference in catalyst weight, increase almost linearly with the average value of $<n>$, indicating that the value of this parameter depends on the extent of deactivation. The parallel behaviour between the values of d and ZnO losses confirms that loss of activity is due to photocorrosion. If the relation between the reaction order and the extent of deactivation is general, then the relationship between catalytic activity and deactivation rate observed for the catalysts of Figure 9 might be coincidence, since there is almost random variation between the values of n and $A_d$, as can be seen in Table 4.

![Figure 10](image.png)

**Figure 10.** Variation of ZnO mass losses after 12 hours of reaction and exponent d of equation (13) with the average reaction order obtained during the stability experiments.

4. **Conclusions**

Zinc oxide nanostructures supported on stainless steel meshes that had been synthesized in a previous work (T.T. Vu, L. del Río, T. Valdés-Solís, and G. Marbán, Mater. Res. Bull., 47 (2012) 1577-1586) were tested for the photocatalytic decomposition of methylene blue under ultraviolet irradiation. A potential reaction
rate equation was used to fit the results of the batch experiments. Because of the existence of different reaction orders and varying catalyst concentrations during the reaction, an activity parameter \( A_c \) was introduced to account for these variations. The best catalyst tested (S2-Ko) showed a catalytic activity higher than that of the reference material P25 TiO\(_2\) (Degussa-Evonik). Its high activity is attributed to a higher quantum yield resulting from the small particle length of the ZnO deposited on the wire meshes. It has been proved that reaction orders of over 1 are due to catalysis deactivation caused by ZnO photocorrosion.

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References


SSWM-supported ZnO photocatalyst


SSWM-supported ZnO photocatalyst


Article III

Fabrication of wire mesh-supported ZnO photocatalysts protected against photocorrosion

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Fabrication of wire mesh–supported ZnO photocatalysts protected against photocorrosion

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ABSTRACT

In this work a catalyst consisting of high surface area ZnO nanoflowers supported on a stainless steel wire mesh was synthesized by hydrothermal growth, and tested for the catalytic photodegradation of methylene blue under UV irradiation. The stability of the photocatalyst was evaluated by assessing the evolution over several reaction stages of catalytic activity and ZnO loss. The initial high activity of this catalyst was followed by a significant decrease after successive reaction cycles due to the dissolution of the ZnO as a consequence of photocorrosion. Impregnation of the catalyst with small amounts of silver enhanced its initial catalytic activity, but failed to produce the photostabilisation of the catalyst that has been reported in the literature. Dip-coating the photocatalyst (either undoped or silver doped) with a diluted polysiloxane solution produced a transparent polysiloxane coating that completely prevented photocorrosion and allowed a stable catalytic activity to be maintained over 8 reaction stages at values higher than those obtained with uncoated catalysts after just 2-3 reactions stages with negligible loss of ZnO.

Keywords: Methylene blue Photocatalysis Photocorrosion ZnO Stainless steel wire mesh

1. Introduction

Heterogeneous photocatalysts are widely used for the destruction of organic pollutants in wastewaters [1]. For this purpose semiconductor particles, such as TiO₂ and ZnO, have attracted widespread attention [2-4]. TiO₂, as a semiconductor oxide, is a very efficient low-cost photocatalyst that is widely available [5].

Zinc oxide shares many of the properties of TiO₂ [6, 7]. Both have similar bandgap energies of around 3.2 eV [6] and it has been found that ZnO nanoparticles may provide a higher quantum yield than TiO₂ nanoparticles [8]. Additionally ZnO has the capacity to absorb a larger fraction of the solar spectrum than TiO₂ [9] and its price is
even lower than that of TiO$_2$ [6]. A major drawback of TiO$_2$ is the technological limitation associated with the recovery and reutilization of fine titania powders, an important disadvantage that prevents its large-scale implementation in photocatalytic processes. On the other hand, ZnO can be easily fabricated by crystal growth on different supports using low temperature methods [10]. In this way monolithic configurations of the catalyst can be produced and applied under practical conditions.

Unfortunately, the application of ZnO as a photocatalyst is limited due to photocorrosion under UV irradiation in aqueous solutions, which results in a decrease in photocatalytic activity [11-13]. Photocorrosion consists of the partial dissolution of Zn and the collapse of the ZnO structure induced by the action of the UV irradiation. Photocorrosion occurs via the following self-oxidation reactions [14-16]:

$$\text{ZnO} + 2h^+ + n\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_{n}^{(2-n)+} + \frac{1}{2}\text{O}_2 + n\text{H}^+$$ (1)

$$\text{ZnO} + 2h^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2}\text{O}_2$$ (2)

where h$^+$ are the positive holes created by the action of UV irradiation. Several research groups have investigated how to reduce ZnO photocorrosion by means of procedures such as depositing silver [17-21], polyaniline monolayers [22], graphitic carbon [23], Nafion films [24], AlSi nanoclays [25] on the surface of the ZnO, via hybridization of ZnO with C$_{60}$ [14] or by depositing ZnO on SiO$_2$ particles [26].

Although the above modifications help to improve the photocatalytic activity of ZnO some problems still persist. For instance, Bessekhouda et al. have reported that the photocatalytic activity of the doped materials is impaired by thermal instability and by an increase in the number of hole/electron recombination centers [27]. Furthermore, photocorrosion is commonly evaluated by its impact on the photocatalytic activity of the materials, whereas the weight loss of catalysts due to ZnO dissolution is not normally measured. Without this information, other factors such as possible changes in the intrinsic activity of the remaining solid ZnO due to surface reorganisation or the photocatalytic activity of colloidal ZnO particles [28] detached from corroded ZnO particles are also overlooked. In short, when testing these materials it is necessary to evaluate simultaneously the evolution of the Zn loss and catalytic activity over successive reaction cycles.

Dastjerdi et al. have demonstrated a novel technique to stabilize photoactive nanoparticles on a textile surface [29] by using polysiloxane (XPs). They used a self-cleaning and antibacterial cloth coated with Ag/TiO$_2$ nanoparticles protected by a
SSWM-supported ZnO photostabilization

small amount of XPs. The thin layer of XPs had the effect of isolating the nanoparticles, thus preventing the exchange of electrons between Ag and TiO$_2$. This exchange causes a red shifted plasmon peak and an impairment of the cloth with a non-aesthetic brown colour. With this protection technique the photocatalytic activity of TiO$_2$ is not negatively affected by the presence of XPs. The present work aims to test this procedure as a method for protecting ZnO nanoparticles against photocorrosion.

In previous works, we tested various procedures for preparing stainless steel wire mesh-supported ZnO catalysts [10]. The catalysts were evaluated for the catalytic photodegradation of methylene blue under ultraviolet irradiation [30]. Some of the tested catalysts showed a higher catalytic activity than that of TiO$_2$ P25 (Evonik). Unfortunately, even the best catalysts became partly deactivated during the reaction due to ZnO photocorrosion. In this work, a novel procedure [31] has been used to prepare a high surface area ZnO catalyst supported on stainless steel wire mesh. In addition, the catalyst was subjected to silver doping by either photodeposition or equilibrium impregnation in order to study their possible positive effects [18, 32] on the activity and stability of the resulting catalyst.

Finally, the effect of XPs coating was thoroughly analysed in order to determine the best conditions for preparing a highly stable catalyst with the best possible catalytic activity for methylene blue decomposition.

2. Experimental

2.1. Catalyst

2.1.1. Materials

All chemical reagents were of analytical grade and were not subjected to additional purification. All of the aqueous solutions were prepared with deionised water. The support was a stainless steel wire mesh [with a 30 µm wire diameter and 40 µm screen opening] provided by CISA. The following reagents were used: zinc acetate dihydrate (Prolabo), silver acetate (99%, Sigma-Aldrich), urea (>99.5%; Fluka), polysiloxane CT208E emulsion supplied by Wacker Finish. The photocatalytic experiments were performed over aqueous solutions of methylene blue monohydrate (>96%; Riedel de Häen).
2.1.2. Synthesis of wire mesh–supported ZnO

The synthesis of wire mesh–supported ZnO was performed on supports consisting of rectangular pieces of wire mesh (5×3 cm²), previously washed with HNO₃ (4M) at 60°C for 4 hours and then with isopropyl alcohol in an ultrasonic bath for 10 minutes.

Mesoporous ZnO nanosheets were synthesized on the surface of the wire mesh by a method that Kakiuchi et al. [31] designed for preparing ZnO on ITO supports. Zinc acetate dihydrate was dissolved together with urea in deionized water. Concentrations of Zn²⁺ and urea in the aqueous solutions were adjusted to 0.05 and 1.0 M, respectively. The pH of the solution was adjusted to 4.88 by using acetic acid. The wire mesh was placed in a Teflon autoclave (100 mL) filled with the growth solution. The autoclave was sealed and hydrothermal ZnO growth proceeded at 80°C for 23 h in a constant-temperature water bath. The ZnO coated-wire mesh was then taken out of the solution, thoroughly washed with deionised water and vacuum-dried at 60°C. Finally the sample was calcined at 200°C for 0.5 h in air.

2.1.3. Silver doped-wire mesh supported-ZnO

To dope the wire mesh–supported ZnO with silver two different methods were employed: equilibrium adsorption impregnation (EAI) and photodeposition (PD). PD allowed Ag nanoparticles to form on the catalyst surface [17, 19], whereas EAI yielded Ag₂O particles that were reduced to Ag under reactive conditions by photogenerated electrons [18]. Silver photodeposition was carried out in a similar way to that employed by Xie et al. with powdered ZnO [19]. The wire mesh supported-ZnO was immersed in a 50 mL aqueous silver acetate solution (12.7 ppm Ag) under stirring and subjected to UV-irradiation in the photocatalytic reactor for 1 hour [17]. Afterwards, the mesh was rinsed with deionized water and dried at room temperature overnight. The Ag/Zn molar ratio in the prepared sample was Ag/Zn=0.0032, as measured by Atomic Absorption Spectroscopy.

Equilibrium adsorption impregnation was carried out by immersing the catalyst in a solution of silver acetate (12.7 ppm Ag) and kept under mechanical agitation for several hours. Afterwards, the metal wire mesh was removed from the impregnation solution and immersed in deionized water under agitation to remove any salt that had not been chemisorbed. Finally, the wire mesh was vacuum dried at 60°C and calcined
in air at 250°C for 30 minutes. The Ag/Zn molar ratio in the prepared sample was Ag/Zn=0.0016, as measured by Atomic Absorption Spectroscopy. This ratio is similar to that considered as optimum in [19].

2.1.4. Preparation of polysiloxane-coated catalysts

Dip-coating with water solutions of polysiloxane (XPs) was applied to both undoped and silver-doped wire mesh-supported ZnO catalysts. A dip-coating device designed and fabricated in our lab was used for this purpose (Fig. 1). This apparatus allows the cycling operation to proceed at a controllable speed following a sequence of dip-coating, air blowing and sample heating. First the substrate (5×5 cm²) was immersed in the XPs solution (0.3-1.5 wt.%) and then slowly extracted at a speed of 2 cm-min⁻¹. The substrate was then passed through the electrical heating section (preheated at 190°C) at the same speed in order to cure the XPs layer. Only one dip-coating cycle was applied.

Figure 1. Dip coating equipment designed and fabricated in our laboratory
2.2. Characterization

2.2.1. Structural characterization

The morphology of the catalysts was studied by means of a scanning electron microscope (SEM, FEI Quanta FEG 650 model) and a transmission electron microscope (TEM, JEM -2100F model) equipped with a detector to perform electron energy loss spectroscopy (EELS). The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA and using Cu Kα radiation (λ = 0.15406 nm). The crystal size values were estimated from the XRD pattern by using Scherrer’s equation (d_{pol}). The instrumental contribution to line broadening was taken into account by using the diffraction pattern of corundum as instrumental standard. Nitrogen adsorption isotherms were performed at -196°C using a Micromeritics ASAP 2020 volumetric adsorption system. The BET surface area was deduced from an analysis of the isotherms in the relative pressure range of 0.04 to 0.20. UV-Vis diffuse reflectance spectroscopy measurements were carried out using a Shimadzu UV-2460 spectrophotometer equipped with an integrating sphere. The spectra were recorded in the range of 200-700 nm. Pure powdered BaSO₄ was used as a reference sample.

Ex-situ X-ray photoelectron spectroscopy (XPS) was carried out by means of a Specs spectrometer, using Mg-Kα radiation (1253.6 eV). The binding energies of the spectra recorded were corrected with the binding energy of adventitious carbon in the C1s region (284.6 eV). The backgrounds were subtracted by means of Shirley baselines. The atomic sensitivity factors stored in the Casa XPS database were used for the quantitative analyses.

2.2.2. Photocatalytic tests

The methylene blue photodegradation experiments were carried out with supported catalysts (1.7×3 cm² strips weighing ~120 mg) in a 400 mL quartz beaker under the illumination of two ring-type UV 22W lamps (Luzchem Ring-Illuminator) which predominantly emit radiation at 351 nm. A small clip fixed to the lower end of a vertical rod was used to hold the catalyst strip. The strip and the holder were immersed in 60 mL of a magnetically stirred aqueous solution of methylene blue, with an initial concentration of 10 mg/L. The catalyst was subjected to seven reaction stages (for a total reaction time of 14 h). After each stage the catalyst was extracted.
from the reaction medium, washed with deionised water, vacuum dried at 60°C, carefully weighed and re-introduced in the reactor for a new stage with a fresh 10 mg/L methylene blue solution. At each reaction stage the solution was first magnetically stirred for 30 min under darkness to ensure adsorption/desorption equilibrium between the dye and the photocatalyst. Next the reactor was exposed to UV lamps for 120 min. Liquid samples were extracted for measurement at fixed reaction times (0, 15, 30, 50, 80 and 120 min). The visible absorption peaks of the analyzed samples were recorded in the 400-800 nm range by means of a UV-Vis spectrometer (Shimadzu UV-2401PC). The true methylene blue concentration was obtained from the visible absorption spectra by means of a recently published deconvolution technique [33] that allows the contribution of reaction intermediates to the spectra to be determined. A photocatalytic analysis was performed using ZnO powder scratched from an undoped wire mesh-supported ZnO catalyst. The powder (10 mg) was suspended in the magnetically stirred liquid for the photocatalytic experiment and the liquid samples for analysis were previously centrifuged to remove the ZnO particles. It was found that the intrinsic catalytic activity of this system was 36% higher than that obtained with the monolithic configuration described above. This difference is ascribed to a higher quantum yield and a better dispersion in the liquid of the suspended powder.

In order to compare the photocatalytic activities of the materials the following factors were taken into account:

(i) the catalyst dosage \( C_{\text{ZnO}} = \frac{w_{\text{ZnO}}}{V} \), where \( w_{\text{ZnO}} \) is the weight of ZnO and \( V \) is the volume of the liquid) increases slightly due to the regular removal of liquid samples for analysis. Thus, the actual catalyst dosage at any time \( t \) can be estimated from the following equation:

\[
C_{\text{ZnO}} = \frac{w_{\text{ZnO}}}{V_0 (1 - b \times t)}
\]  

(3)

where \( V_0 \) is the initial liquid volume and \( b \) is a constant that can be evaluated by linear regression;

(ii) the reaction rate can be expressed by the potential equation:

\[
- \frac{dC_{\text{MB}}}{dt} = kC_{\text{ZnO}} C_{\text{MB}}^n
\]  

(4)
where \( C_{MB} \) is the methylene blue concentration at a given time \( t \), \( k \) is the reaction rate constant \((m_{MB}^{1-n} \cdot m_{ZnO}^{-1} \cdot t^{-n} \cdot \text{min}^{-1})\) and \( n \) is the apparent reaction order. Factor \( C_{ZnO} \) is introduced to account for the known dependence of the reaction rate on the catalyst dosage in the absence of screening effects [2,34-36]. Therefore, under chemical control the reaction constant \( k \) should be independent of the catalyst dosage.

For \( n=1 \), equation (4) is coincident with the well-known Langmuir-Hinshelwood equation for diluted solutions [37]. In this case, the resolution of equation (4) yields:

\[
C_{MB} = C_{MB,0} \exp\left[-k C_{ZnO,0} (1.05^n t)\right] \tag{5}
\]

whereas for \( n \neq 1 \):

\[
C_{MB} = \left\{C_{MB,0}^{-1} - (1-n)k C_{ZnO,0} (1.05^n t)\right\}^{1-n} \tag{6}
\]

where \( C_{ZnO,0} \) is the catalyst dosage at \( t=0 \). By fitting the concentration values from these equations with the experimental values of \( C_{MB} \) at different times, the values of \( k \) and \( n \) can be obtained. However, the comparison of catalytic activities cannot be performed with the values of \( n \) are identical. To overcome this problem, we used the following parameter to evaluate the intrinsic catalytic activity of the samples:

\[
A_{ZnO} = \frac{1}{t_0.5 C_{ZnO,0}} \tag{7}
\]

where \( t_0.5 \) is the semiconversion time (min). Parameter \( A_{ZnO} \) allows the intrinsic activities of the catalysts to be compared at the same initial methylene blue concentration. In principle this parameter is independent of the catalyst dosage [30]. Calculation of \( t_0.5 \) can be performed by re-arranging equations (5) and (6) for \( C_{MB}=0.5 \times C_{MB,0} \). Thus, for \( n=1 \):

\[
A_{ZnO} = \frac{b}{C_{ZnO,0} \left[1 - \exp\left(-\frac{-0.693 b}{k C_{ZnO,0}}\right)\right]} \tag{8}
\]

whereas for \( n \neq 1 \):

\[
A_{ZnO} = \frac{b}{C_{ZnO,0} \left[1 - \exp\left(-\frac{C_{MB,0}^{1-n} - 1}{k C_{ZnO,0} (1-n)}\right)\right]} \tag{9}
\]
This parameter allows the intrinsic activity of different catalysts to be compared on a ZnO mass basis, but in a series of reaction stages performed with the same catalyst it is necessary to consider how the ZnO losses affect the absolute catalytic activity. In this situation it is convenient to employ the inverse of the semiconversion time for a fixed initial ZnO dosage (333 mg/L):

\[
\frac{1}{t^{0.5}} = A_{ZnO} \times 333 \times \frac{C_{ZnO,0}}{C_{ZnO,i}}
\]  \hspace{1cm} (10)

where \( C_{ZnO,0}^{i} \) is the catalyst dosage at the beginning of the first reaction stage (UV time=0) and \( C_{ZnO,i} \) is the catalyst dosage at the beginning of the reaction stage under analysis, in which the catalyst displays the intrinsic activity \( A_{ZnO} \).

**Acronyms**

- ZnO-i: wire mesh supported-ZnO after having been subjected to \( i \) reaction stages.
- ZnO(0.3X)-i: wire mesh supported-ZnO coated with XPs from a 0.3 wt.% XPs solution after having been subjected to \( i \) reaction stages.
- ZnO(Ag)-i: Ag doped-wire mesh supported-ZnO after having been subjected to \( i \) reaction stages. If not indicated, Ag doping is performed via Equilibrium Adsorption Impregnation (EAI).
- ZnO(Ag)(0.3X)-i: Ag doped-wire mesh supported-ZnO coated with XPs from a 0.3 wt.% XPs solution after having been subjected to \( i \) reaction stages. If not indicated, Ag doping is performed via Equilibrium Adsorption Impregnation (EAI).

**3. Results and Discussion**

**3.1. Unmodified wire mesh supported-ZnO**

Fig. 2 shows a SEM image of the ZnO-0 sample (fresh wire mesh supported ZnO). As can be seen ZnO has grown and uniformly covers the microwires of the mesh. The ZnO deposits for all the prepared samples amount to 18.7 ± 5.0 wt.% of the total mass of the coated wire mesh and consist of interconnected nanosheets which are approximately 20-50 nm thick (inset of Fig. 2). This ZnO structure is very open (with voids of 1-3 μm) and has a high BET surface area (75 m²/g on a ZnO mass basis). The XRD pattern of the ZnO-0 sample is shown in Fig. 3. The indexed peaks correspond to the hexagonal wurtzite structure, according to JCPDS card No. 79-2205. The main
characteristic of this pattern is the high (100)/(002) intensity ratio ($I_{100}/I_{002}=3$), which evidences the exposure of a large proportion of polar surfaces, which is thought to be the key for a high photocatalytic activity [38]. The crystal size of ZnO nanoparticles, as evaluated by the Scherrer equation, is relatively small ($13 \pm 1$ nm).

![ZnO-0 SEM image](image)

**Figure 2.** SEM image of ZnO-0

Fig. 4 shows the results of the MB photodegradation performed with wire mesh supported-ZnO. As can be seen, in the first reaction stage all the MB is degraded in less than one hour, though the catalytic activity is significantly reduced in successive reaction stages. This loss of activity is undoubtedly a consequence of the photocorrosion process, which causes extensive dissolution of the solid ZnO. This is clearly appreciated in Fig. 5, where SEM images of the fresh ZnO-0 sample and of the same sample after having been subjected to 7 reaction stages (ZnO-7) are shown. As can be observed, a significant amount of the initially present ZnO has disappeared from the surface of the wire mesh.
**Figure 3.** XRD spectra of different supported catalysts

**Figure 4.** Methylene blue concentration decay curves for ZnO-i (i = 1 to 7)
The photocorrosion process dissolves a large part of the ZnO, as can be appreciated in Fig. 6. In this figure, the UV time only includes the summation of the reaction times for the successive stages under ultraviolet irradiation. It does not include the adsorption steps under darkness. Each point in the plots stands for one reaction stage (60-120 min). After each stage the catalyst was cleaned with deionized water, dried, weighed and subjected to the next reaction stage. In Fig. 6, the baseline represents the losses of ZnO for a blank experiment in the absence of radiation. These losses are due to manual handling (i.e. fixing the catalyst in the holder after weighing at each stage), which, after seven stages, amounts to less than 3 wt.%. Under reactive conditions, the vast majority of ZnO is lost during the first stage (56.0 wt.%, after the baseline correction, as shown in Figure 6 and indicated in Table 1), whereas after the seventh stage the lost amount of ZnO has increased to 77.6 wt.%. However, the absolute catalytic activity ($1/t_{a3}^*$), evaluated by equation (10), is much higher in this first stage than in the successive stages (Fig. 6), in which the ZnO losses are not as high as in the first stage.

![Figure 5. SEM images of ZnO-0, ZnO-7, ZnO(Ag)-0 and ZnO(Ag)-7](image-url)
ZnO colloidal particles detached from the corroded ZnO particles probably contribute significantly to the catalytic activity in the first experiment [28]. However, they do not contribute in successive reaction stages, because the MB solution has been renewed. It should also be pointed out that almost 100% of the ZnO detached from the mesh during the photocatalytic test is dispersed or dissolved in the liquid, and only minute traces of ZnO remain as solid particles that can be separated from the liquid by centrifugation. The photocorrosion process causes a clear change in the ZnO crystals. The XRD peak (002) completely disappears (ZnO-7 pattern in Fig. 3). This implies that the non-polar surfaces are significantly reduced by the corrosion process and, as a result, the intrinsic catalytic activity ($A_{\text{ZnO}}$) of the catalyst should be favoured [38].

![Figure 6. Variation of absolute activity ($1/t^{*0.5}$) and ZnO losses during successive reaction stages performed with different supported catalysts. The baseline represents ZnO losses in the absence of UV radiation](image)
However, as can be seen in Table 1, parameter $A_{ZnO}$ for ZnO-1 is twice that of ZnO-7. The reason for this may be the loss of specific surface area as a consequence of photocorrosion. However, the BET analyses only revealed a reduction in specific surface area of from 75 m²/g (ZnO-0) to 56 m²/g (ZnO-7), which can not account for the greater reduction in the $A_{ZnO}$ parameter. The reorganisation of the ZnO nanosheets due to photocorrosion probably causes some degree of nanosheet packing. This would hardly affect the value of the specific surface area but it would cause an increase in the extent of the “dark areas” (see insets in Fig. 5 of the SEM images corresponding to ZnO-0 and ZnO-7), and thus would have a negative effect on the quantum yield. In addition, the density of the centers for electron-hole recombination might increase due to the photocorrosion process.

**Table 1.** Surface atomic relations of Si to Zn obtained by XPS

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Zn</th>
<th>ZnO losses after 7 reaction stages (baseline corrected) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-0</td>
<td>0</td>
<td>77.6</td>
</tr>
<tr>
<td>ZnO(0.3X)-0</td>
<td>0.13</td>
<td>17.1</td>
</tr>
<tr>
<td>ZnO(0.6X)-0</td>
<td>1.18</td>
<td>9.7</td>
</tr>
<tr>
<td>ZnO(Ag)(0.3X)-0</td>
<td>0.96</td>
<td>8.3</td>
</tr>
</tbody>
</table>

**3.2. Ag doped-wire mesh supported-ZnO**

Silver doping of the wire mesh supported-ZnO samples should lead to an enhancement of catalytic activity and endow the catalysts with a better stability against photocorrosion [17-20]. Ag nanoparticles on the semiconductor surface act as electron sinks, which provide sites for the accumulation of photogenerated electrons, increase the separation of electrons and holes, and improve photocatalytic activity [17]. Fig. 5 shows the appearance of a silver doped-wire mesh supported-ZnO (ZnO(Ag)-0) prepared by EAI. It can be seen that it is very similar to that of the undoped catalyst (ZnO-0), without any conspicuous accumulations of silver. Contrary to expectations, doping of the catalyst did not produce photostabilisation of the zinc oxide, as is demonstrated by the extensive loss of ZnO detected in the SEM image of ZnO(Ag)-7 (Fig. 5). The ZnO losses for both doped samples (EAI and PD) are very similar to those corresponding to the undoped catalyst (Fig. 6), though their catalytic activities show some differences. Thus, the absolute catalytic activity of the silver doped-catalyst prepared by equilibrium adsorption impregnation shows a clear enhancement with respect to the undoped catalyst in the first reaction stage.
However, its activity decreases abruptly in the second reaction stage, remaining more or less constant in successive stages. The silver doped-catalyst prepared by photodeposition is less active than the undoped catalyst, even in the first reaction stage. Again, the photocorrosion process for the silver doped-catalyst reduces the extent of non-polar surfaces, as is reflected by the decrease in the (002) peak of the XRD spectrum of ZnO(Ag)-7 with respect to that of Zn(Ag)-0 (Fig. 3). This did not cause an increase in the intrinsic catalytic activity of the catalyst (A_{ZnO}), which, as in the case of the undoped catalyst, clearly decreased between the first and the seventh reaction stage (Table 1).

3.3. XPs coated-wire mesh supported-ZnO

In view of the poor photostability achieved by doping the ZnO based-catalysts with silver, we coated the catalysts with solutions of polysiloxane (XPs) in different concentrations, following the idea of Dastjerdi et al. [29]. This procedure reduced the surface area of the catalysts but did not affect the crystal structure of ZnO. Thus, when the catalysts were coated with XPs solution (1.0 wt.%) the specific surface area decreased to 28 m²/g (on a ZnO mass basis) though the XRD pattern remained unchanged (ZnO(1.0X)-0 in Fig. 3).

Fig. 7 shows a SEM image of ZnO(1.0X)-0. The macroscopic appearance of this catalyst is very similar to that of ZnO-0 (Fig. 5), without any conspicuous accumulations of silicon based-coating. After seven reaction stages the morphology of the ZnO nanosheets has changed to an apparently denser material (see inset in ZnO(1.0X)-7 in Fig. 7) though the zinc oxide seems to remain well adhered to the surface of the wire mesh. In fact, the crystal structure of this “apparently denser” material is practically identical to that of the fresh catalyst, as can be appreciated in the comparison of the XRD patterns for ZnO(1.0X)-0 and ZnO(1.0X)-7 (Fig. 3).

Fig. 8(a-c) shows HRTEM images of ZnO(0.3X)-0. It can be seen that the size of the nanoparticles is rather homogeneous, with an average nanoparticle size of 11.2 ± 2.3 nm, similar to that obtained by XRD (13 ± 1 nm). The lattice spacing of approximately 2.8 Å between adjacent lattice planes (Fig. 8c) corresponds to the (100) plane of the hexagonal crystalline wurtzite type structure, with space group P63mc, which indicates the exposure of the polar surfaces.
No silicon-based particles were visually observed in the images, contrary to what was reported by Siddiquey et al. for silica-coated ZnO particles prepared with TEOS [39], although these authors used a much higher silica content (TEOS/ZnO weight ratios in the range 0.1-0.8). The distribution of silicon and zinc throughout a selected nanoparticle was studied by electron energy loss spectroscopy (EELS) elemental mapping (Fig. 8 d-e). As can be seen, there is a homogeneous distribution of Si throughout the nanoparticle (Fig. 8d). From the combined XRD and HRTEM analyses it can be concluded that XPs is homogeneously distributed over the surface of ZnO as a monolayer and no changes occurred in the ZnO lattice structure after it was dip-coated with XPs.

**Figure 7.** SEM images of ZnO(1.0X)-0, ZnO(1.0X)-7, ZnO(Ag)(0.3X)-0, ZnO(Ag)(0.3X)-7
The surface composition of the catalysts listed in Table 1 was examined by XPS analysis. All the characteristic binding energy peaks corresponding to the expected elements, i.e. Zn, Si, and O, were found, except in the case of the silver-doped catalyst (ZnO(Ag)(0.3X)-0) for which Ag was not visible in the survey scans. The absence of a signal for silver might be explained by the fact that the amount of Ag doped on the surface of ZnO was very small or because silver was shielded by XPS after the dip-coating step.

![HRTEM and EELS mappings](image)

**Figure 8.** HRTEM of ZnO(0.3X)-0 (Figs. a–c) and EELS mappings for Si (d) and Zn (e)

XPS analyses also show that the amount of surface carbon, which in metallic samples is generally thought to come from the pump oil in the vacuum system of the XPS instrument itself [18], increases linearly with the amount of surface silicon introduced by dip coating. This must be due to the presence of carbon from alkyl groups of XPS that have not been totally decomposed by the thermal treatment at 190°C. The C/Si atomic ratio in the original XPS is 8, whereas, after correction for adventitious carbon, the ratio obtained by XPS in the dip-coated samples is 1.4, which indicates that 83% of the original carbon was released during the thermal treatment.
at 190°C. Since the cured polysiloxane chains should have a C/Si ratio of 2 [29], the polysiloxane chains covering the ZnO nanoparticles are defective in methyl groups.

The diffuse reflectance absorption spectra of samples ZnO-0 and ZnO(0.6X)-0 are shown in Fig. 9. ZnO(0.6X)-0 exhibited almost the same absorbance edge as the undoped ZnO-0 sample but for a slightly lower absorption in the UV region and a slightly higher adsorption in the visible region, the latter probably due to the presence of carbon in the dip-coated sample. It seems reasonable to conclude therefore that the XPs coating in sample ZnO(0.6X)-0 is almost completely transparent to the incoming radiation. Fig. 10 shows the evolution curves of the ZnO losses and absolute catalytic activity ($1/t^{0.5}$) during consecutive reaction stages corresponding to wire mesh supported-ZnO catalysts coated with different XPs solutions.

![Figure 9](image_url)  
**Figure 9.** UV-vis diffuse reflectance spectra corresponding to ZnO-0 and ZnO(0.6X)-0 samples.

As can be appreciated, the catalytic activity of the coated catalysts in the first reaction stage is lower than that of the uncoated catalyst, although it remains practically unaltered in successive reaction stages. After 3-4 reaction stages, the activity of the coated catalysts becomes greater than that of ZnO-i. The loss of ZnO by the coated catalysts diminishes with the increase in the concentration of XPs in the
coating solution, although even in the case of the least concentrated solution the ZnO losses are around 4 times lower than in the case of the uncoated catalysts. In the search for a compromise between catalytic activity and ZnO loss it can be seen that the best catalyst is ZnO(1.0X), because its catalytic activity after seven reaction stages is similar to those of ZnO(0.3X) and ZnO(0.6X) and its loss of ZnO, corrected with respect to the baseline, is zero.

Since the catalytic activity of the silver doped-catalyst (EAI) is higher than that of the undoped catalyst in the first reaction stage (Fig. 6), one would expect coating the silver doped-catalyst to produce a better performing catalyst than ZnO(1.0X). Therefore, we coated two silver doped-catalysts with XPs solutions of different concentrations (0.3 and 1.0 wt.%).

![Figure 10. Variation of absolute activity \(1/t^*0.5\) and ZnO losses during successive reaction stages performed with supported catalysts protected with XPs](image)

The silver-doped catalyst coated with 1.0 wt.% XPs solution did not show any catalytic activity at all. This result can be explained by the data presented in Table 1, which shows the surface atomic relation of Si to Zn obtained by XPS for different
samples. Sample ZnO(Ag)(0.3X) contains an amount of silicon that is similar to that of sample ZnO(0.6X) though the concentration of the XPs solution used in the dip-coating stage for ZnO(Ag)(0.3X) was half that used for ZnO(0.6X). It seems that the presence of Ag contributes to the capture of a higher amount of XPs in the dip coating process. The similar silicon contents in both samples is also the reason for their similar ZnO losses (Table 1), which are undoubtedly dependent on the silicon content. Therefore, the inactive silver doped catalyst coated with 1.0 wt.% XPs must have a silicon content that is even higher than that of ZnO(1.5X)-0 which, as can be seen in Fig. 10, is already relatively inactive. From the results shown in Table 1 it can be concluded that the ZnO surface becomes quite stable for Si/Zn atomic ratios of around 1.

A tentative mechanism for the photocatalytic reaction on the XPs coated ZnO particles comprises the photoexcitation of the ZnO particles by the incoming UV radiation through the transparent XPs monolayer, the generation of electron-hole pairs on the ZnO electronic bands, the migration of the generated excitons through the XPs monolayer towards the external surface of the coated particles and the final photodegradation reactions on that surface. A too thick XPs layer (Si/Zn >> 1, as in ZnO(1.5X); Fig. 10) provokes the exciton recombination before reaching the external surface of the XPs coating (and thus the loss of catalytic activity) whereas a too thin layer (Si/Zn < 1) is insufficient to protect the ZnO particles from the action of water (photocorrosion reaction (1)).

On the other hand, the ZnO(Ag)(0.3X) catalyst displayed a relatively high catalytic activity which was accompanied by a significant reduction in the loss of ZnO (Table 1). The SEM images of the fresh (ZnO(Ag)(0.3X) 0) and recycled (ZnO(Ag)(0.3X)-7) catalysts (Fig. 7) show almost identical changes to those observed between ZnO(1.0X)-0 and ZnO(1.0X)-7, i.e., although no loss of ZnO can be appreciated, the morphology of the ZnO nanosheets has changed to an apparently more dense material. Again, the XRD pattern of ZnO(Ag)(0.3X)-0 is similar to that of ZnO-0, and has remained unchanged after seven reaction cycles (Fig. 3).

Fig. 11a shows the results of MB photodegradation performed with the ZnO(Ag)(0.3X) catalyst. All the reaction curves are located in a narrow region, indicating that catalytic activity has been maintained over successive reaction stages. The average reaction curve is represented by a dashed line in Fig. 11b and can be compared with the reaction curves produced by the uncoated catalyst. Although
coating the catalyst clearly reduces its catalytic activity in the first reaction stage, it produces a better performing material in the following stages. Fig. 12 shows that this catalyst is also superior in performance to ZnO(0.3X) and produces a smaller loss of ZnO (8.3 wt.% after seven reaction stages, corrected with respect to the baseline) although in this respect the best catalyst is still ZnO(1.0X) with no ZnO losses.

**Figure 11.** Methylene blue concentration decay curves for ZnO(Ag)(0.3X)-i and ZnO(Ag)-i (i = 1 to 8)

Table 2 provides a summary of the catalytic results for the main catalysts subjected to one and seven reaction stages. The high photostability supplied by XPs coating is offset by a loss of activity, which nevertheless is much higher than that obtained with the uncoated catalysts after a few reaction cycles. Part of the activity lost by coating with XPs is due to a decrease in active surface area, though there is also a decrease in intrinsic activity provoked by the XPs coating. Thus, ZnO(1.0X)-1 displays 18% of the intrinsic activity of ZnO-1 (100×0.37/2.03), whereas if only the reduction in specific surface area is taken into account, ZnO(1.0X)-1 should retain 37% of the activity of ZnO-1 (100×28/75). For the silver doped-catalysts, ZnO(Ag)(0.3X)-1 retains 28% of the intrinsic activity of ZnO(Ag)-1 (100×0.80/2.77). The loss of activity associated with the silicon coating might be due to the incorporation of centres of electron-hole recombination. In any case, the values of intrinsic activity (AZnO) displayed by ZnO(1.0X)-i and, especially, ZnO(Ag)(0.3X)-i are comparable to, or higher
than, those obtained with similar materials, as reported in [30], with the additional feature of having a much greater photostability.

Table 2. Summary of catalytic results for catalysts subjected to one and seven reaction stages

| Catalyst           | $1/t^{*0.5} \times 10^5$ (min$^{-1}$) | $A_{\text{ZnO}} \times 10^4$ (mgZnO L$^{-1}$ min$^{-1}$) | ZnO losses (baseline corrected) (wt.%)
<table>
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<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-1</td>
<td>6.69</td>
<td>2.03</td>
<td>56.0</td>
</tr>
<tr>
<td>ZnO-7</td>
<td>0.61</td>
<td>0.94</td>
<td>77.6</td>
</tr>
<tr>
<td>ZnO(Ag)-1</td>
<td>9.33</td>
<td>2.77</td>
<td>58.2</td>
</tr>
<tr>
<td>ZnO(Ag)-7</td>
<td>0.82</td>
<td>0.98</td>
<td>72.0</td>
</tr>
<tr>
<td>ZnO(1.0X)-1</td>
<td>1.24</td>
<td>0.37</td>
<td>0.7</td>
</tr>
<tr>
<td>ZnO(1.0X)-7</td>
<td>1.26</td>
<td>0.38</td>
<td>-0.4</td>
</tr>
<tr>
<td>ZnO(Ag)(0.3X)-1</td>
<td>2.67</td>
<td>0.80</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnO(Ag)(0.3X)-7</td>
<td>2.36</td>
<td>0.78</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Figure 12. Variation of absolute activity ($1/t^{*0.5}$) and ZnO losses during successive reaction stages performed with catalysts consisting of Ag doped-wire mesh supported-ZnO coated with XPs
4. Conclusions

In summary, we have synthesized a catalyst consisting of high surface area ZnO nanoflowers supported on stainless steel wire mesh. Doping the catalyst with silver by means of equilibrium impregnation produced an increase in the initial catalytic activity towards methylene blue photodegradation under UV irradiation, but a high degree of photocorrosion was also observed. The photocorrosion process reduced the extent of non-polar surfaces in the ZnO nanosheets although this was not accompanied by the expected increase in intrinsic activity. Dip-coating ZnO and ZnO(\text{Ag}) catalysts with diluted polysiloxane solutions produced a homogeneous and transparent XPs coating that provoked the photostabilisation of the catalysts, especially where the surface Si/Zn atomic ratios were over 1. The catalytic activity of the coated catalysts in the first reaction stage was lower than that of the uncoated catalyst, although after a few reaction stages the activities of the coated catalysts were clearly superior to those of the uncoated catalysts. Both the loss of ZnO and catalytic activity during the reaction in the case of the coated catalysts decreased with a greater content of XPs in the coating solution. A compromise between ZnO loss and catalytic activity showed ZnO(1.0X) and ZnO(\text{Ag})(0.3X) to be the optimal catalysts in terms of photocatalytic activity and photostability. The values of intrinsic activity displayed by these catalysts are comparable to, or higher than, those obtained with similar materials, with the additional advantage that they show a much greater photostability.

Acknowledgements

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References

Annex

A simple visible spectrum deconvolution technique to prevent the artefact induced by the hypsochromic shift from masking the concentration of methylene blue in photodegradation experiments

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A simple visible spectrum deconvolution technique to prevent the artefact induced by the hypsochromic shift from masking the concentration of methylene blue in photodegradation experiments

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This paper analyzes the experimental evaluation of methylene blue concentration applied during photocatalytic experiments. In most studies a satisfactory evaluation of the concentration of methylene blue by means of visible spectroscopy is masked by the presence of intermediates during the reaction, resulting in an overestimation of the amount of methylene blue present. The deconvolution technique described in the present study solves this problem by estimating the contribution by intermediates to the visible spectrum. In the photodegradation of methylene blue by Degussa P25 TiO₂ particles the main intermediate detected in the visible spectral region was azure A, produced from the gradual demethylation of azure B. The methylene blue concentrations obtained if the artefact is not taken into account give lower values for the kinetic rate constants of photocatalytic degradation than those provided by this novel deconvolution technique.

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1. Introduction

Semiconductor metallic oxides such as TiO₂ or ZnO are typically used in the photocatalytic degradation of organic compounds in water [1-4]. To test the photocatalysts in laboratory experiments, dyes such as methylene blue are often employed [5-9] because they represent a sizeable fraction (over 0.7 million tons) of the organic compounds produced each year, whose disposal in effluent water streams has a considerable impact on the environment.

In most experimental strategies the concentration of methylene blue is analyzed by applying absorption spectroscopy to the visible spectral region of liquid samples from which the catalyst particles have been previously separated. The relation
between absorbance and concentration is obtained by calibrating with methylene blue solutions of different concentrations. To analyze the concentration of methylene blue during photodegradation experiments some authors use the absorbance at the maximum absorption wavelength though most researchers employ the absorbance at a fixed wavelength, typically in the 664-668 nm range, which corresponds to the maximum absorption wavelength for unreacted methylene blue. This procedure is chosen because the maximum absorption wavelength shifts to lower values (hypsochromic shift) during the degradation process. It is known that this shift is produced by the formation of reaction intermediates that present absorption maxima at lower wavelengths than methylene blue \([10]\). Thus, according to some authors [11-13], the photocatalytic degradation of methylene blue by TiO\(_2\) takes place via the sequential decomposition of methyl groups, through the formation of azure B and azure A (also azure C, thionine and phenothiazine). To take into account this phenomenon some researchers use liquid chromatography to separate the intermediate products (e.g. [11]), and then analyze them by means of mass or visible spectrometry. Other authors recognize the formation of these intermediates but do not apply the necessary corrections when evaluating the concentration of methylene blue by means of visible spectroscopy (e.g. [9,12,14]). Most authors however simply disregard the existence of intermediates (e.g. [5,6,8]) and evaluate the concentration of methylene blue from visible spectra that are almost certainly composed of spectra of different compounds.

The formation of intermediate compounds in methylene blue photodegradation can also be inferred from the shape of the kinetic curves representing methylene blue concentration decay, in which a shoulder can be observed at intermediate reaction times (e.g. Fig.6 in [15] (TiO\(_2\)-Cu films), Fig. 7 in [16] (ZnO), Figs. 4 and 5 in [17] (Zn\(_{1.6}\)Cu\(_0.4\)S)), a feature that is not mentioned in the works previously mentioned. Thus, in most cases the methylene blue concentration evaluated by visible absorption is wrongly estimated because of the presence in the spectra of peaks corresponding to intermediate compounds. Yogi et al. [10] tried to deal with this artefact in their analysis of the decomposition of methylene blue by Au-TiO\(_2\) films by means of visible spectroscopy. They started from the premise that the spectra at different reaction times resulted from the absorption of several species (methylene blue, azure A, azure B, azure C and thionine) and that the absorbance of the multicomponent system would be equal to the sum of the absorbances of each component. By solving the resulting equation system (3125 simultaneous equations based on the Beer-Lambert
Evaluation of true methylene blue concentration

law) they were able to estimate the evolution of the concentration of the different species with the reaction time. This procedure yielded some very interesting results while at the same time it revealed the following flaws: the variation in the amount of dimeric methylene blue with the methylene blue concentration was not considered; the azure C concentration was estimated to be negative; and only the evolution of the species inputted into the multicomponent system can be followed.

The dimeric form of methylene blue is apparent in the visible spectrum of methylene blue in the form of a shoulder at ~616 nm [18]. The specific form of the equilibrium constant for the dimer formation is \( K = \frac{1-X}{2C-X^2} \), where \( X \) is the fraction of dye molecules existing in monomeric form and \( C \) is the total concentration of methylene blue that can be calculated as \( C = C_{\text{mon}} + 2C_{\text{dim}} \). This implies that the concentration of the dimeric form of methylene blue increases with the increase in the total concentration of methylene blue. However, some authors [19] consider that the shoulder at ~616 nm cannot be produced by the presence of the dimer since, according to their calculations, its concentration in water is always about 106 times lower than that of the monomer (Fig. 2 in [19]). We suspect that these authors used the “dissociation” constant evaluated in [18] as a “dimerization” constant and, because of this “misuse”, they obtained such an odd result. In fact, if the dissociation constant provided in [18] is applied, the percentage of dimer in solution for an initial methylene blue concentration of 10 mg/L is quite high (9.9%).

In this study we propose a deconvolution procedure that permits an unambiguous evaluation of the methylene blue concentration during photodegradation experiments, allowing the absorption peaks ascribed to intermediate products to be evaluated without the need for previous assumptions concerning peak positions and taking into account the variation of dimeric methylene blue with the concentration of methylene blue in solution.

2. Experimental

The photocatalytic methylene blue degradation experiment was carried out with 20 mg of commercial TiO₂ particles (Degussa P25) in a 400 mL quartz beaker under the illumination of two ring-type UV 22W lamps (Luzchem Ring-Illuminator) which predominantly emit radiation at 351 nm. The particles were introduced in 60 mL of an aqueous solution of methylene blue, of an initial concentration of 10 mg/L. The
suspension was magnetically stirred for 30 min under darkness to ensure the adsorption/desorption equilibrium between the dye and the photocatalyst. Next the suspension was exposed to the UV lamp. Samples were extracted for measurement after various reaction times, and centrifuged to remove the particles before analysis. The visible absorption peaks of the analyzed samples were recorded in the 400-800 nm range by means of a UV-Vis spectrometer (Shimadzu UV-2401PC).

**Figure 1.** Visible spectra of methylene blue solutions in water (7.0 and 2.3 mg/L). P1 to P6 are the peaks obtained by Gaussian deconvolution.
3. Deconvolution procedure

3.1. Methylene blue calibration

The procedure described below has been tested with the methylene blue photodegradation reaction. However it can be applied to any reaction in which the concentration of the main species is evaluated by absorption spectroscopy. The calibration of the methylene blue concentration in aqueous solution was performed in the 0-12 mg/L range. Fig. 1 shows the visible spectra of the 7.0 and 2.3 mg/L solutions. To perform a Gaussian deconvolution of the spectrum a linear baseline between the lowest point at the left of the spectrum and the point at 794 nm was set. Six Gaussian peaks (P1 to P6 in Fig. 1) were found to be necessary to obtain a correct deconvolution of the original spectra. The convolved curves match almost exactly the experimental curves, as can be appreciated in Fig. 1. P1 and P2 are the main peaks that represent the monomeric and dimeric methylene blue species, respectively [18]. Table 1 shows all of the parameters obtained from the Gaussian deconvolutions. As can be seen, the peak positions, \( \lambda_i \), and standard deviations, \( \sigma_i \), were independent of the solution concentration, whereas the normalized areas of the peaks, \( f_i \) (\( \Sigma f_i = 1 \)), were found to change with the concentration and follow different trends. Thus, \( f_4 \) and \( f_6 \) remained constant for all the methylene blue solutions, \( f_1 \) and \( f_5 \) decreased with the increase in the methylene blue concentration (the peaks being ascribed to monomeric methylene blue [18]) and \( f_2 \) and \( f_3 \) increased with the increase in the methylene blue concentration (the peaks being ascribed to dimeric methylene blue [18]). Once the values of the peak areas were obtained for the different solutions it was possible to construct the upper plot in Fig. 2. As can be seen, \( f_i \) to \( f_1 \) ratios follow second order polynomial trends with the absorbance of peak P1 (\( A_1 \)) at the mean wavelength (666 nm). The polynomial and regression coefficients are shown in Table 2. The lower plot in Fig. 2 displays the calibration data that allow the methylene blue concentration to be related to the absorbance of peak P1 (\( A_1 \)). This parameter is calculated as follows:

\[
A_1 = \frac{f_i}{\sigma_i \sqrt{2\pi}} A_T
\]  

(1)

where \( A_T \) is the total area of the visible spectrum (nm) before normalization. A polynomial fitting of the data displayed in Fig. 2 yields the following calibration equation:
In conclusion, with this procedure it is possible to build up the whole spectrum for methylene blue with only the values of \( f_1 \) and \( A_7 \), since the rest of the parameters are known (Table 1) or have known relations with \( f_1 \) and \( A_7 \) (equation (1) and Table 2).

A classical calibration procedure would involve relating the values of methylene blue concentration to the absorbance of the maximum in the original spectra (in our spectra the maximum was located at 664 nm). For comparison purposes we deduced the following equation for the classical calibration of methylene blue:

\[
C_{MB} = 0.466A_{664}^2 + 3.764A_{664}
\]  

(3)

**Table 1.** Gaussian parameters for P1 to P6 peaks (Figure 1) obtained from the deconvolution of the visible spectra for methylene blue solutions of different concentrations

<table>
<thead>
<tr>
<th>Peak parameters</th>
<th>Methylene blue concentration (mg/L)</th>
</tr>
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<tr>
<td></td>
<td>11.7</td>
</tr>
<tr>
<td>( \lambda_1 ) (nm) (^a)</td>
<td>( \lambda_2 ) (nm)</td>
</tr>
<tr>
<td>664.0</td>
<td>615.9</td>
</tr>
<tr>
<td>( \sigma_1 ) (nm) (^b)</td>
<td>( \sigma_2 ) (nm)</td>
</tr>
<tr>
<td>14.7</td>
<td>23.4</td>
</tr>
<tr>
<td>( f_1 )</td>
<td>( f_2 )</td>
</tr>
<tr>
<td>0.396</td>
<td>0.443</td>
</tr>
<tr>
<td>0.414</td>
<td>0.429</td>
</tr>
<tr>
<td>0.427</td>
<td>0.417</td>
</tr>
<tr>
<td>0.439</td>
<td>0.406</td>
</tr>
<tr>
<td>0.447</td>
<td>0.396</td>
</tr>
</tbody>
</table>

\(^a\) Mean wavelength for the Gaussian distribution  
\(^b\) Standard deviation  
\(^c\) Peak area for the normalized spectrum (\( \Sigma f_i=1 \))
Evaluation of true methylene blue concentration

Figure 2. Upper plot: variation in f_i-to-f_1 ratios with the absorbance of peak P1 from visible spectra obtained with methylene blue solutions of different concentrations. Lower plot: variation of methylene blue concentration with the absorbance of peak P1 at the mean wavelength
Table 2. Parameters from the fitting of the values of f_{i} to f_{1} ratios with the absorbance of peak P1 from visible spectra obtained with methylene blue solutions of different concentrations

<table>
<thead>
<tr>
<th>f_{i} to f_{1} ratios</th>
<th>f_{i}/f_{1} = A\times A_{1}^{2} + B \times A_{1} + C</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R^{2}</th>
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<tr>
<td>f_{2}/f_{1}</td>
<td>5.22\times10^{-2}</td>
<td>-8.78\times10^{-3}</td>
<td>8.79\times10^{-1}</td>
<td>0.998</td>
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<td>f_{3}/f_{1}</td>
<td>1.06\times10^{-2}</td>
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<td></td>
</tr>
<tr>
<td>f_{4}/f_{1}</td>
<td>2.76\times10^{-3}</td>
<td>-1.72\times10^{-3}</td>
<td>7.92\times10^{-2}</td>
<td>0.997</td>
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<tr>
<td>f_{5}/f_{1}</td>
<td>-8.29\times10^{-4}</td>
<td>-1.55\times10^{-2}</td>
<td>1.46\times10^{-1}</td>
<td>0.998</td>
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<tr>
<td>f_{6}/f_{1}</td>
<td>8.58\times10^{-4}</td>
<td>-5.34\times10^{-4}</td>
<td>2.46\times10^{-2}</td>
<td>0.997</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Deconvolution of visible spectra with the contribution of unknown intermediates

The procedure for evaluating the methylene blue concentration as well as the contribution of unknown intermediates to the visible spectra obtained during the photodegradation experiment consists in finding the peaks that, together with those of methylene blue, best fit the spectra. To this end the following steps were followed:

1. A baseline was established between the lowest point at the left end of the spectrum and the point at 794 nm.
2. The total area (AT) between the profile of the spectrum and the baseline was evaluated.
3. The spectrum was normalized so that the total area would be equal to one (Σfi=1).
4. The initial values for the unknown peaks (area fractions fi>6, mean wavelengths, λi>6, and standard deviations, σi>6) and for the methylene blue peaks were inputted. In the case of the methylene blue peaks the only variable to be fitted was f_{1}, since the rest of parameters are known (Table 1) or have known relations with f_{1} and A_{T} (Table 2).
5. A minimization algorithm was set to fit f_{1} and the values of the parameters for the new peaks (i>6). Absorbance A_{i} was then calculated by means of equation (1) and the methylene blue concentration by means of equation (2).

In order to implement these steps on an easy-to-use interface we designed a Microsoft Excel sheet with visual basic macros making use of the Microsoft Solver complement to minimize the error.
3. Discussion of results

It was found that in most of the spectra obtained during the reaction only three peaks were needed for deconvolution in addition to those corresponding to methylene blue. Fig. 3 shows the spectrum obtained after 19 minutes of reaction together with the peaks obtained by the deconvolution technique.

![Figure 3](image)

**Figure 3.** Visible spectrum of a sample obtained after 19 min of reaction together with the peaks obtained by the deconvolution technique. Bold peaks (P7, P8, P9) are ascribed to intermediates; thin peaks are ascribed to methylene blue.

The peaks ascribed to methylene blue are represented by the thin lines, whereas the extra peaks (P7, P8 and P9) are displayed using bold lines. P7, P8, P9 were located at mean wavelengths of 530.9, 611.2 and 648.4 nm, respectively, and they maintained these positions throughout the reaction, though their relative areas varied. This can be appreciated in Fig. 4, where only the extra peaks and their convolved profiles are represented for different reaction times.

As can be seen, the decreasing area of peak P9 during the reaction produces a hypsochromic shift in the convolved spectrum of the intermediate products. Fig. 5 shows the temporal evolution of the absorbances at mean wavelengths for the extra
peaks (P7, P8 and P9) together with those for peak P1, corresponding to methylene blue, and for a peak (P10) that started to emerge in the longest reaction times at a mean wavelength of 667 nm, although its significance was always minimal. It can be seen that the absorbances of P7, P8 and P9 vary in a way that would be expected of intermediate products; they increase at the beginning of the reaction and start to decrease when the methylene blue concentration has fallen to almost zero.

Figure 4. Fraction of the visible spectra for samples obtained at different reaction times corresponding to intermediate compounds as evaluated by the deconvolution technique.
Having managed to discriminate between the spectrum corresponding to methylene blue and that due to the formation of intermediates, we are now in a position to calculate the concentration of methylene blue during the reaction. However we still know nothing about the nature of the intermediates. These can be expected to be mainly azure A and azure B and, to a lesser extent, azure C, thionine and phenothiazine [11-13]. Fig. 6 shows the visible spectra of aqueous solutions of azure A, B and C taken from the literature [20]. The deconvolution of these spectra yields the peaks that are displayed in the figure. As can be seen the azure A and azure B spectra contain three peaks, whose Gaussian parameters (mean wavelengths and standard deviations) are very similar to those of P7, P8 and P9 (see Fig. 4). The ratios of the absorbance of the peak at ~650 nm to the absorbance of the peak at 609-614 nm are 1.15, for azure B, and 0.34, for azure A. Assuming that peaks P8 (at 611.2 nm) and P9 (648.4 nm) are composites of the peaks at 609-614 nm and at ~650 nm for azure A and azure B we can use the following equation to estimate the proportion of these compounds in the spectra shown in Fig. 4:

\[
\text{%Azure A} = 100 - \text{%Azure B} = 100 \times \frac{1.15 - \frac{A_9}{A_8}}{1.15 - 0.34}
\]

(4)

where A8 and A9 are the values of absorbance at the mean wavelength corresponding to peaks 8 and 9, respectively.

![Figure 5](image_url)

**Figure 5.** Temporal evolution of the absorbances at the mean wavelengths for P1 (methylene blue) and the peaks derived for intermediate compounds (P7 to P10)
Figure 6. Visible spectra of azure A, azure B and azure C (10 μM aqueous solutions); original data taken from [20]. Curve deconvolutions performed in this study.
Fig. 7 shows the estimated speciation of azure A and B obtained by means of equation (4). From the figure it can be deduced that the main intermediate product is azure A that is formed by the gradual demethylation of azure B, which in turn is a product of the demethylation of methylene blue. At reaction times of over ~100 min both azure A and B have been degraded to other products that do not absorb radiation in the visible spectral region (Fig. 5). The results displayed in Figs. 5 and 7 are congruent with those obtained by Yogi et al. [10].

Nevertheless, the main purpose of the deconvolution procedure is to avoid the artefact arising from the presence of these intermediate compounds in the evaluation of the concentration of methylene blue. Fig. 8 shows the evolution of the concentration of methylene blue with the reaction time as evaluated by three different methods: (i) by using the classical calibration equation (3) fed with the values of absorbance at the maximum point of the visible spectra, (ii) by using equation (3) fed with the values of absorbance at 664 nm and (iii) by using equation (2) fed with the values of absorbance of peak P1 at the mean wavelength. There are significant differences between the three procedures, which proves that evaluation of the concentration of methylene blue without taking into account the presence of intermediates yields higher values than those obtained by means of equation (2) (deconvolution technique). Very often the concentration values are used to derive
kinetic rate constants \((k)\) from first order reaction equations derived from the Langmuir-Hinshelwood kinetic model [21]. The simplest form of this model yields the following equation:

\[
C_{MB} = C_0 e^{-kt} \tag{5}
\]

where \(C_0\) is the methylene blue concentration at \(t=0\). The dashed lines in Fig. 8 represent the curve fittings to equation (5) with the values of \(k\) also shown in the figure. It can be seen that by ignoring the artefact when evaluating the methylene blue concentration the kinetic rate constants turn out to be significantly lower than that obtained by employing the methylene blue concentration as calculated by means of our deconvolution technique. In the view of the different results shown in Fig. 8, future studies devoted to methylene blue degradation should clearly state whether the artefact masking the evaluation of methylene blue concentration has been taken into account or not.

**Figure 8.** Evolution of the methylene blue concentration with the reaction time as evaluated by: (i) using Eq. (3) with the values of absorbance at the maximum absorption wavelength in the visible spectra, (ii) using Eq. (3) with the values of absorbance at 664 nm and (iii) using Eq. (2) with the values of absorbance of peak P1 at its mean wavelength (deconvolution technique). Dashed lines represent the curve fittings to Eq. (5) with the values of \(k\) also shown in the figure.
Evaluation of true methylene blue concentration

5. Conclusions

The presence of intermediates during the photocatalytic degradation of methylene blue in aqueous solution masks the determination of its concentration when classical evaluation methods by means of visible spectroscopy analyses are employed. The deconvolution procedure described in this work circumvents this artefact by estimating the contribution of intermediates to the visible spectrum. In the photodegradation of methylene blue with Degussa P25 TiO$_2$ particles the main intermediate detected in the visible spectral region was azure A resulting from the gradual demethylation of azure B. The methylene blue concentrations obtained if the artefact was not taken into account were higher than those evaluated by the deconvolution technique and provided lower values of kinetic rate constants for the photocatalytic degradation.

Acknowledgements

Tan T. Vu is grateful to CSIC for the award of a JAE predoc grant.

References


2. **Block II: Sacrificial template synthesis of nanostructured metal oxides supported on stainless steel wire mesh and their applications**

![Image of synthesis, Fenton-like reaction, photostabilization, photocatalysis, and hydrogen production]

**Figure 11. Schematic illustration of the research activities described in Block II**

High surface area metal oxide structures supported on a substrate have been the subject of intensive research in recent years. In this block we refer to experiments performed as part of this thesis involving the fabrication of stainless steel wire mesh (SSWM)-supported metal oxides nanostructures and
their application in areas such as the degradation of contaminants in water or hydrogen production from bioalcohols. The main achievement of this work has been the successful development of a new synthesis strategy, based on the sacrificial template accelerated hydrolysis (STAH) technique, described in Article IV. The methodology is based on the use, as template, of highly polar ZnO nanosheets supported on SSWM. In this article we describe the synthesis of SSWM-supported high surface area CuO, α-Fe₂O₃, CeO₂, and TiO₂, and report the results of testing the α-Fe₂O₃ nanostructures in a Fenton-like reaction for degrading methylene blue in aqueous solutions. Articles V, VI and VII present several examples of application of single and binary metal oxides synthesized by means of the same procedure. Article V illustrates the use of SSWM-supported CdₓZn₁₋ₓO photocatalysts for methylene blue degradation in water under ultraviolet and visible irradiation, the main objective of the work being to obtain a stable photocatalyst inserting cadmium atoms into the ZnO structure. Article VI analyses the photocatalytic activity of TiO₂ nanoparticles supported on SSWM and reveals that the activity of the best catalyst synthesized is superior to that of the standard catalyst P25 TiO₂. Finally, Article VII reports for the first time the use, as catalyst, of a high surface area Ni₀.₇Zn₀.₃O solid solution supported on a SSWM substrate. This new catalyst has a remarkable activity in the production of hydrogen from methanol. Figure 11 illustrates the relevant details of the work contained in this block.

2.1. Sacrificial template accelerated hydrolysis for the synthesis of SSWM-supported high surface area metal oxides

Hard template methods have recently been employed for synthesizing unsupported metal oxide particles with a high surface area [25-28]. However, these methods involve several synthesis steps, including the removal of the template, that make them costly in terms of time and reactants. Sacrificial template accelerated hydrolysis (STAH) is a novel hard exotemplating
technique that allows metal oxide nanotubes to be synthesized via the hydrolysis of metal ions in mild conditions with the simultaneous dissolution of the template [73]. The common feature of the syntheses reported until now has been that the template is made up of non-polar ZnO nanowires or nanorods and the metal oxides obtained are in the form of nanotubes. Although not specifically stated in these works, it is clear that the metal oxide nanotubes obtained exhibit a low specific surface area and a low yield on the substrate, which is generally indium tin oxide (ITO). In the present work we have employed a novel template consisting of SSWM-supported polar ZnO nanosheets. The template displays a high surface area (80 m² g⁻¹) and a large proportion of polar surfaces, contrary to the non-polar ZnO nanorods typically used in the standard STAH technique. The polar template makes it possible to obtain metal oxides with porous nanosheet-like structures, high surface areas (up to 275 m² g⁻¹ in the case of TiO₂, as reported in articles IV and VI) and in high yields (up to 40 wt.% for Ni₀.7Zn₀.3O, as reported in article VII). The main results of the synthesis are set out in Article IV (Sacrificial template synthesis of high surface area metal oxides. Example: an excellent structured Fenton-like catalyst, Vu et al. Applied Catalysis B: Environmental, 152-153 (2014) 51-58). This method has also been applied for the synthesis of the materials included in Articles V, VI and VII.

The STAH procedure starts with the hydrolysis of the metal ions used as precursor for the synthesis of the supported metal oxides. The acidic character of the ions affects the final degree of Zn substitution that can be achieved. Thus, strongly acidic cations (pKₐ > -9.5), such as Fe³⁺, Ce³⁺, Cu²⁺, etc., permit the total substitution of ZnO giving rise to pure metal oxide nanostructures supported on the mesh. On the other hand, in the case of weakly acidic cations, with pKₐ values below -9.5, only partial substitutions are obtained, leading to the formation of mixed oxides MₓZn₁₋ₓO (i.e., M = Ni²⁺ or Cd³⁺).

As the template employed in this work has a large proportion of polar surfaces, when acidic ions are used special care has to be taken in order to
avoid the complete dissolution of the template before the formation of new metal oxide on the ZnO scaffold. This problem has been solved by adding the solution of the more acidic ions (i.e., Fe\(^{3+}\)) dropwise, i.e., the salt solution is slowly pumped by means of a syringe pump into the plastic flask containing the template in water, while the flask is shaken in an orbital shaker at room temperature.

The degree of replacement of ZnO by metal oxide can be controlled by changing the time of reaction or the concentration of the metal ions in the synthesis solution, with the limitations indicated above. Degrees of substitution as high as 98 mol\% can be achieved. In general, the specific surface area of the substituted material increases with the degree of substitution. For the highest substitution degrees, the metal oxide nanostructures exhibit high specific surface areas which are in the range of 37-275 m\(^2\) g\(^{-1}\) depending on the metal oxide synthesized and the calcination temperature used. It is important to note that the specific surface areas of the metal oxides obtained in this work are significantly higher than those reported in literature for materials prepared by means of the conventional STAHT technique [75]. This improvement can be explained by the large polar surface and high surface specific area of the ZnO structures used as template in this work.

The yield of the synthesized metal oxides with respect to the SSWM support varies from ~12 wt.% (TiO\(_2\)) to ~40 wt.% (Ni\(_{0.7}\)Zn\(_{0.3}\)O). The metal oxide yield can be maximized by increasing the ZnO load in the original template (Article VII). In correspondence with their high surface area, the crystal sizes of the metal oxides are fairly small (5-8 nm). The morphologies of the metal oxides are a replica of the morphology of the ZnO nanosheets used as template. It is important to note that these nanosheets show a good adhesion to the SSWM support.

In summary, we have successfully demonstrated that it is possible to synthesize nanosized metal oxides supported on SSWM substrates using the STAHT method with a SSWM-supported ZnO template that has a high surface
Results and Discussion: Block II

area and a large proportion of polar surfaces. The nanostructures obtained exhibit several important properties: a) high specific surface area values which are at least one order of magnitude higher than those previously reported for metal oxides prepared by the standard STAH method, b) a high purity and yield and c) a good adhesion to the SSWM substrate.

2.2. Applications of SSWM-supported metal oxides obtained via STAH

2.2.1. Oxidative degradation of contaminants by means of a Fenton-like process

The abatement of organic contaminants by a heterogeneous Fenton process (or a Fenton-like reaction) using hydrogen peroxide and iron oxides as catalyst has recently generated great interest [130]. However, the use of iron oxides in a powder form entails several drawbacks such as the difficult separation of the catalyst particles from the reaction medium. To overcome this problem, we have used high surface area $\alpha$-Fe$_2$O$_3$ nanosheets (220 m$^2$ g$^{-1}$) supported on SSWM substrates as a structured Fenton-like catalyst for the oxidative degradation of methylene blue in aqueous solutions. The results are summarised in Article IV (Sacrificial template synthesis of high surface area metal oxides. Example: an excellent structured Fenton-like catalyst, Vu et al. Applied Catalysis B: Environmental, 152-153 (2014) 51-58).

The Fenton-like reaction has been performed in a continuous flow monolithic reactor, consisting of a SSWM-supported $\alpha$-Fe$_2$O$_3$ catalyst rolled around a stainless steel wire and inserted into a silicone tube with an internal diameter of 4 mm. The degree of methylene blue conversion is monitored as a function of the residence time. Over 80% conversion is obtained at the highest residence time tested in this work ($\tau=6.5$ min). The catalyst shows an outstanding stability during a single experiment and over several reaction cycles.
In addition, the intrinsic catalytic activity of the α-Fe₂O₃ particles has been compared to that of other particulate catalysts reported in literature. To this end, the α-Fe₂O₃ particles have been scratched from the wire mesh and subsequently tested in a batch experiment. It has been found that the α-Fe₂O₃ particles prepared in this work show a better performance than that reported for the highly active Fe₂O₃@mesoporous SiO₂ particles [154]. This high catalytic activity can be attributed to the high surface area of the STAH-synthesized material, which provides a higher number of electron transfer sites between H₂O₂ molecules and ferric ions and gives rise to the generation of a large number of reactive radicals.

2.2.2. Photocatalytic activity of SSWM-supported CdₓZn₁₋ₓO under ultraviolet and visible irradiation

As discussed in Block I, ZnO (and SSWM-supported ZnO) suffers from deactivation under UV irradiation due to the photocorrosion phenomenon. Although there are some recent works that indicate that the coupling of CdO and ZnO oxides could help to prevent the recombination of excitons, improve the absorption of solar light and increase the photocatalytic activity of ZnO [128], a study of CdO-ZnO structures alone to prevent photocorrosion has not yet been undertaken. Additionally, to the best of our knowledge, CdO-ZnO nanostructures have always been synthesized in powder form. In this work, the synthesis of SSWM-supported CdO-ZnO mixed oxides has been achieved for the first time. The synthesis strategy employed consists of the formation of CdₓZn₁₋ₓO nanostructures via the hydrolysis of Cd²⁺ ions in the vicinity of ZnO supported nanostructures, by applying the STAH technique to the SSWM-supported polar ZnO template described in Article IV. The most important results derived from this work are summarised in Article V (Nanostructured stainless steel wire mesh-supported CdₓZn₁₋ₓO: a stable photocatalyst under visible and ultraviolet irradiation, Vu et al., submitted, 2014).
In aqueous medium the cadmium ion is a weakly acidic cation with a pKa of -9.7, and, \textit{a priori}, the basic synthesis method reported in article IV should permit only partial substitution, producing a mixed CdO-ZnO oxide. At room temperature, low substitution degrees (≤6 mol%) are obtained for Cd to Zn molar ratios in the synthesis solution below or equal to 5. The substitution degree is not increased even when the temperature is increased to 90°C. However, when sodium citrate is added to the synthesis solution and this is heated at 90°C, the substitution kinetic rate increases drastically and a maximum substitution degree of around 20 mol% is obtained (Cd/Zn molar ratio = 5). The nanosheet-like morphology of the synthesised material has been found to be similar to that of the SSWM-supported ZnO template.

An EDX analysis of the sample reveals a homogeneous distribution of cadmium on the ZnO nanosheets. The specific surface area of the Cd-substituted materials calcined at 350°C is around 37 m² g⁻¹, regardless of the degree of substitution. XRD analysis shows that CdO can only be identified as a minor separate phase when the amount of Cd is around 20 mol%. Additionally, the XRD peaks of Cd-substituted ZnO phase shows a slight deviation from those of pure ZnO. This suggests the formation of a CdxZn1−xO solid solution in which cadmium is replacing part of the zinc atoms in the hexagonal structure of ZnO. XPS analyses reveals a profile of the Cd concentration in the substituted ZnO layer, as a result of which the stoichiometric formula changes gradually from ZnO in the bulk to CdO on the surface, for the catalyst with the highest substitution degree (x=0.2).

The photocatalytic activity of SSWM-supported CdxZnO1−xO (x=0.00, 0.01, 0.05 and 0.20) for methylene blue decomposition has been studied both under visible and ultraviolet irradiation. We observe that a small amount of cadmium in the CdxZn1−xO nanostructures (x=0.05) drastically reduces the photocorrosion under UV light. Although SSWM-supported CdxZn1−xO exhibits a lower initial photocatalytic activity than the SSWM-supported ZnO after only three reaction stages the activity of the Cd-substituted catalyst is already higher than that of the non-substituted catalyst, and it remains practically
unchanged during the seven stages tested in this work (14 hours). With respect to the mass losses due to photocorrosion, we observe an active phase loss of only 8 wt.% after 7 reaction stages for a sample containing 5.3 mol% Cd. This behaviour differs from that of the pure ZnO which suffers a weight loss of around 78 wt.% under similar conditions. In this work it has been found for the first time that the incorporation of a small amount of cadmium significantly reduces ZnO deactivation due to photocorrosion. Under visible irradiation Cd-substitution leads to a very slight enhancement of the photocatalytic activity, with the material with 1.1 mol% Cd showing the highest enhancement on a total mass basis (ZnO plus CdO) with no deactivation.

In summary, a simple straightforward route for the synthesis of Cd$_x$Zn$_{1-x}$O mixed oxide catalysts ($x=0.01-0.20$) supported on a wire mesh has been achieved. This solid solution exhibits a good activity as photocatalyst under both ultraviolet and visible irradiation and a high stability.

2.2.3. Photocatalytic activity of SSWM-supported TiO$_2$ nanostructures

The STAH technique has been used previously for the synthesis of TiO$_2$ nanotubes supported on silicon, FTO and ITO substrates employing ZnO nanorods/nanowires as templates [74, 155, 156]. A consequence of the nanotube morphology is that the TiO$_2$ materials exhibit low surface areas. In contrast, the SSWM-supported TiO$_2$ nanosheets reported in Article IV have a very high surface area, and therefore this material is suitable for application in catalytic or photocatalytic reactions. In the case of TiO$_2$ not only the surface area, but also the crystallinity and the ratio of the photocatalytic phases, anatase and rutile, have to be taken into account. A crystallized anatase material with a small grain size and a high surface area is the preferred form for TiO$_2$ photocatalysts [157-159]. Heating TiO$_2$ at a high temperature is a simple method to transform the amorphous TiO$_2$ phase into small crystals of
Results and Discussion: Block II

anatase, which grow upon continuous heating, and then change to rutile at higher temperatures [160]. Crystallization from amorphous TiO\(_2\) to anatase and then from anatase to rutile usually occurs in the temperature ranges of 450-550°C and 600-700°C, respectively. We have varied these parameters (anatase/rutile ratio, crystal size and crystallinity) by using different calcination temperatures in the synthesis of the SSWM-supported TiO\(_2\) nanosheets and have tested the catalysts obtained for the photodegradation of methylene blue in aqueous solution. The results of this work are included in Article VI (High surface area stainless steel wire mesh-supported TiO\(_2\) prepared by sacrificial template accelerated hydrolysis. A monolithic photocatalyst superior to P25 TiO\(_2\) by Vu et al., submitted, 2014).

The purity of the SSWM-supported TiO\(_2\) prepared in this work is very high (the degree of substitution of ZnO is 98 mol%), and the average yield for all the samples is 11.8±2.0 wt.% with respect to the SSWM support. The TiO\(_2\) on the surface of SSWM is formed by thin nanosheets (length: 5-7 μm) with crystals in the 3-6 nm range. A series of SSWM-supported TiO\(_2\) samples have been calcined at different temperature (250°C-700°C) in order to study the effect of the calcination temperature on the composition, texture and photodegradation activity of the catalysts.

The TiO\(_2\) nanosheets exhibit a very high specific surface area, that decreases with the calcination temperature from 275 m\(^2\)g\(^{-1}\) (250°C) to 42 m\(^2\)g\(^{-1}\) (650°C). However the surface area values of the synthesized samples are higher than the values reported in the literature for similar materials. For instance, P25 TiO\(_2\) powder calcined at 500°C for 2 hours has a specific surface area of 52 m\(^2\)g\(^{-1}\) [161], whereas, with the same calcination procedure, the SSWM-supported TiO\(_2\) has a specific surface area of 87 m\(^2\)g\(^{-1}\).

The TiO\(_2\) sample calcined at a relatively low temperature (250°C) contains mainly a mixture of anatase and amorphous TiO\(_2\) and a minor rutile-like phase of ZnO-TiO\(_2\) solid solution, derived from the presence of residual ZnO (around 2 wt.% ZnO). This phase might have been formed due to Zn\(^{2+}\) promoting the
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transformation of anatase to rutile during the room temperature synthesis of TiO$_2$. When the temperature increases this phase probably splits into anatase and ZnO, which would explain the reduced presence of the rutile-like phase on approaching 650°C. At 700°C the thermodynamic transformation of anatase to rutile is clear, the rutile content of the sample reaching a value of over 20%.

The photocatalytic activity of the SSWM-supported TiO$_2$ catalysts has been tested for the photodegradation of methylene blue (MB) under UV irradiation. We observe that the sample calcined at 250°C presents a relatively high catalytic activity due to its very high specific surface area (275 m$^2$ g$^{-1}$). For the sample treated at 375°C, the specific surface area has decreased to 126 m$^2$ g$^{-1}$, with a parallel decrease in the number of active centers for photocatalysis, which explains its significantly lower catalytic activity. On increasing the calcination temperature to 450°C, a very sharp increase of the catalytic activity is observed, which is attributed to the transformation of amorphous TiO$_2$ into crystalline anatase of small crystal size. For calcination temperatures between 450 and 600°C, a slight decrease in the catalytic activity is observed, due to a reduction in specific surface area and a parallel increment of anatase crystal size caused by sintering. This temperature region is the optimal region of calcination for using these catalysts for the photodegradation of methylene blue. Beyond 600°C the reduction in catalytic activity is more severe, as a consequence of the onset of rutile formation.

We have analyzed the photocatalytic activity of TiO$_2$ particles scratched from the SSWM ($T_c = 450$ and 500°C) and the results have been compared to those obtained for a commercial P25 TiO$_2$ catalyst. The TiO$_2$ particles prepared in the present work exhibit a better performance than the P25 TiO$_2$ particles. This is due to their higher specific surface area and smaller rutile content than those of the P25 TiO$_2$ particles.

In summary, it has been found that the calcination temperature significantly affects the composition, crystallinity, textural properties and photocatalytic activity of SSWM-supported TiO$_2$ catalysts. The STAH synthetic
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route opens the door for the fabrication of structured TiO$_2$ photocatalysts which can be easily incorporated into monolithic reactors. The best catalytic performance is obtained with the catalyst calcined at 450°C, this catalyst exhibiting twice as much intrinsic catalytic activity as P25 TiO$_2$.

2.2.4. Production of H$_2$ from methanol by using a SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O catalyst

The ability of the zinc atoms to be incorporated into the NiO rocksalt crystal structure and to form a solid solution of formula Ni$_{0.7}$Zn$_{0.3}$O was recognized long ago [162, 163]. The synthesis of this solid solution usually requires a high temperature (more than 500°C) for the incorporation of zinc [164]. To our knowledge this solid solution has only been tested for its photoluminescence [165] and electroluminescence [166] properties. In this work, the room-temperature synthesis of a high surface area Ni$_{0.7}$Zn$_{0.3}$O solid solution by sacrificial template accelerated hydrolysis (STAH) has been achieved for the first time. We have also shown that this material is a good catalyst for the production of hydrogen from methanol. The results obtained are described in Article VII (Novel high surface area stainless steel wire mesh supported Ni$_{0.7}$Zn$_{0.3}$O solid solution prepared by room temperature sacrificial template accelerated hydrolysis. Application in the production of hydrogen from methanol by Vu et al., Applied Catalysis B: Environmental, accepted, http://dx.doi.org/10.1016/j.apcatb.2014.05.005, 2014).

The first objective of this work was to synthesize NiO with a high yield and purity by changing two operational parameters: reaction time and the Ni/Zn molar ratio in the synthesis solution. However, this optimization process leads to a maximum Ni/(Zn+Ni) molar ratio of only 0.7.

By using different characterization techniques (TPR, XRD and XPS) we are able to conclude that what we have obtained is in fact an oxygen-defective solid solution with an empirical formula of the type
Nanostructured metal oxides supported on SSWM

$\text{Zn}^{(2-\sigma)^+}_{0.30}\text{Ni}^{(2-\delta)^+[\text{bulk}]}_{0.28}\text{Ni}^{2+ [\text{surf}]}_{0.25}\text{Ni}^{3+}_{0.17}\text{O}_{1.085-0.15\sigma-0.14\delta}$ with a slightly distorted rocksalt crystal structure. This bimetallic compound has a high specific surface area of 100 $\text{m}^2\text{g}^{-1}$. A SEM analysis of the SSWM-supported mixed oxide reveals that it is composed of nanosheets analogous to those of the ZnO used as template. TEM analysis shows that these nanosheets are made up of three-dimensionally interconnected nanograins of $\sim 7 \text{ nm}$ size.

We have tested the catalytic activity of the SSWM-supported $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ catalysts obtained in different yields (20, 35 and 40 wt.%) for the production of hydrogen by methanol steam reforming (MSR) and methanol decomposition (MD). The catalytic performance for the MSR reaction has been investigated in the 300-450°C temperature range for long isothermal stages (15 h each). The catalysts are gradually reduced during the catalytic tests on increasing the reaction temperature and they then maintain a high catalytic activity towards methanol conversion in the testing stage at decreasing temperatures (450 to 300°C). It is observed that at temperatures below 400°C the catalysts are not very selective and consequently large amounts of CO are produced. However, when the temperature reaction is higher than 400°C there is an improvement in the hydrogen yield and in the carbon selectivity towards CO$_2$, especially for the longest contact time. This suggests that the steam reforming process needs longer contact times and/or higher steam pressures for the water gas shift reaction to increase the H$_2$ yield and the carbon selectivity towards CO$_2$.

The MD reaction over the SSWM-supported $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ catalysts has been investigated at temperatures in the 200-325°C range and for long isothermal stages of 10 h. Methanol decomposition occurs with high conversion degrees and hydrogen yields in the 250-350°C temperature range. In spite of some catalyst deactivation due to coke deposition, which is more noticeable at the highest weight hourly space velocity, this catalyst has been found to be among the most active catalysts ever reported in the literature [38].

In brief, we demonstrate the feasibility of preparing a high surface area $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ solid solution supported on a flexible substrate (SSWM) by a room
Results and Discussion: Block II

temperature synthesis procedure. Once reduced, the catalyst exhibits an excellent activity for H₂ production via a methanol steam reforming reaction in the 300-450°C temperature range, although the carbon selectivity towards CO₂ is rather limited. This material has been found to be a very active and selective catalyst for the decomposition of methanol in the 250-350°C temperature range, although it undergoes a slight deactivation due to the formation of coke deposits.
Article IV

Sacrificial template synthesis of high surface area metal oxides.
Example: an excellent structured Fenton-like catalyst

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Sacrificial Template Synthesis of High Surface Area Metal Oxides. Example: An Excellent Structured Fenton-like Catalyst
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ABSTRACT

Standard sacrificial template synthesis allows metal oxide nanotubes to be produced from ZnO nanowires. In spite of their high interest in several technological fields, the low surface area of these nanotubes is a drawback for most applications. Here we report for the first time the sacrificial template synthesis of stainless steel wire-mesh (SSWM) supported metal oxides of high technological interest (CuO, CeO₂, α-Fe₂O₃ and TiO₂) with specific surface area values (84-275 m² g⁻¹) that are at least one order of magnitude higher than that of metal oxide nanotubes. The key to achieving this outstanding result was the use of a novel template (SSWM-supported ZnO nanosheets) with a large proportion of polar surfaces. As an example of application of these materials, a structured reactor with a highly active SSWM-supported α-Fe₂O₃ catalyst was successfully tested for the continuous Fenton-like degradation of aqueous Methylene Blue.

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1. Introduction

Metal oxides of high surface area are used in many applications such as heterogeneous catalysis, wastewater conditioning, the electrochemical storage of energy, sensing, etc [1-5]. There is a great need to develop versatile low temperature synthesis methods for the preparation of nanosized metal oxides with an elevated specific surface area and a high yield on the external surface of flexible metallic supports that will allow microdevices with excellent heat transfer and electrical conductivity properties to be built. Among these supports stainless steel wire meshes (SSWM) of micrometric dimensions have been used with great success for supporting high surface area cobalt and zinc oxides [6, 7]. In this work, a low temperature
method for obtaining nanosized metal oxides supported on SSWM is presented. To demonstrate the potential of this invention, one of the obtained materials (SSWM-supported α-Fe₂O₃) was successfully employed as a structured catalyst for the continuous degradation of aqueous methylene blue (MB) via the heterogeneous Fenton-like reaction with hydrogen peroxide [8, 9].

2. Experimental

2.1. Preparation method

The support was SSWM [with a wire diameter of 30 µm and a screen opening of 40 µm] provided by CISA. The SSWM-supported ZnO was synthesized as described in [7]. In summary, Zinc acetate dihydrated was dissolved together with urea in deionized water. Concentrations of Zn²⁺ and urea in the aqueous solutions were adjusted to 0.05 and 1.0 M, respectively. The pH of the solution was adjusted to 4.88 by using acetic acid. The wire mesh was placed in a Teflon autoclave (100 ml) filled with the growth solution. The autoclave was sealed and hydrothermal ZnO growth proceeded at 80°C for 23 h in a constant-temperature water bath. The ZnO coated-wire mesh was then taken out of the solution, thoroughly washed with deionised water and vacuum-dried at 60°C. Finally the sample was calcined at 200°C for 0.5 h in air.

To fabricate the copper, cerium and titanium oxides by means of the basic synthesis method, the as-synthesized SSWM–supported ZnO templates were immersed in plastic flasks containing 50 mL water solutions of metallic salts. For the preparation of TiO₂ boric acid was added to the solution at a H₃BO₃/K₂TiF₆ molar ratio of 3/1. The closed flasks were subjected to shaking at RT in an orbital shaker for different durations of time in order to obtain different degrees of metal substitution. To synthesize the iron oxides by the dropwise synthesis method, water solutions (50 mL) of iron (III) nitrate or iron (II) sulphate were slowly pumped with a syringe pump into plastic flasks containing 50 mL of water and the SSWM–supported ZnO templates, while the flasks were shaken in an orbital shaker at RT. Afterwards, the samples were taken out of the flasks and washed with deionized water, vacuum-dried at 60°C for 30 min and calcined in air at 250°C (in the case of copper, cerium, iron (ex-Fe²⁺) and titanium oxides) or at 275°C (in the case of iron (ex-Fe³⁺) oxide) for 2 hours. The calcination temperatures were selected after TGA analyses of the different samples.
2.2. Material characterization

The chemical composition of the metal oxides was evaluated by means of atomic absorption spectroscopy. The morphology of the samples was studied by scanning electron microscopy (SEM, FEI Quanta FEG 650 model) and transmission electron microscopy (TEM, JEM -2100F). The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA using Cu-Kα radiation (λ = 0.15406 nm). The BET specific surface area of the samples was evaluated by means of N₂ adsorption isotherms (-196°C) obtained on a Micromeritics ASAP 2020 analyser. Raman spectra from 100 to 1400 cm⁻¹ were obtained at room temperature using a T64000 System (Horiba).

2.3. Heterogeneous Fenton-like reaction

Fenton-like degradation of methylene blue in aqueous solutions was performed with SSWM-supported α-Fe₂O₃ catalysts in two modes; batch and continuous operation. All reactions were carried out in the dark to avoid the influence of light. No acid or base was added to adjust the pH value of the reaction solution. A batch reaction experiment was carried out in order to compare the catalytic activity of the α-Fe₂O₃ powder obtained in this work (scratched from the wire mesh-supported material) with that of yolk-shell structured Fe₂O₃@mesoporous SiO₂ particles reported by Cui et al. [10]. The reaction was performed in a magnetically stirred reactor at room temperature, at the same reaction conditions used by Cui et al. [10] (0.5 g·L⁻¹ α-Fe₂O₃, 50 mg·L⁻¹ MB, 18 g·L⁻¹ H₂O₂). Liquid samples were taken for measurement at given reaction times and centrifuged to remove the α-Fe₂O₃ particles. The visible absorption peaks of the analyzed samples were recorded in the 400-800 nm range by means of a UV-Vis spectrometer (Shimadzu UV-2401PC). The concentration of MB was evaluated from calibration curves using the absorbance at 664 nm.

For the continuous operation mode, a SSWM-supported α-Fe₂O₃ catalyst with dimensions of 2.5 cm × 5 cm (36 mg α-Fe₂O₃) was rolled around a stainless steel wire and inserted into a silicone tube with an internal diameter of 4 mm (Figure 8). A 50 mL solution containing 50 mg·L⁻¹ MB and 18 g·L⁻¹ H₂O₂ was introduced into a syringe coated with a black tape (not shown in Figure 2). The MB/H₂O₂ solution was then slowly injected by means of a syringe pump into the silicone tube containing the SSWM-supported α-Fe₂O₃ (Figure 2). Experiments at different residence times
(pumping rates) were performed. For a given experiment the concentration of the exit solution was analyzed every 5 mL and found to be quite stable during the entire experiment. The final degree of MB degradation was expressed as the average value of all measurements (<C/C0>).

3. Results and Discussion

3.1. Sacrificial template synthesis of high surface area metal oxides

Of the many synthesis methods described in the scientific and patent literature, mainly for making unsupported metal oxides, hard templating methods are known to be among the most effective in producing high surface area metal oxides in powder form [11,12]. However, these methods involve several synthesis steps, including the removal of the template by oxidation or dissolution. Sacrificial template-accelerated hydrolysis (STAH) is a novel hard exotemplating technique [13] that consists in the formation of metal oxide nanotubes via the hydrolysis of metal ions in the vicinity of ZnO nanowires, generally supported on ITO. Hydrolysis is favoured by the removal of protons due to the simultaneous dissolution of the ZnO scaffold, which is the distinctive characteristic of this technique. Thus, its main advantage over other classical hard templating approaches is that there is no need for a template removal step. Initially used for the synthesis of Fe2O3 nanostructures with a high lithium-ion storage capacity [13-15] STAH has also been applied in the preparation of platinum and palladium nanotubes for electrocatalysis and chemical sensing [16,17], NiO-based electrodes [18,19], CeO2 nanotubes [20], and active electrocatalysts consisting of mixtures of noble metal nanotubes [21]. The common feature of all these publications is that the ZnO template is made up of nanowires or nanorods and the metal oxides obtained are in the form of nanotubes, with the exception of the ZnO-α-Fe2O3 nanosheets described by Qin et al. [14], which have a higher specific surface area (27 m² g⁻¹) than nanotube-based materials. The values of the specific surface area and yields of these nanotubes have not been reported in any of the revised papers though their geometrical characteristics (e.g. nanotube diameters of hundreds of nanometers) suggest that their associated specific surfaces areas and yields are low.

As an example of a nanotube-precursor template, Figure 1a shows a SEM image of a SSWM-supported ZnO sample. The synthesis of this sample has been described in a previous work [22] (denoted there as S0-Bai). It consists of typical hexagonal prisms of
large size, very low specific surface area and with a small proportion of polar planes (top of the prisms). Figure 1b shows the prisms after they have been immersed in an aqueous solution of iron (III) nitrate. As can be seen, the iron oxide only forms on the external (non-polar) surface of the prisms (as detected by EDX) whereas their inner cores are hollowed out by the etching action of the protons released via the hydrolysis of Fe$^{3+}$ on the top (polar) surface of the prisms. A scheme of this mechanism is shown in Figure 1. This is a similar mechanism to that proposed by Feng et al. [20].

**Figure 1.** (a) SEM images of a SSWM-supported ZnO sample consisting of typical ZnO prisms. (b) SEM images of the same sample after it has been immersed in an aqueous solution of iron (III) nitrate. Drawing) STAH mechanism for a highly acidic cation (Fe$^{3+}$) at ambient conditions or mildly acidic cations under hydrothermal conditions on non-polar ZnO prisms
We discovered that the main difference between the ZnO template used to produce moderate surface area ZnO-α-Fe₂O₃ nanosheets [14] and that displayed in Figure 1a or those used in the works describing the production of nanotubes is to be found in their polarity. The XRD pattern of the ZnO in the ZnO-α-Fe₂O₃ nanosheets has a (100)/(002) intensity ratio higher than 1 (Figure 3 in [14]), which indicates that the ZnO crystals have a greater proportion of polar surfaces [23] than the typical ZnO nanowires employed in other works (e.g.[13]). The latter present a low (100)/(002) intensity ratio (I₁₀₀/I₀₀₂<<1), which evidences the exposure of a large proportion of non-polar surfaces [22,23]. It follows from this that metal oxide nanotubes are only produced from non-polar ZnO nanowires.

It should also be noted that when Fe³⁺ is used as precursor (a strongly acidic cation) the STAH reaction occurs readily at ambient conditions over the non-polar ZnO nanowires [13-15], whereas when much less acidic cations are used, such as Ni²⁺ [18] or Ce³⁺ [20] more drastic conditions are needed to produce the nanotubes. Only when the more polar ZnO is used is it possible to obtain ZnO-α-Fe₂O₃ nanosheets at ambient conditions with mildly acidic cations (Fe²⁺) [14], although up to now there has been no report in the literature on the synthesis of pure metal oxides with polar ZnO. This suggests that, contrary to what Feng et al. affirm [20], the nucleation of metal oxides is not prevented on the polar faces by an electrostatic effect, but by the increased rate of dissolution of the polar faces due to the high acidity of the metallic cations (Fe³⁺). On the other hand, when the metallic cations are less acidic, as in [14], the polar surfaces can be partially substituted by metal oxides.

From this deduction, the following questions naturally arise. Would a highly polar ZnO template be completely dissolved by the action of a strongly acidic cation? Would the formation of pure and very high surface area metal oxides be possible at ambient conditions with less acidic cations on a polar ZnO template?

In the present work we have tried to answer these questions by using a high surface area SSWM-supported ZnO template, the preparation of which has been reported in detail elsewhere [7] (Figure 2). This material displays a high specific surface area (80 m² g⁻¹) on a ZnO mass basis and a high yield (20.5 wt.%). Furthermore the ZnO nanosheets show a good adhesion to the support and have a large proportion of polar surfaces (see XRD pattern in Figure 2).

Using the template shown in Figure 2 we attempted to synthesize metal oxides of practical technological interest from aqueous solutions of their metal ions, and
established a clear relation between the value of the pKa (minus decimal logarithm of the hydrolysis constant) and the result obtained by applying the STAH method at ambient conditions (Table 1).

Figure 2. SEM images and XRD pattern corresponding to the polar SSWM-supported ZnO template (SSWM-ZnO). Scheme of the STAH method and images of some SSWM-supported metal oxides

When the basic synthesis method (see Experimental section) was used with Fe$^{3+}$ (a strongly acidic cation), the large amount of H$^+$ produced dissolved the ZnO nanosheets completely before any precipitation of iron oxide started to occur on their surface. In principle, this result answers the first question that we addressed in the preceding discussion: a highly polar ZnO template is completely dissolved by the action of a strongly acidic cation. However, if the iron (III) nitrate solution is supplied dropwise (dropwise synthesis method) onto the piece of SSWM-ZnO when it is immersed in water, iron oxide clearly forms on the SSWM surface. This result corroborates the previous view expressed above that it is local acidity in the vicinity of the polar surfaces that controls the ZnO dissolution rate. When the acidic cation is supplied...
surfaces that controls the ZnO dissolution rate. When the acidic cation is supplied dropwise the local acidity and the ZnO dissolution rate are lower and therefore the deposition of iron oxide on the polar ZnO surface is not impeded.

**Table 1.** Values of pKa and STAH results at ambient conditions for the ions used as metal oxide precursors

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>pKa [30,31]</th>
<th>STAH method</th>
<th>Material obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiF₆²⁻</td>
<td>-</td>
<td>SSWM-ZnO in the precursor solution with H₃BO₃ as a fluoride scavenger [32,33]</td>
<td>Single oxides</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>-2.2</td>
<td>Precursor solution added dropwise to SSWM-ZnO (by means of a syringe pump)</td>
<td></td>
</tr>
<tr>
<td>Ce³⁺</td>
<td>-5.7</td>
<td>SSWM-ZnO in the precursor solution</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺ a)</td>
<td>-8.0</td>
<td>SSWM-ZnO in the precursor solution. Gradual oxidation of Fe⁵⁺ to Fe³⁺ (best results obtained with a syringe pump)</td>
<td></td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>-9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>-9.7</td>
<td>SSWM-ZnO in the precursor solution</td>
<td>Mixed oxides b)</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>-9.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>-10.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Although in most cases the precursor salts were the corresponding nitrates, in the case of copper the specific surface area of the resulting oxide is strongly dependent on the counterion of the precursor salt. Thus, copper nitrate gave rise to a pure oxide with a specific surface area of around 18 m² g⁻¹, whereas copper acetate yielded a copper oxide with a specific surface area of 84 m² g⁻¹. This was due to the hydrolysis of the acetate that produced a slight increase in the pH of the solution [34], thereby slowing down the dissolution of ZnO and causing the CuO to be more uniformly dispersed on the remaining ZnO surface; b) For weakly acidic cations, with pKa values below around -9.5, only partial substitutions were obtained, leading to mixed oxides which will be the subject of a future work.

On the other hand, for values of pKa in the range of aprox. -9.5 to -5 (mildly acidic cations such as Cu²⁺ and Ce³⁺) the basic synthesis method allows total substitution to take place and metal oxides with a purity of over 95% and high yields are obtained.

Since the preparations were carried out at RT and ambient pressure, the main substitution parameters used for the polar SSWM-ZnO template were (i) the aqueous metal ion to zinc molar ratio (R_{metal/Zn}) and (ii) the substitution time (t_{s}). To maximize the purity of the metal oxides obtained (degree of metal substitution; M/(M+Zn) molar...
ratio in the metal oxides) during the synthesis, first the $R_{M/Zn}$ parameter was varied, while the substitution time was kept fixed (Figure 3a) and then the optimal values of $R_{M/Zn}$ (larger dots in Figure 3a) were selected and the substitution time was changed (Figure 3b).

From Figures 3a and 3b it is clear that all of the metal oxides can be prepared with a purity of over 95 mol% provided the appropriate synthesis parameters are selected. It is also to be noted that with the STAH method it is possible to obtain high surface area mixtures of ZnO with the different metal oxides. The surface area of the prepared materials depends on the degree of metal substitution. Except in the case of SSWM-ZnO substituted with Cu (ex-nitrate) the specific surface area increases with the degree of substitution (Figure 3c).

For the highest values of purity, the metal oxides show elevated values of specific surface area that range from 18 m$^2$ g$^{-1}$ (CuO (ex-nitrate)) to 275 m$^2$ g$^{-1}$ (TiO$_2$). As can be observed in Figure 3c, the specific surface area of the iron oxide obtained in this work is more than eight times higher than the highest specific surface area reported in literature for materials prepared by the STAH method [14]. The values of specific surface area obtained are, in general, higher in the case of the synthesized metal oxides than in the case of the original ZnO. This may be due to the restricted growth of the metal hydroxide nuclei inside the electrostatic field of the polar ZnO surface. Table 2 summarizes the main physical properties of the synthesized metal oxides.

**Figure 3.** Effect of a) $R_{M/Zn}$ and b) substitution time ($t_s$) on the degree of metal substitution. c) Variation of the specific surface area with the degree of metal substitution for different SSWM-supported metal oxides.
Table 2. Tailoring the synthesis of stainless steel wire mesh-supported ZnO

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Synthesis method</th>
<th>Yield [wt.%]</th>
<th>Purity [mol%]</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>Pore size maxima [nm]</th>
<th>Crystal size [nm]</th>
<th>XRD</th>
<th>TEM</th>
<th>BET</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO template</td>
<td>Vu et al.[7]</td>
<td>20.5</td>
<td>100.0</td>
<td>80</td>
<td>16, 109</td>
<td>13</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>CuO (ex-acetate)</td>
<td>Basic $R_{\text{M/Zn}}=1.5$ $t_s=1$ day</td>
<td>22.2</td>
<td>95.3</td>
<td>84</td>
<td>53</td>
<td>8</td>
<td>6</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>Basic $R_{\text{M/Zn}}=5$ $t_s=5$ days</td>
<td>26.6</td>
<td>95.6</td>
<td>122</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$ (ex-Fe$^{2+}$)</td>
<td>Basic $R_{\text{M/Zn}}=2$ $t_s=2$ day</td>
<td>18.3</td>
<td>95.1</td>
<td>166</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$ (ex-Fe$^{3+}$)</td>
<td>Basic $R_{\text{M/Zn}}=1.1$ $t_s=2$ days</td>
<td>13.5</td>
<td>97.6</td>
<td>220</td>
<td>3, 12</td>
<td>-</td>
<td>3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>Basic $R_{\text{M/Zn}}=1.5$ $t_s=1$ day</td>
<td>11.6</td>
<td>97.8</td>
<td>275</td>
<td>4</td>
<td>5</td>
<td>3-6</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

When we used iron (II) sulphate with the basic synthesis method we succeeded in obtaining $\alpha$-Fe$_2$O$_3$ but not with a very high value of purity or surface area (64 mol% purity, $S_{\text{BET}} = 42$ m$^2$ g$^{-1}$, $t_s = 2$ days, $R_{\text{M/Zn}} = 1.1$) as occurred in the case of Qin et al. [14]. Fe$^{2+}$ is slowly oxidized to Fe$^{3+}$ in an aqueous solution and this may have affected the Fe$_2$O$_3$ deposition rate during the synthesis. We therefore applied the dropwise synthesis method with this cation and found that the specific surface area of the iron oxide obtained increased dramatically to a value of 166 m$^2$ g$^{-1}$ with a purity of over 95 mol%, probably as a result of a faster oxidation of the highly diluted Fe$^{2+}$ within the flask containing the SSWM-supported ZnO piece. The use of the SSWM-ZnO template with 20.5 wt.% ZnO yielded almost pure metal oxides in amounts that ranged from $\sim$12 wt.% (TiO$_2$) to $\sim$27 wt.% (CeO$_2$). Figure 2 shows photographs of the different SSWM-supported metal oxides obtained while Figure 4 shows the XRD patterns of the metal oxides. The dashed lines mark the positions of the peaks ascribed to the SSWM support.

The patterns for zinc, copper, cerium and titanium oxides correspond to the crystal structures of zincite (ZnO), tenorite (CuO), cerianite (CeO$_2$) and anatase (TiO$_2$), respectively. The crystal sizes of the metal oxides obtained by applying the Scherrer
STAH Method. Example: A Fenton-like catalyst

equation to the XRD spectra, are fairly small (5-8 nm). The iron oxides show patterns of ill-crystallized materials which are difficult to ascribe to any known crystal structure, whereas the peaks of the spectrum corresponding to titanium dioxide are too wide to discard the possible presence of rutile. To facilitate identification in these cases we used Raman analysis and obtained the spectra shown in Figure 5. As can be seen, the spectra are coincident with those of hematite α-Fe₂O₃ [24] and pure anatase TiO₂[25].

![XRD patterns of the different SSWM-supported metal oxides](image)

**Figure 4.** XRD patterns of the different SSWM-supported metal oxides

The morphologies of the metal oxides are presented in Figure 6. As can be seen, the macroscopic morphology of the ZnO template (Figure 2) was more or less
unchanged after the substitution process. The metal oxides are arranged in arrays of thin nanosheets that have a homogenous length distribution in the 5-7 μm range.

Figure 5. Raman patterns of the ill-crystallized SSWM-supported metal oxides

The high resolution TEM images shown in Figure 6 evidence that the nanosheets are formed by nanograin with sizes in the 3-6 nm range (Table 2). This result is in good agreement with the crystal sizes evaluated by XRD or BET analyses, the latter based on the assumption of spherical nanoparticles (Table 2). The three-dimensionally interconnected nanograin give rise to the high porosity of the macroscopic nano sheets. In the electron diffraction patterns of the SSWM-supported metal oxides (Figure 6) all the dominant diffraction rings can be indexed to the planes of the same phases analysed by XRD (Figure 4) and Raman spectroscopy (Figure 5).

To test the degree of adhesion between the metal oxide particles and the SSWM, rectangular pieces were introduced into plastic flasks which were then mechanically shaken for several hours at 1200 rpm in order to cause the SSWM pieces to impact continuously and at high speed against the internal walls of the flasks. After 15 hours of testing the SSWM pieces still retained their initial weight.
Figure 6. SEM and TEM images of the SSWM-supported metal oxides
3.2. Fenton-like degradation of Methylene Blue

To test the potential of the present invention we chose the heterogeneous Fenton-like degradation of Methylene Blue (MB). This is an advanced oxidation process that employs iron-based catalysts to promote a reaction between ferrous ions and hydrogen peroxide for producing reactive radicals. It is a proven and effective technology for the destruction of a large number of hazardous and organic pollutants [8,9]. The use of $\alpha$-Fe$_2$O$_3$ catalysts in powder form involves a series of technical challenges, the most important of which is the separation of the nanosized particles from the reaction medium. To overcome this problem, in this work the SSWM-supported $\alpha$-Fe$_2$O$_3$ material was employed directly as a structured catalyst for the Fenton-like degradation of methylene blue in aqueous solutions.

First, the activity of the high surface area iron oxide was evaluated. To do this $\alpha$-Fe$_2$O$_3$ particles (ex-Fe$^{3+}$) scratched from the surface of the wire mesh were tested in a batch experiment, as described in the Experimental section.

Figure 7 shows the variation of relative MB concentration ($C/C_0$) versus reaction time. The data obtained under the same reaction conditions by Cui et al. [10] for a yolk-shell structured $\alpha$-Fe$_2$O$_3$@mesoporous SiO$_2$ catalyst are also plotted for purposes of comparison. These authors described the activity of their catalyst as “outstanding” [10]. As can be observed in Figure 7, the structured Fe$_2$O$_3$@mesoporous SiO$_2$ nanoreactor shows a high degree of MB adsorption in the absence of H$_2$O$_2$ (time < 0), due to the mesoporous SiO$_2$ layer, whereas the high surface area Fe$_2$O$_3$ prepared in this work does not show any trace of MB adsorption, probably due to chemical incompatibility since there is no other reason why the pore system of the particles (Table 2) should not be readily accessible to the MB molecules. When H$_2$O$_2$ was poured into the reaction vessel (time = 0), reactive radicals were immediately formed on the surface of the iron oxide particles by the action of the hydrogen peroxide and reacted in solution with the MB molecules, causing their degradation. The better performance of the iron oxide particles prepared in this work with respect to the highly active structured Fe$_2$O$_3$@mesoporous SiO$_2$ nanoreactor [10] (Figure 7) must be ascribed to their much larger active surface areas, causing an increased number of electron transfers between H$_2$O$_2$ molecules and ferric ions and, therefore, a larger production of reactive radicals.
Stainless steel wire mesh (SSWM)-supported metal oxide catalysts have been revealed in the recent years by our group as a very promising structured catalytic system [6,7,22,26-28]. Following this path, a continuous Fenton-like reaction system for the degradation of MB was designed in this work in order to use the SSWM-supported α-Fe₂O₃ catalyst, as described in the Experimental section. An image of the reactor is shown in Figure 8. We investigated the MB conversion as a function of the residence time. As can be observed in the graph of Figure 8, over 80% conversion was obtained at the highest residence time tested in this work. The catalyst showed good stability during a single experiment and over several reaction cycles. The conversion values obtained in five consecutive cycles were comprised within the standard deviation limits plotted in Figure 8. Leaching of iron is expected to be minimal considering the initial pH of the testing solution (5.7) [29]. Its performance justifies further research and the development of continuous mode Fenton-like reaction systems employing supported metal oxides prepared by sacrificial template synthesis.

Figure 7. Results of Fenton-like degradation of MB in the dark for the α-Fe₂O₃ (ex-Fe³⁺) particles scratched from the wire mesh (0.5 g·L⁻¹ α-Fe₂O₃, 50 mg·L⁻¹ MB, 18 g·L⁻¹ H₂O₂). As a comparison, the data obtained under the same conditions by Cui et al. [10] for a highly active yolk-shell structured Fe₂O₃@mesoporous SiO₂ nanoreactor are also plotted.
Figure 8. Continuous Fenton-like reaction system using a SSWM–supported $\alpha$-Fe$_2$O$_3$ catalyst for the degradation of MB in aqueous solution. The graph shows the variation of the MB relative concentration in the exiting solution as a function of residence time.

4. Conclusion

In summary, a general method for producing nanosized metal oxides supported on stainless steel wire meshes is presented. The method is based on the Sacrificial Template Accelerated Hydrolysis of strongly or mildly acidic cations in aqueous solution. The sacrificial template is a high surface area SSWM-supported ZnO material with a large proportion of polar surfaces. The nanosized metal oxides (CuO, CeO$_2$, $\alpha$-Fe$_2$O$_3$, and TiO$_2$) are obtained in high yields (12-27 wt.%), adhere well to the SSWM pieces and exhibit a high specific surface area (84-275 m$^2$ g$^{-1}$) which are one order of magnitude higher than those previously reported for metal oxides prepared by the STAH method. Until now this method has only been able to produce pure metal oxide nanotubes of low surface area which are mainly applied in electrochemical applications [13-21]. The breakthrough of the present contribution is that it shows how to apply the STAH method in the fabrication of advanced functional materials of high surface area that can compete in many other fields, such as heterogeneous catalysis, photocatalysis, environmental remediation, micro-reactors, etc, against high surface area materials prepared by more complex techniques. As proof of the potential of this method we designed a structured reactor with a SSWM-supported $\alpha$-Fe$_2$O$_3$ catalyst that was successfully used for the continuous Fenton-like degradation of aqueous Methylene Blue.
Acknowledgements

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References


Nanostructured stainless steel wire mesh-supported Cd$_x$Zn$_{1-x}$O: a stable photocatalyst under visible and ultraviolet irradiation

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Nanostructured stainless steel wire mesh-supported Cd$_x$Zn$_{1-x}$O: a stable photocatalyst under visible and ultraviolet irradiation

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ABSTRACT
In this work, high surface area stainless steel wire mesh-supported Cd$_x$Zn$_{1-x}$O catalysts (x=0.01-0.20) were successfully synthesised and tested for the photodegradation of methylene blue in water under UV and visible light. The solid solution, prepared at low temperature by means of sacrificial template accelerated hydrolysis, shows a cadmium concentration profile in which the external surface contains more cadmium than the bulk and a maximum average cadmium content of 20 mol%. The presence of the cadmium in the catalyst protects the photocatalyst against photocorrosion. Under visible irradiation both undoped and doped catalysts show significant degrees of catalytic activity and stability.

Keywords:
ZnO
Cd$_x$Zn$_{1-x}$O solid solution
Sacrificial Template
Photocatalysis
Methylene blue

1. Introduction
Nanostructured semiconductors are attracting widespread attention due to certain properties that make them suitable for many applications including photocatalysis, an advanced green technology for the removal of organic compounds in water [1-3]. ZnO is a promising material for heterogeneous photocatalysis because of its low production cost, its non-toxicity and high absorption efficiency that ensures a quantum yield even greater than that of TiO$_2$ [4, 5].

The large bandgap of ZnO (3.37 eV) makes it active mainly under UV light, but this represents less than 5% of the solar spectrum. Furthermore, its application under UV light ZnO is inefficient due to its tendency towards photocorrosion according to the following self-oxidation reactions:

$$\text{ZnO} + 2\text{h}^+ + n\text{H}_2\text{O} \rightarrow \text{Zn(OH)}(2-n)^+ + \frac{1}{2}\text{O}_2 + n\text{H}^+ \quad (1)$$

$$\text{ZnO} + 2\text{h}^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2}\text{O}_2 \quad (2)$$

where h$^+$ are the positive holes created by the action of UV irradiation.

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Several authors have studied the attenuation of ZnO photocorrosion by different procedures including silver deposition [6, 7]. In the case of SSWM-supported ZnO we have recently found that Ag itself is not enough to prevent photocorrosion and better results are obtained by combining Ag doping with a protective layer of polysiloxane [8]. Attempts have also been made to improve the photocatalytic activity of ZnO under solar or visible irradiation by applying techniques such as non-metal doping [9-11], the addition of transition metals [12] and the use of coupled semiconductors, including TiO$_2$/ZnO [13]. Additionally, some recent works have analysed the viability of cadmium doping [14-17] to improve the photoactivity of ZnO under visible irradiation. Cadmium oxide has a bandgap of around 2.2 eV, so that Cd$_x$Zn$_{1-x}$O nanostructures are active in the visible range. Coupling CdO and ZnO could help to prevent the electron-hole recombination, enhance the absorption of solar light and increase the photocatalytic activity of ZnO [15].

For industrial applications, the use of supported nanostructures is of great interest since the handling of the catalyst is easier, and common operational problems such as loss of catalyst or complicated separation methods from the reaction medium, typical of powder catalysts are avoided. It is for these reasons that the manufacture of catalysts in monolithic configurations is essential in advanced photodegradation processes. ZnO has been synthesized on several substrates such as ITO [18], silica [19], crystal or polyester films [20], poly-ethylene fibres [21] and stainless steel wire mesh (SSWM) [8, 22, 23]. The latter has been proved to be a good support for the synthesis of many metal oxides [24], and it offers a number of interesting advantages for micro-reactor applications, such as a good thermal and electronic conductivity, a high flexibility, low cost synthesis and a wide availability. Recently, we have developed a room temperature method based on the sacrificial template accelerated hydrolysis (STAH) technique to produce a variety of single and mixed oxides of high surface area on the surface of SSWM pieces [24]. The method employs a SSWM-supported ZnO template with a high surface area and a large proportion of polar surfaces, which is the distinctive feature that sets it apart from the standard STAH technique [25-27].

In the present work we have employed the STAH technique to synthesize CdO-substituted ZnO supported on SSWM and analysed its photocatalytic activity and stability for the degradation of methylene blue dye under ultraviolet and visible irradiation.


2. Experimental

2.1. Catalyst synthesis

SSWM [wire diameter: 30 μm; screen opening: 40 μm] provided by CISA was used as the support. The SSWM-supported ZnO was synthesized as described elsewhere [8]. In brief, zinc acetate dihydrated and urea were dissolved in deionized water (0.05 and 1 M, respectively) and the pH was adjusted to 4.88 with acetic acid. The wire mesh was placed in a Teflon autoclave (100 ml) filled with the growth solution. The autoclave was sealed and hydrothermal ZnO growth proceeded at 80°C for 23 h. The ZnO coated-SSWM was then thoroughly washed with deionised water and vacuum-dried at 60°C. Finally, the sample was calcined at 210°C for 1 h in air.

To prepare the cadmium-substituted catalyst, the sacrificial template accelerated hydrolysis method was applied. In this method, the SSWM-supported ZnO template was immersed in a solution of cadmium nitrate in water at low temperature (25-90°C). The cadmium to zinc molar ratio in the flasks (R_{Cd/Zn} from 1 to 10) was varied in order to see the effect this would have on the final degree of cadmium substitution. The use of sodium citrate as a complexing agent [28] (20 mM in the synthesis solution) was also analyzed in order to establish its effect on the substitution kinetics. The SSWM-supported ZnO piece was immersed in the synthesis solution for 1-3 days. Finally, the substituted catalyst was thoroughly washed with deionized water, vacuum-dried at 60°C for 30 min and calcined in air at 350°C for 2 hours. The calcination temperature was selected on the basis of a previous TGA experiment.

2.2. Catalyst characterization

The chemical composition of the metal oxides was evaluated by means of atomic absorption spectroscopy (Shimadzu AA-6300). The morphology of the samples was studied by means of scanning electron microscopy (SEM, FEI Quanta FEG 650 model). The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA using Cu-Kα radiation (λ = 0.15406 nm). The crystal size values were estimated from the XRD pattern by Scherrer’s equation (d_{XRD}). The instrumental contribution to line broadening was taken into account.

The BET specific surface area of the samples was evaluated by means of N₂ adsorption isotherms (-196°C) obtained with a Micromeritics ASAP 2020 analyser. The
BET surface area was deduced from an analysis of the isotherms in the relative pressure range of 0.04 to 0.20. Ex-situ X-ray photoelectron spectroscopy (XPS) was carried out on a Specs spectrometer, using Mg-Kα or Al-Kα (30 eV) radiation emitted from a double anode at 50 W. The binding energies of the resulting spectra were corrected with the binding energy of adventitious carbon (284.6 eV) in the Cls region. The backgrounds were corrected by Shirley baselines. UV-vis diffuse reflectance spectroscopy measurements were carried out in a Shimadzu UV-2460 spectrophotometer equipped with an integrating sphere. The spectra were recorded in the 200-700 nm range using powdered BaSO₄ as reference material.

2.3. Photocatalytic tests

_Ultraviolet irradiation:_ methylene blue (MB) photodegradation experiments were carried out over supported catalysts (1×5 cm² strips ~120 mg) in a 400 mL quartz beaker under the illumination of two ring-type UV 22W lamps (Luzchem Ring-Illuminator) which predominantly emit radiation at 351 nm. A strip of catalyst was clipped onto the end of a metal rod which was then vertically immersed in 60 mL of a magnetically stirred aqueous solution of methylene blue, with an initial concentration of 10 mg L⁻¹. The catalyst was subjected to seven reaction stages (for a total reaction time of 14 h). After each stage the catalyst was extracted from the reaction medium, washed with deionised water, vacuum dried at 60°C, carefully weighed and reintroduced into the reactor for a new stage with a fresh 10 mg L⁻¹ MB solution. At each reaction stage the solution was first mechanically stirred for 30 min under darkness to ensure adsorption/desorption equilibrium between the dye and the photocatalyst. Next the reactor was exposed to UV lamps for 120 min. Liquid samples were extracted for measurement at fixed reaction times (0, 15, 30, 60, 90 and 120 min).

_Visible irradiation:_ the experiments under visible irradiation were performed with a 400W NAV® 4Y® lamp which emitted radiation in the visible range with the maximum peak centered at 600 nm, under identical reaction conditions as for the UV experiments. The photocatalyst was tested in 3 reaction stages (total reaction time: 13.5 hours). After each photocatalytic test, the photocatalyst was washed thoroughly with deionized water and vacuum-dried at 60°C. At each reaction stage, liquid samples were extracted for measurement at set times (0, 15, 30, 60, 90, 120, 150,
180, 210 and 270 min). In this work only the results of the first reaction stage are shown, since the second and third stages yielded identical results to the first one.

The process of MB degradation was tracked by UV-Vis spectrometry (Shimadzu UV-2401PC). The visible absorption peaks of the analyzed samples were recorded in the 300-800 nm range. The real methylene blue concentration was obtained from the visible absorption spectra by means of a deconvolution technique [29] that allows the contribution of the reaction intermediates to the spectra to be determined.

In order to compare the photocatalytic activity of the materials the following factors were considered:

i) the catalyst dosage \( C_C \) (\( C_C = w_C/V \), where \( w_C \) is the weight of the catalyst disregarding the support and \( V \) is the volume of the liquid). \( C_C \) increases slightly as a consequence of the periodic sampling. Thus, at any particular time the actual catalyst dosage can be calculated from the following equation:

\[
C_C = \frac{w_C}{V_0(1-bt)}
\]

(3)

where \( V_0 \) is the liquid volume at \( t=0 \) and \( b \) is a constant that can be evaluated by linear regression.

ii) the reaction rate which can be expressed by the potential equation

\[
\frac{dC_{MB}}{dt} = kC_C^n
\]

(4)

where \( C_{MB} \) is the methylene blue concentration at a given time \( t \), \( k \) is the reaction rate constant (\( \text{mg}_{MB} \cdot \text{mg}_{C}^{-1} \cdot \text{L}^{-1} \cdot \text{min}^{-1} \)) and \( n \) is the apparent reaction order. As indicated in [8], under chemical control the reaction constant \( k \) must be independent of the catalyst dosage.

For \( n=1 \), equation (4) is coincident with the well-known Langmuir-Hinshelwood equation for diluted solutions [30]. In this case, the resolution of equation (4) yields:

\[
C_{MB} = C_{MB,0}\exp\left[-kC_{C,0}(1+b)\ln(1-(1-bt))\right]
\]

(5)

whereas for \( n\neq1 \):

\[
C_{MB} = \left(C_{MB,0}^{\frac{1}{n}}-(1-n)kC_{C,0}(1+b)\ln(1-(1-bt))\right)^{\frac{1}{1-n}}
\]

(6)
where $C_{C,0}$ is the catalyst dosage at $t=0$. By fitting the concentration values from these equations to the experimental values of $C_{MB}$ at different times, the values of $k$ and $n$ can be obtained. However, the comparison of catalytic activities cannot be performed with the values of $k$ unless the values of $n$ are identical. To overcome this problem, we used the following parameter to evaluate the *intrinsic catalytic activity* of the samples:

$$A_c = \frac{1}{t_{0.5} C_{C,0}}$$  \hspace{1cm} (7)

where $t_{0.5}$ is the semiconversion time (min). Parameter $A_c$ allows the intrinsic activities of the catalysts to be compared at the same initial methylene blue concentration. In principle this parameter is independent of the catalyst dosage [23]. $t_{0.5}$ can be calculated by rearranging equations (5) and (6) for $C_{MB}=0.5 \times C_{MB,0}$. Thus, for $n=1$:

$$A_c = \frac{b}{C_{C,0} \left[1 - \exp \left( \frac{-0.693 b}{k C_{C,0}} \right) \right]}$$  \hspace{1cm} (8)

whereas for $n \neq 1$:

$$A_c = \frac{b}{C_{C,0} \left[1 - \exp \left( \frac{C_{MB,0} \left(0.5^{1-n} - 1\right) b}{k C_{C,0} (1-n)} \right) \right]}$$  \hspace{1cm} (9)

This parameter allows the intrinsic activity of different catalysts to be compared on a catalyst mass basis, but in a series of reaction stages performed with the same catalyst it is necessary to take into account the fact that catalyst losses affect the *absolute catalytic activity*. For this purpose it is convenient to employ the inverse of the semiconversion time for a fixed initial catalyst dosage (333 mg L$^{-1}$):

$$\frac{1}{t_{0.5}} = A_c \times 333 \times \frac{C_{C,0}}{C_0}$$  \hspace{1cm} (10)

where $C_{C,0}^0$ is the catalyst dosage at the beginning of the first reaction stage (time=0) and $C_{C,0}$ is the catalyst dosage at the beginning of the reaction stage under analysis, in which the catalyst displays the intrinsic activity $A_c$. 
3. Results and Discussion

3.1. Structure and morphology of SSWM-supported CdO-ZnO

CdO-ZnO catalysts were synthesised in this work following a sacrificial template accelerated hydrolysis procedure (STAH), a novel hard exotemplating technique that consists in forming metal oxide nanostructures via the hydrolysis of metal ions in the vicinity of a ZnO template [24-27]. Hydrolysis is favoured by the removal of protons due to the simultaneous dissolution of the ZnO scaffold, which is the distinctive characteristic of this technique.

In previous works [8,24] we synthesized a SSWM-supported ZnO material with a large proportion of polar surfaces [(100)/(002) XRD peaks ratio higher than 1]. The template in this study displays a high specific surface area on a ZnO mass basis (80 m² g⁻¹ for samples calcined at 210°C and 36 m² g⁻¹ for samples calcined at 350°C), a high yield (20.5 wt.%) and a good adhesion of the ZnO nanosheets to the SSWM support. When using strongly or mildly acidic cations in aqueous solution with this ZnO template, the STAH technique can be applied to the synthesis of high surface area pure oxides (TiO₂, CuO, CeO₂, α-Fe₂O₃) and these are obtained with a purity of over 95% and in high yields [24]. By controlling the synthesis conditions it is possible to obtain partial substitution degrees of the ZnO template. In the case of weakly acidic cations, with pKa values below or around -9.5, the basic synthesis method permits only partial substitutions, which results in mixed oxides [24]. Cadmium ion is a weakly acidic cation with pKa of -9.7, and therefore only partial substitution can be expected at low temperature.

We first tried out room temperature substitution using solutions of cadmium nitrate and substitution times (tₛ) of 1 to 3 days. Figure 1 shows that, with this method, low substitution degrees (≤6 mol.%) were obtained for values of Cd to Zn molar ratios (RCd/Zn) in the synthesis solution of below or equal to 5, even when the temperature was increased to 90°C. However, when sodium citrate was added to the synthesis solution as a complexing agent [28], the substitution kinetic rate increased dramatically and a substitution degree of around 20 mol% was obtained for RCd/Zn=5 (Figure 1). Higher values of RCd/Zn resulted in no further improvement of the substitution degree, proving that, in the conditions of this work, a maximum replacement of Zn by Cd of approximately 20 mol% can be achieved.

Apart from the pure SSWM-ZnO supported catalyst (either calcined at 210°C or at
350°C) three samples with 1.1 \((t_s=1\text{ day}, T=25°C)\), 5.3 and 20.3 mol\% Cd (those enclosed by circles in Figure 1) were selected for further testing. These materials exhibited elevated BET surface areas of 37.5, 37.4 and 39 m\(^2\) g\(^{-1}\) respectively, and remained practically unchanged from that of the ZnO-support calcined at 350°C (36 m\(^2\) g\(^{-1}\)).

![Graph showing effect of \(R_{Cd/Zn}\) on the degree of cadmium substitution](image)

**Figure 1.** Effect of \(R_{Cd/Zn}\) on the degree of cadmium substitution

SEM images of the catalyst with 5.3 mol\% Cd are shown in Figure 2. Fig. 2a shows that the morphology of the catalyst remained basically unchanged after the substitution process with respect to that of the ZnO template (see images in previous literature [8, 24]). The Cd-Zn nanostructures are organized in arrays of thin nanosheets that are approximately 20-50 nm thick (Fig. 2b) and have a homogenous length distribution in the 2-5 μm range. The yield of Cd-Zn nanostructures for all the synthesised samples amounted to 21±1 wt.% of the total mass of the coated wire mesh. The detailed elemental distribution of this material was obtained by EDX mapping (Figs. 2c-e), which revealed a homogeneous distribution of cadmium in the ZnO nanosheets.
SSWM-supported Cd$_x$Zn$_{1-x}$O photocatalysts

Figure 2. SEM images and EDX mapping of the SSWM-supported CdO-ZnO sample containing 5.3 mol% Cd

X-ray diffraction patterns obtained from the ZnO (calcined at 350°C) and CdO-ZnO composite structures with different degrees of Cd substitution are shown in Figure 3. The peaks located at 31.8, 34.5, 36.2° correspond to zincite with a wurtzite structure (JCPDS 70-8070). CdO can only be identified when the amount of Cd is over 20 mol% by small peaks that match the position of the JCPDS 5-0640 pattern for CdO. All the substituted catalysts show a slight deviation from the peaks of pure zincite. This suggests the formation of a Cd$_x$Zn$_{1-x}$O solid solution where cadmium is replacing part of the zinc atoms in the hexagonal structure of ZnO [14]. This can be seen from Figure 4 which shows that the (101) plane spacing increases with the increase in cadmium content, as one would expect given the larger ionic radius of Cd$^{2+}$ (Zn$^{2+}$ and Cd$^{2+}$ radii are 74 and 97 pm, respectively [31]). The crystal sizes of the Cd$_x$Zn$_{1-x}$O nanostructures ($x>0$), as evaluated by Scherrer’s equation from the XRD spectra in Figure 3, 10.9±0.9 nm, are smaller than that of the undoped ZnO sample calcined at 350°C (14 nm) and similar to that of the ZnO sample calcined at 210°C (~12 nm). Since the Cd$_x$Zn$_{1-x}$O samples were prepared from ZnO templates calcined at 210°C, it can be
concluded that the inclusion of Cd in the wurtzite-like crystals prevents them from growing during the subsequent calcination step up to 350°C.

Figure 3. XRD patterns of the ZnO and CdO-ZnO composite nanostructures with different Cd substitution degrees (calcination temperature = 350°C). Stars indicate the JCPDS 70-8070 pattern for ZnO and triangles the JCPDS 5-0640 pattern for CdO
SSWM-supported Cd$_x$Zn$_{1-x}$O photocatalysts

Figure 4. Variation in (101) plane spacing with Cd content for the different Cd$_x$Zn$_{1-x}$O catalysts calcined at 350°C

The exact mechanism via which the solid solution is formed by sacrificial template accelerated hydrolysis is unclear. In principle there is no apparent thermodynamic reason why the solubility of Cd in ZnO cannot exceed 20 mol%. A number of preparation methods of Cd$_x$Zn$_{1-x}$O solid solutions (i.e. pulsed laser deposition, metal organic vapor deposition and molecular beam epitaxy) are described in the literature [32-35]. In these works, the degree of Cd substitution varies over a wide range from x=0.07 [32] to x=0.7 [35]. On the basis of this variation and the XRD results, we propose a mechanism for the low temperature formation of Cd$_x$Zn$_{1-x}$O, an illustration of which is provided in Fig. 5. In this mechanism, the hydrolysis of a cadmium ion (or citrate-complexed cadmium ion) generates the intermediate species Cd(OH)$^+$ and a proton in the vicinity of the highly polar ZnO template. ZnO is simultaneously etched by the proton to form Zn(OH)$^-$. The Cd(OH)$^+$ species reacts inside the crystal network position that is abandoned by the outgoing Zn(OH)$^-$, occupying its place within the network as CdO, while liberating a second proton to complete the hydrolysis process and to permit the formation of Zn$^{2+}$ via the reaction Zn(OH)$^-+H^+\rightarrow$Zn$^{2+}+H_2$O. The presence of citrate as a complexing agent probably accelerates the initial hydrolysis rate of Cd$^{2+}$, thereby increasing the rate of substitution. The degree of substitution is higher in the outer layers of the zincite crystal, giving rise to a Cd profile (Fig. 5). When the external layer has been almost totally replaced by Cd, its structure
undergoes a rearrangement from wurtzite towards a CdO rocksalt crystal structure with small peaks corresponding to this species appearing in the XRD spectrum (upper spectrum in Figure 3). At this point, the external CdO layer prevents further etching of the ZnO crystal and the reaction stops. Under the conditions used in this work, the replacement of zinc by cadmium produces a solid solution with an average stoichiometric formula of Cd$_{0.2}$Zn$_{0.8}$O, although within the crystal structure the species changes gradually from ZnO (bulk) to CdO (external layer). This hypothesis is confirmed by the results of the XPS analysis performed on the sample with 5.3 mol% Cd. Analysis of the Cd3d and Zn2p regions showed that the surface amount of Cd varies from 10.7 mol% with a Mg-Kα radiation source to 7.1 mol% with a Al-Kα radiation source. Both types of radiation interact with the outermost layers of the sample, though Al-Kα radiation has the power to penetrate more deeply. Thus cadmium is more concentrated on the surface of the sample than within the bulk, in accordance with the profile illustrated in the inset of Figure 5.

Figure 5. Schematic representation of the proposed mechanism of formation of Cd$_x$Zn$_{1-x}$O via low temperature sacrificial template accelerated hydrolysis

Figure 6 shows the DRS spectra corresponding to the SSWM-supported ZnO (calcined at 210°C) and Cd$_x$Zn$_{1-x}$O materials. Considering the narrow band gap of the CdO materials, the optical absorbance region of SSWM-supported Cd$_x$Zn$_{1-x}$O can be expected to be in the visible region. From Figure 6 it can be seen that there is a shift to the red when the amount of Cd increases from 0 to 20 mol%. This shift in the DRS spectrum is also reflected in the changing colour of the samples (inset of Figure 6). These results suggest that greater photocatalytic efficiency could be achieved with Cd$_x$Zn$_{1-x}$O than with pure ZnO in the visible region.
**Figure 6.** Diffuse reflectance spectra (DRS) of the pure SSWM-supported ZnO (calcined at 210°C) and the Cd-substituted SSWM-supported ZnO. Inset: colour changes with Cd content.

**Figure 7.** Kubelka-Munk absorption plots obtained from the spectra in Figure 6.
Additional evidence of the red shift of Cd-doped samples is provided in Fig. 7, in which the Kubelka-Munk absorption curves are represented. The intersection between the linear fit and the photon energy axis gives $E_g$ values that vary from 3.1 eV for 0.0 mol% Cd to 2.81 eV for 20.3 mol% Cd. In this last sample there are two $E_g$ values that can be attributed to the presence of two different phases, the external CdO ($E_g$=2.27 eV in Figure 7) and the Cd$_x$Zn$_{1-x}$O solid solution ($E_g$=2.81 eV).

3.2. Photocatalytic activity and photostability of SSWM-supported Cd$_x$Zn$_{1-x}$O under UV light

As pointed out above, one of the main drawbacks to the use of ZnO in practical applications under UV irradiation is its photocorrosion degradation in water solutions. Several strategies have been applied in the literature in an attempt to obtain more stable materials, including our previous work with SSWM-supported ZnO [8]. Figure 8 shows the activity towards methylene blue decomposition displayed by the SSWM-supported catalysts with 0.0 and 5.3 mol% Cd, when tested under identical conditions as those in [8]. It is clear that, although in the first three stages the catalyst with 5.3 mol% Cd has a lower activity than the pure ZnO catalyst calcined at 210°C, its activity is higher after the third stage and practically remains unchanged during seven cycles, contrary to what occurs with the pure ZnO catalyst, which undergoes severe deactivation over the seven reaction stages due to ZnO photocorrosion. Table 1 and Figure 9 summarize the activity of the Cd-substituted samples. It should be pointed out that the activity is similar to the best previous results achieved with silver and polysiloxane [8], but in the case of the Cd-substituted catalysts the synthesis procedure is shorter since there is one synthesis step less. In the literature, doping with Ag and Cd simultaneously has been shown to be very effective for ensuring the reusability of the catalyst under visible irradiation [15], but to the best of our knowledge this is the first time that Cd by itself has successfully prevented the photocorrosion of ZnO. The best results in this study were obtained with the sample containing 5.3 mol% Cd. The lower activity of the sample containing 20.3 mol% Cd can be attributed to the detrimental effect of the external CdO layer. This is confirmed by the increase in absolute activity during the successive stages of this sample (Figure 9), which occurs at the same time as the loss of the CdO layer during the reaction, as verified by XRD analysis of the sample after 2 hours of reaction (Figure 3). It is noticeable that the loss of the CdO layer during the first stage of reaction occurs without a net loss of material (Table 1). This result suggests that under ultraviolet
SSWM-supported \( \text{Cd}_{x}\text{Zn}_2\text{O} \) photocatalysts

radiation there is a reorganization of the structure that causes the incorporation of CdO phase into the \( \text{Cd}_x\text{Zn}_{2-x}\text{O} \) phase.

Figure 8. Methylene blue concentration curves corresponding to 7 consecutive reaction stages for the catalysts with 0.0 (calcined at 210°C) and 5.3 mol% Cd

Table 1. Catalytic activity for ZnO-based catalysts supported on SSWM tested for several reaction stages

<table>
<thead>
<tr>
<th>mol% Cd (stage)</th>
<th>( \frac{1}{t} \times 10^2 ) (min(^{-1}))</th>
<th>( A_c \times 10^4 ) (mgC(^{-1})-L(^{-1})-min(^{-1}))</th>
<th>ZnO losses (baseline corrected) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 (1)(^a)</td>
<td>6.69</td>
<td>0.10</td>
<td>56.0 (0.35)</td>
</tr>
<tr>
<td>0.0 (7)(^a)</td>
<td>0.61</td>
<td>0.11</td>
<td>77.6 (0.36)</td>
</tr>
<tr>
<td>0.0 (1)(^b)</td>
<td>0.36 (0.36)</td>
<td>0.09</td>
<td>0.30 (0.36)</td>
</tr>
<tr>
<td>0.0 (7)(^b)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11 (0.36)</td>
</tr>
<tr>
<td>1.1 (1)</td>
<td>1.69</td>
<td>0.50</td>
<td>8.2 (0.42)</td>
</tr>
<tr>
<td>1.1 (7)</td>
<td>0.99</td>
<td>0.12</td>
<td>18.3 (0.42)</td>
</tr>
<tr>
<td>5.3 (1)</td>
<td>1.92</td>
<td>0.57</td>
<td>2.1 (0.40)</td>
</tr>
<tr>
<td>5.3 (7)</td>
<td>1.98</td>
<td>0.11</td>
<td>7.9 (0.40)</td>
</tr>
<tr>
<td>20.3 (1)</td>
<td>0.57</td>
<td>0.17</td>
<td>0.0 (0.49)</td>
</tr>
<tr>
<td>20.3 (7)</td>
<td>0.72</td>
<td>0.12</td>
<td>-0.4 (0.49)</td>
</tr>
</tbody>
</table>

\(^a\) Material calcined at 210°C.
\(^b\) Material calcined at 310°C
\(^c\) In brackets: values on a ZnO mass basis
**Figure 9.** Variation in absolute activity ($1/t^{*0.5}$) and ZnO losses during successive reaction stages performed with the pure SSWM-supported ZnO (calcined at 210°C) and the Cd substituted SSWM-supported ZnO catalysts. The baseline indicates ZnO losses in the absence of UV irradiation for the pure SSWM-supported ZnO catalyst.

Figure 10 shows SEM images of the SSWM-supported Cd$_x$Zn$_{1-x}$O samples with $x=0$ (calcined at 210°C) and $x=0.053$, before the reaction and after seven reaction stages under UV light. The macroscopic structure of the ZnO is almost completely destroyed after 7 reaction cycles. The addition of Cd does not change the macroscopic appearance of the initial catalyst which is essentially composed of nanosheets. After seven reaction stages, the nanosheets became thicker but negligible losses of material apart from those expected by manual handling are produced, as indicated in Figure 9 and Table 1 (7.9% lost after 7 cycles in the case of the sample containing 5.3 mol% Cd compared to >77% lost in the case of the pure ZnO sample).
3.3. Photocatalytic activity and photostability of SSWM-supported Cd$_x$Zn$_{1-x}$O catalysts under visible light

Only a few works deal with the use of Cd-doped ZnO for photocatalysis under visible or solar light, either alone [14, 16, 17, 36] or together with Ag [15]. The positive effect of Cd doping under visible irradiation is generally attributed to an improvement in charge separation. In the materials used in this work the stainless steel wire mesh may also have contributed to charge separation. The diffuse reflectance spectra in Figures 6 and 7, and the values of calculated $E_g$ suggest that the Cd-doped catalysts
would be active under visible irradiation. The behaviour of the different catalysts under visible irradiation is shown in Figure 11.

![Figure 11. Methylene blue concentration decay curves under visible irradiation for SSWM-supported Cd$_x$Zn$_{1-x}$O catalysts](image)

Small differences in activity for the different catalysts can be observed, which might be due to slight differences in catalyst weight. A better comparison can be made on the basis of absolute catalytic activity ($1/t_{0.5}^*$) and intrinsic catalytic activity ($A_C$), the values of which are presented in Table 1. This table also shows that the weight losses during one reaction stage under visible irradiation are negligible, in accordance with what is usually reported for photocatalysis with Zn-based materials under visible light. From these results there can be no doubt that the undoped SSWM-supported ZnO catalyst displays activity under visible irradiation, even though $E_g=3.13$ eV ($\lambda=396.5$ nm). This activity is one order of magnitude lower than that under UV light, but nevertheless it contradicts the findings of previous works that report the inactivity of ZnO under visible radiation [10, 11]. In the present study the catalytic activity of ZnO cannot be attributed solely to the negligible amount of UV radiation emitted by the lamp, since theoretical calculations predict that the response
would be much lower. From the results in Table 1, it can be seen that Cd-doping produces a very limited enhancement of photocatalytic activity, with the material with 1.1 mol% Cd showing a higher enhancement on a total mass basis (ZnO plus CdO). However, if only ZnO is considered as the active phase, then the improvement in catalytic activity due to Cd-doping is more significant, and the more heavily substituted sample (20.3 mol% Cd) is the one that displays a higher catalytic activity.

4. Conclusions

High surface area stainless steel wire mesh-supported Cd$_x$Zn$_{1-x}$O catalysts ($x=0.01$-0.20) were successfully synthesised and tested for the photodegradation of methylene blue under UV and visible UV light. The solid solution, prepared at low temperature by sacrificial template accelerated hydrolysis, presents a cadmium concentration profile in which the external surface contains more cadmium than the bulk, and the maximum average cadmium content is 20 mol%. Cd-doping allows the photocatalyst to be stabilised against photocorrosion by means of a simple synthesis procedure. Under visible irradiation both undoped and doped catalysts show significant degrees of catalytic activity and stability.

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Article VI

High surface area stainless steel wire mesh-supported TiO$_2$ prepared by sacrificial template accelerated hydrolysis. A monolithic photocatalyst superior to P25 TiO$_2$

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High surface area stainless steel wire mesh-supported TiO₂ prepared by sacrificial template accelerated hydrolysis. A monolithic photocatalyst superior to P25 TiO₂

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ABSTRACT

High surface area stainless steel wire mesh-supported TiO₂ catalysts were prepared by sacrificial template accelerated hydrolysis using highly polar SSWM-supported ZnO templates. The monolithic catalysts were tested for the photodegradation of methylene blue in aqueous solution under UV irradiation. The calcination temperature of the catalysts was observed to have a determinant effect on their catalytic activity. The optimum calcination temperature range was 450-600°C, in which a combination of high surface area (50-90 m²/g), a high degree of crystallinity and a minimum rutile content yielded the best catalytic results, with maximum catalytic activity appearing for a calcination temperature of 450°C. The most active catalyst prepared in this work displayed twice the catalytic activity of the reference catalyst, P25 TiO₂.

Keywords:
TiO₂
Sacrificial Template
Photodegradation
Methylene blue
P25 TiO₂

1. Introduction

Titania (TiO₂) is considered to be one of the most useful semiconducting metal oxides and is employed in applications ranging from sensors to photonic crystals [1], energy storage [2, 3], solar cells [4], micro-optoelectronics [5] and photocatalysis [3]. Its band gap energy (Eg=3.2 eV) allows the absorption of UV light, generating electrons (e⁻) and holes (h⁺), which can subsequently induce redox reactions for the degradation of organics in wastewaters. TiO₂ offers a number of advantages, including its low cost, relatively high photocatalytic activity, low toxicity and high chemical stability [6]. It has been established that the TiO₂ material must have a highly crystalline structure to enhance the generation and migration of photogenerated electrons/holes [7]. A high specific surface area is also of critical importance for increasing the number of redox reaction sites on the catalyst surface. TiO₂ has three main crystalline phases: brookite, anatase, and rutile, of which the last two are photocatalytically active. Although rutile has lower band gap energy than anatase, from a photocatalytic point of view anatase is undoubtedly the more active phase due

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to its higher reduction potential and lower recombination rate of electron-hole pairs. A highly crystallized anatase phase material with a small grain size and elevated surface area is therefore the preferred combination for TiO$_2$-based photocatalysts [8-10]. Calcination at high temperatures is a simple method to induce the crystallization of amorphous TiO$_2$ produced from sol-gel processes. Typically, amorphous TiO$_2$ is first transformed into small crystals of metastable anatase, which grow upon continuous heating, and then change to rutile crystals as the temperature increases [11]. Crystallization from amorphous TiO$_2$ to anatase and then from anatase to rutile usually occurs in the temperature ranges of 450-550°C and 600-700°C, respectively.

These properties (high surface area and crystallinity) are clearly apparent in the well-known commercial TiO$_2$ material Aeroxide® P25 TiO$_2$, which is a reference material in most works dealing with catalytic photodegradation of organics in wastewaters. P25 TiO$_2$ has around 87 wt.% anatase and 13 wt.% rutile, a crystal size of about 20 nm and a specific surface area of around 55 m$^2$ g$^{-1}$ [12]. However, P25 TiO$_2$ shares the common disadvantage of all particulate materials, i.e. it has to be separated from the reaction medium by means of energy-consuming methods. According to Evonik, the company that fabricates P25 TiO$_2$, handling AEROXIDE® Fumed Metal Oxides such as “P25” requires sophisticated handling due to the fineness and fluffy nature of the powder. To circumvent this drawback it is necessary to find suitable monolithic configurations for TiO$_2$. TiO$_2$ monolithic photocatalysts can be prepared using various procedures, such as the extrusion of commercial nanopowders and binders [13], using sol-gel with titanium alkoxides, with or without templates [14-16], the impregnation of cordierite monoliths with titanium alkoxides and their subsequent calcination to fabricate an optical fiber honeycomb reactor [17], the impregnation of alumina monoliths with colloidal TiO$_2$ nanoparticles [18], the immersion of microchannel monoliths or transparent monoliths in sol-gel grown dispersions of nanoparticles (dip-coating) [19, 20], the chemical vapour deposition of TiCl$_4$ on silicon-coated substrates [21], etc. In recent years, a new method referred to as either liquid phase deposition (LPD) or sacrificial template accelerated hydrolysis (STAH) has been used to prepare TiO$_2$ nanorods, nanotubes or nanosheets on silicon-based, FTO, ITO or stainless steel wire mesh (SSWM) substrates from templates based on non-polar ZnO nanorods [22-24] or polar ZnO nanosheets [25, 26]. Geometrical considerations suggest that the specific surface area of the materials derived from polar ZnO templates is much higher than that of the materials consisting
of nanorods or nanotubes, though until now only in one work by Vu et al. [26] has the specific surface area of the nanosheet-based material been reported (275 m² g⁻¹ on a TiO₂ mass basis). The very high surface area of this material and the flexibility of its monolithic support (micrometric stainless steel wire mesh) make it an ideal candidate for testing in photodegradation reactions.

In this work, we have tested for the first time high surface area SSWM-supported TiO₂ catalysts prepared by sacrificial template accelerated hydrolysis for the photodegradation of methylene blue in aqueous solutions under ultraviolet irradiation. Special attention has been focussed on the effect of the calcination temperature on the composition, texture and photodegradation activity of the catalysts.

2. Experimental

2.1. Preparation method

The support was a SSWM [with a wire diameter of 30 μm and a screen opening of 40 μm] provided by CISA. The SSWM-supported ZnO was synthesized as described in [27]. In summary, zinc acetate dihydrated was dissolved together with urea in deionized water. Concentrations of Zn²⁺ and urea in the aqueous solutions were adjusted to 0.05 and 1.0 M, respectively. The pH of the solution was adjusted to 4.88 by using acetic acid. The wire mesh was placed in a Teflon autoclave (100 mL) filled with the growth solution. The autoclave was sealed and hydrothermal ZnO growth was allowed to proceed at 80°C for 23 h in a constant-temperature water bath. The ZnO coated-wire mesh was then taken out of the solution, thoroughly washed with deionised water and vacuum-dried at 60°C. Finally the sample was calcined at 210°C for 1 h in air.

To fabricate the titanium oxide the as-synthesized SSWM–supported ZnO templates were immersed in plastic flasks containing a 50 mL water solution of K₂TiF₆ (titanium to zinc molar ratio, Rₜi/Zn=1.5) and boric acid at a H₃BO₃/K₂TiF₆ molar ratio of 3/1. The closed flasks were subjected to shaking at RT in an orbital shaker for 1 day until a substitution degree of around 98% was achieved [26]. Afterwards, the samples were washed with deionized water, vacuum-dried at 60°C for 30 min and calcined in air at a temperature in the 250-700°C range for 2 hours.
2.2. Material characterization

The chemical composition of the metal oxides was evaluated by means of atomic absorption spectroscopy. The morphology of the samples was studied by scanning electron microscopy (SEM, FEI Quanta FEG 650 model) and transmission electron microscopy (TEM, JEM-2100F). The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA using Cu Kα radiation (λ = 0.15406 nm). The crystal size values were estimated from the XRD pattern by using Scherrer’s equation (d_{XRD}). The instrumental contribution to line broadening was taken into account. The BET specific surface area of the samples was evaluated by means of N₂ adsorption isotherms (-196°C) obtained on a Micromeritics ASAP 2020 analyser. UV-VIS diffuse reflectance spectroscopy measurements were carried out using a Shimadzu UV-2460 spectrophotometer equipped with an integrating sphere. The spectra were recorded in the range of 200-700 nm. Pure BaSO₄ powder was used as a reference sample.

2.3. Photocatalytic tests

The methylene blue photodegradation experiments were carried out using supported catalysts (1×5 cm² strips weighing ~100 mg) in a 400 mL quartz beaker under the illumination of two ring-type UV 22W lamps (Luzchem Ring-Illuminator) which predominantly emit radiation at 351 nm. A small clip fixed to the bottom of a vertical rod was used to hold the catalyst strip. The strip and the holder were immersed in 60 mL of an aqueous solution of methylene blue, with an initial concentration of 10 mg/L. The catalyst was then rotated at 120 r.p.m, firstly for 30 min under darkness to ensure adsorption/desorption equilibrium between the dye and the photocatalyst and then under the irradiation of the UV lamps for 120 min. Liquid samples were extracted for measurement at set reaction times (0, 15, 30, 60, 90 and 120 min). The visible absorption peaks of the analyzed samples were recorded in the 400-800 nm range by means of a UV-Vis spectrometer (Shimadzu UV-2401PC). The true methylene blue concentration was obtained from the visible absorption spectra by means of a deconvolution technique [28] thereby making it possible to determine the contribution of the reaction intermediates to the spectra. For comparison purposes photocatalytic analyses were performed using either P25 TiO₂ powder or TiO₂ powders scratched from selected wire mesh-supported TiO₂ samples. The powder (10 mg) was suspended in the magnetically stirred methylene blue
solution for the photocatalytic experiment and the liquid samples subjected to analysis were previously centrifuged to remove the TiO₂ particles.

In order to compare the photocatalytic activity of the materials the following factors were taken into account:

(i) the catalyst dosage, which in the case of monolithic catalysts \( C_C = \frac{w_{\text{TiO}_2}}{V} \), where \( w_{\text{TiO}_2} \) is the weight of TiO₂ and \( V \) is the volume of the liquid) increases slightly due to the regular removal of liquid samples for analysis. Thus, the actual catalyst dosage at any time \( t \) can be estimated from the following equation:

\[
C_C = \frac{w_{\text{TiO}_2}}{V_0 (1 - b \times t)}
\]  

where \( V_0 \) is the initial liquid volume and \( b \) is a constant that can be evaluated by linear regression. For the experiments with powdered samples the catalyst dosage remains constant \( (b = 0) \);

(ii) the reaction rate, which can be expressed by the potential equation:

\[
-\frac{dC_{\text{MB}}}{dt} = kC_{C}C_{\text{MB}}^{n}
\]  

where \( C_{\text{MB}} \) is the methylene blue concentration (mg\( \text{MB L}^{-1} \)) at a given time \( t \) (min), \( k \) is the reaction rate constant (mg\( \text{MB} \cdot \text{mg}_{\text{TiO}_2}^{-1} \cdot \text{L}^{-1} \cdot \text{min}^{-1} \)) and \( n \) is the apparent reaction order. Factor \( C_C \) (mg\( \text{TiO}_2 \cdot \text{L}^{-1} \)) is introduced to account for the known dependence of the reaction rate on the catalyst dosage in the absence of screening effects [29-32]. Therefore, under chemical control the reaction constant \( k \) should be independent of the catalyst dosage.

For \( n = 1 \), equation (2) is coincident with the well-known Langmuir-Hinshelwood equation for diluted solutions [33]. Depending on the values of \( C_C \) and \( n \), the methylene blue concentration can be evaluated by any of the equations (3) to (6) listed in Table 1.

By fitting the concentration values from these equations to the experimental values of \( C_{\text{MB}} \) at different times, the values of \( k \) and \( n \) can be obtained. However, the catalytic activities, expressed by the values of \( k \), cannot be compared unless the values of \( n \) are identical. To overcome this problem, we used the following parameter to evaluate the ***intrinsic catalytic activity*** of the samples:
\[ A_C = \frac{1}{t_{0.5}C_{C,0}} \]  

where \( t_{0.5} \) is the semiconversion time (min). Parameter \( A_C \) allows the intrinsic activities of the catalysts to be compared on a TiO\(_2\) mass basis using the same initial methylene blue concentration. In principle this parameter is independent of the catalyst dosage [34], although it is affected by mass transfer limitations and the quantum yield. \( t_{0.5} \) can be calculated by rearranging equations (3) to (6) for \( C_{MB}=0.5 \times C_{MB,0} \). Depending on the values of \( C_C \) and \( n \), parameter \( A_C \) (mgTiO\(_2\) L\(^{-1}\) min\(^{-1}\)) can be evaluated from any of the equations (8) to (11) listed in Table 1.

Table 1. Equations for evaluating \( C_{MB} \) and the activity parameter \( A_C \) under different conditions

<table>
<thead>
<tr>
<th>Equation</th>
<th>Conditions</th>
<th>( C_{MB} ) (mg·L(^{-1}))^(a)</th>
<th>( A_C ) (mgL(^{-1})·min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3) ( \frac{k}{0.693} )</td>
<td>( C_C=\text{constant}^1 ) ( n=1 )</td>
<td>( C_{MB,0} \exp \left( -kC_{C,0}t \right) )</td>
<td>( C_{C,0} ) ( \exp \left( -0.693 \frac{bC_{C,0}}{kC_{C,0}} \right) )</td>
</tr>
<tr>
<td>(4) ( \frac{b}{0.693} )</td>
<td>( C_C \neq \text{constant}^2 ) ( n=1 )</td>
<td>( C_{MB,0} \exp \left( -kC_{C,0}(1+b) \ln \left[ 1/(1-bt) \right] \right) )</td>
<td>( C_{C,0} ) ( \left[ 1-\exp \left( -0.693 \frac{b}{kC_{C,0}} \right) \right] )</td>
</tr>
<tr>
<td>(5) ( \frac{k(n-1)}{0.5^{1-n}-1} )</td>
<td>( C_C=\text{constant}^1 ) ( n \neq 1 )</td>
<td>( \left[ C_{MB,0} - (1-n)kC_{C,0} \right] \exp \left( \frac{k(n-1)}{0.5^{1-n}-1} \right) )</td>
<td>( \frac{k(n-1)}{0.5^{1-n}-1} )</td>
</tr>
<tr>
<td>(6) ( \frac{b}{0.693} )</td>
<td>( C_C \neq \text{constant}^2 ) ( n \neq 1 )</td>
<td>( \left[ C_{MB,0} - (1-n)kC_{C,0} \right] \exp \left( \frac{k(n-1)}{0.5^{1-n}-1} \right) )</td>
<td>( C_{C,0} ) ( \left[ 1-\exp \left( -0.693 \frac{b}{kC_{C,0}[1-n]} \right) \right] )</td>
</tr>
</tbody>
</table>

1. Powdered catalyst
2. Monolithic catalyst
3. \( C_{MB,0} \) = initial MB concentration (mgMB·L\(^{-1}\)); \( C_{C,0} \) = catalyst dosage at \( t=0 \) (mgTiO\(_2\)·L\(^{-1}\))

3. Discussion of results

3.1. Characterisation of the SSWM-supported TiO\(_2\) catalysts

SSWM-supported TiO\(_2\) samples were synthesised in this work following a sacrificial template accelerated hydrolysis procedure (STAH), a novel hard exotemplating technique that consists in forming metal oxide nanostructures via the hydrolysis of
metal ions in the vicinity of a ZnO template [26, 35-37]. Hydrolysis is favoured by the removal of protons due to the simultaneous dissolution of the ZnO scaffold, which is the distinctive characteristic of this technique.

In previous works [26, 27] we synthesized a SSWM-supported ZnO material with a large proportion of polar surfaces [(100)/(002) XRD peaks ratio higher than 1]. This template displays a high specific surface area on a ZnO mass basis (80 m² g⁻¹ in the case of samples calcined at 210°C), a high yield (20.5 wt.%) and a good adhesion of the ZnO nanosheets to the SSWM support. When strongly or mildly acidic cations are used in aqueous solution in combination with this ZnO template, the STAH technique can be applied to synthesize high surface area pure oxides (TiO₂, CuO, CeO₂, α-Fe₂O₃) and these are obtained with a purity of over 95% and in high yields [26]. In the case of SSWM-supported TiO₂ we were able to produce samples with a 98% degree of purity, in average yields of 11.8±2.0 wt.% on the SSWM support for all samples and with a very large specific surface area of 275 m² g⁻¹ (on a TiO₂ mass basis) in the case of the

**Figure 1.** Photography, SEM images and a TEM image of a SSWM-supported TiO₂ sample calcined at 250°C
sample calcined at the lowest temperature (250°C). Figure 1 contains images of a SSWM-supported TiO₂ sample calcined at 250°C. The morphology of the catalyst remained basically unchanged after the substitution process with respect to that of the ZnO template (compare the SEM images in Figure 1 with those reported in the previous literature [26, 27]). The white and flexible sample (photograph in Figure 1) is formed by TiO₂ homogeneously covering the SSWM in the form of thin nanosheets with a length distribution in the 5-7 μm range (SEM images), composed of nanograins 3-6 nm in size (TEM image) the stacking of which is responsible for the high porosity of the sample. Figure 2 shows the variation in specific surface area with the calcination temperature. There is a continuous decrease in the BET surface area with the increase in calcination temperature, though the surface area values are still very high. For instance, P25 TiO₂ powder calcined at 500°C for 2 hours has a specific surface area of 52 m² g⁻¹ [12], whereas, with the same calcination procedure, the SSWM-supported TiO₂ has a specific surface area of 87 m² g⁻¹.

![Figure 2](image_url)

**Figure 2.** Variation of the specific surface area (on a TiO₂ mass basis) of the SSWM-supported TiO₂ samples with the calcination temperature

XRD analyses were conducted to assess the effect of the calcination temperature on the crystal size and the anatase content of the SSWM-supported TiO₂ samples. Figure 3 shows the XRD plots for two samples calcined at 375 and 700°C. The crystal size values were evaluated by applying Scherrer’s equation to the (101) peak at 25.3°, whereas the anatase content was determined from the heights of the peaks
corresponding to anatase (I\textsubscript{\alpha}, (101) peak at 25.3°) and rutile (I\textsubscript{\beta}, (110) peak at 27.0-27.4°) using the equation in the figure [38, 39]. In the case of the samples with broader peaks (smaller crystal sizes) the overlapping peaks necessitated a deconvolution procedure to find the exact values of crystal size, I\textsubscript{\alpha} and I\textsubscript{\beta}, as illustrated by the curve for the sample calcined at 375°C (Figure 3). The rutile content of the samples was evaluated by subtracting the percentage of anatase from 100. Two samples were prepared at each calcination temperature and analysed by XRD according to the procedure explained above. Figure 4 shows the “apparent” rutile content and the crystal size (d\textsubscript{\text{XRD}}) of all the samples analyzed. The qualifier “apparent” is used here for reasons that will be explained below. Although rutile is thermodynamically stable in the whole temperature range [11], anatase is kinetically favoured at low temperatures. The sample calcined at the lowest temperature has a relatively high rutile content (~9%). From this temperature up to 650°C the rutile content decreases to a lower value range (3-8%). This observation contravenes the generally accepted rule that rutile cannot be transformed into anatase [11]. It should be noted however that the small, though conspicuous, shoulders detected in the samples calcined at T\textsubscript{c}\leq650°C, ascribed initially to rutile, present an average maximum at 27.0±0.2° in the XRD plots, well below the maximum at 27.4° detected for the sample calcined at 700°C (Figure 3). In addition the rutile crystal size is much smaller at T\textsubscript{c}\leq650°C (7.4±2.6 nm) (randomly distributed over the temperature range) than at 700°C (18.6±1.3 nm). It is probable that what we have termed “apparent” rutile phase at T\textsubscript{c}\leq650°C is really a solid solution of the residual ZnO (around 2 wt.%) and TiO\textsubscript{2}, that has a crystal structure similar to that of rutile. This rutile-like phase may have formed during the room temperature synthesis of TiO\textsubscript{2} due to the well-known promotion effect that Zn\textsuperscript{2+} has on the transformation of anatase to rutile [11, 40]. The possibility of synthesizing solid solutions of binary oxides at low temperature with the STAH method has already been pointed out in a previous work [26] and is currently an important topic of research in our laboratory. When the temperature is increased this phase probably splits into anatase and ZnO, which would explain its reduced presence on approaching 650°C. At 700°C the thermodynamic transformation of anatase to rutile becomes more evident, with the rutile content of the sample reaching a value of >20%. This temperature is higher than the transition onset temperature generally reported, which is around 600°C [11]. The relative amount of amorphous TiO\textsubscript{2} in the samples can be deduced from the degree of crystallinity (DOC), defined as the ratio of the (101) anatase peak height (subtracting the baseline) to the total height including the background of the XRD diffractogram [41]. We found that the DOC increased from
0.28 at 250°C to 0.45 at 450°C and to 0.59 at 700°C. Therefore, there is a significant presence of amorphous TiO₂ at 250°C.

With regards to the size of the anatase crystals, there is a clear increase from 6 to 10 nm in the 250-375°C temperature range (Figure 4), while at the same time there is a marked decrease in specific surface area from 275 to 126 m² g⁻¹ (Figure 2). From 375 to 450°C a small, but clear, decrease in crystal size, from 10 to 8 nm is discernible. Then, after this local minimum, there is a continuous increase in anatase crystal size from ~8 (450°C) to ~21 nm (700°C).

![Figure 3. XRD plots for SSWM-supported TiO₂ calcined at 375 and 700°C, and the method of calculating the anatase percentage from the height of the peaks](image)

To some extent the calcination temperature also affects the optical absorbance of the SSWM-supported TiO₂ catalysts. Figure 5 shows the DRS spectra corresponding to two SSWM-supported TiO₂ samples (calcined at 450 and 700°C) and P25 TiO₂ powder. As can be seen for the region below 350 nm, the sample calcined at 700°C shows a slightly lower optical absorbance than P25 TiO₂ or the sample calcined at 450°C. The band gap energy values evaluated from the Kubelka-Munk absorption curves are 3.3, 3.3 and 3.2 eV, for the P25 TiO₂ particles and for the SSWM-supported samples calcined at 450 and 700°C, respectively.
Figure 4. Variation of the anatase crystal size ($d_{XRD}$) and apparent rutile content with the calcination temperature of the SSWM-supported TiO$_2$ catalysts

Figure 5. Diffuse reflectance spectra (DRS) of the SSWM-supported TiO$_2$ catalysts (calcined at 450 and 700°C) and P25 TiO$_2$ particles
3.2. Photocatalytic activity of the SSWM-supported TiO₂ catalysts

The main advantage of the photocatalysts prepared in this work is their monolithic configuration, which allows them to be retrieved from the reaction medium without the need for a costly separation stage. The micrometric stainless steel wire meshes are very flexible and can be rolled up to fit in the reaction chamber of a tubular micro-reactor, as described in [26, 42], or they can be fitted to rotating holders in batch reactors for the photodegradation of organic materials in water as in [27] and the present work. The kinetic results of the methylene blue photodegradation experiments conducted with the SSWM-supported TiO₂ catalysts or with the powdered catalysts were processed using the equations in Table 1, as mentioned in the Experimental section, to obtain the intrinsic catalytic activity parameter, A∞, for the different catalysts. We used the equations for n>1 to ensure a more accurate fitting of the experimental results. Figure 6 shows the variation of A∞ with the calcination temperature for the tests performed with the SSWM-supported catalysts fitted to a rotating holder immersed in the methylene blue solution. The sample calcined at 250°C, which is a mixture of anatase, amorphous TiO₂ and a small amount of what we have described as a ZnO-TiO₂ solid solution with a crystal structure similar to that of rutile, presents a relatively high catalytic activity, which is ascribed to its large specific surface area (275 m² g⁻¹). At 375°C, the specific surface area of the sample has been halved, to a value of 126 m² g⁻¹, with a concomitant decrease in the number of active centers for photocatalysis. This explains the marked reduction in catalytic activity with respect to the sample calcined at 250°C (Figure 6). From 375 to 400°C degrees there is a notable increase in catalytic activity, which is coincident with a slight diminution of anatase crystal size (Figure 4). We attribute this to the transformation of amorphous TiO₂ to crystalline anatase of small crystal size. The average crystal size of the anatase phase in this temperature region is derived from the combination of the crystal size of the anatase resulting from the room temperature synthesis, which increases with the rise in temperature from 250 to 375°C in a typical sintering phenomenon (Figure 4), and the small crystal size of the anatase resulting from the transformation of amorphous TiO₂. This explains the unexpected diminution in size of the anatase crystals and the marked increase in catalytic activity, which is undoubtedly a consequence of the higher degree of crystallinity in the anatase phase. From 450 to 600°C there is a slight decrease in the catalytic activity, which is attributed to a diminution of specific surface area (from 91 to ~51 m² g⁻¹) and a parallel increment in anatase crystal size (from 8 to 14 nm) due to
sintering. This temperature region, which has been highlighted in Figure 6 by a grey shadow, is considered to be the optimal region of calcination for preparing the catalysts destined for the photodegradation of methylene blue. From 600 to 650°C there is a notable decrease in catalytic activity, which cannot be ascribed to any marked change in specific surface area (Figure 2), anatase crystal size or apparent rutile content (Figure 4). However, it is well known that the onset of the transformation from anatase to rutile occurs at around 600°C [11] in a nucleation process at anatase (112) twin boundaries [43], and therefore the rutile nuclei that are formed around the anatase crystals might alter their photocatalytic properties before the amount of the rutile phase surpasses the detection limit of the X-Ray diffractometer. It is for this reason that the decrease in catalytic activity from 600 to 650°C is ascribed to the onset of rutile formation, as indicated in Figure 6. A further decrease in catalytic activity at temperatures over 650°C is attributed to the presence of rutile (over 20%) and a decrease in the number of active centers in the anatase phase when $d_{\text{XRD}}$ increases and $S_{\text{BET}}$ decreases.

![Figure 6](image_url)

**Figure 6.** Variation of the catalytic activity ($A_C$) with the calcination temperature for the SSWM-supported catalysts fitted to a rotating holder immersed in the methylene blue solution.
For comparison purposes, 10 mg of powder scratched from the most active SSWM-supported catalysts (Tc=450 and 500°C) and 10 mg of P25 TiO2 were tested in the batch photodegradation of methylene blue under the same experimental conditions. Figure 7 shows the decay of the methylene blue concentration corresponding to the three catalysts. By comparing the A_c values in Figure 6, obtained from equation 10, with those in Figure 7, it can be deduced that the catalytic activity of SSWM-supported catalysts with a monolithic configuration is around 30% that of the particles scratched from the surface of the stainless steel wire mesh. This is due to the fact that the loose particles are more evenly distributed in the liquid, which is beneficial for the mass transfer of methylene blue to the active centers of the catalyst and, undoubtedly, for the quantum yield. In this work we employed a simple setup for testing monolithic catalysts consisting of a wire mesh strip rotating inside the liquid bulk, as described in the Experimental section. Other configurations based on quartz micro-reactors that reduce the mass transfer path and increase the quantum yield are to be tested in the near future.

![Graph](image)

**Figure 7.** Methylene blue concentration decay curves for the particulate samples scratched from the SSWM-supported TiO2 catalysts (calcined at 450 and 500°C) and the P25 TiO2 particles. The values of A_c for the different catalysts are also included in the figure.
As can be seen in Figure 7, the TiO$_2$ samples prepared in this work are more active than the P25 TiO$_2$ particles. The $A_c$ values in the figure indicate that the TiO$_2$ particles prepared by STAH and calcined at 450°C show twice the catalytic activity for the photodegradation of methylene blue in an aqueous solution than the P25 TiO$_2$ particles. The superiority of the STAH-prepared particles can be ascribed to their larger specific surface area and smaller rutile content with respect to the P25 TiO$_2$ particles (i.e., a higher density of anatase active centers) for the same degree of crystallinity (the same calcination temperature).

4. Conclusions

Stainless steel wire mesh-supported TiO$_2$ catalysts were prepared by sacrificial template accelerated hydrolysis using highly polar SSWM-supported ZnO templates. The calcination temperature of the catalysts significantly affects the composition, crystallinity, the textural properties and the photocatalytic activity of the catalysts. Thus, at 250°C the catalyst, which is mainly composed of anatase and amorphous TiO$_2$ and, to a lesser extent, a ZnO-TiO$_2$ rutile-like solid solution, the amount of which decreases with the increase in the calcination temperature, has a high specific surface area (275 m$^2$ g$^{-1}$) and shows a remarkable catalytic activity for the photodegradation of methylene blue in aqueous solution. At 375°C the anatase crystal size has grown considerably and both the specific surface area and the catalytic activity have experienced a parallel decrease. In the 375-450°C range the transformation of amorphous TiO$_2$ into small anatase crystals provokes a diminution in anatase crystal size and a marked increase in catalytic activity, which reaches its highest value at 450°C. From this temperature to 600°C the catalytic activity undergoes a gradual reduction as a consequence of the loss of active centers due to sintering. Beyond 600°C the reduction in catalytic activity is more severe, as a consequence of the onset of rutile formation. The most active catalyst prepared in this work shows a catalytic activity which is twice that of the reference catalyst P25 TiO$_2$.

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References


SSWM-supported TiO₂ photocatalysts


Article VII

Novel high surface area stainless steel wire mesh supported Ni$_{0.7}$Zn$_{0.3}$O solid solution prepared by room temperature sacrificial template accelerated hydrolysis. Application in the production of hydrogen from methanol

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Novel high surface area stainless steel wire mesh supported \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{O} \) solid solution prepared by room temperature sacrificial template accelerated hydrolysis. Application in the production of hydrogen from methanol

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**ABSTRACT**

This work describes for the first time the room temperature synthesis of a high surface area \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{O} \) solid solution by sacrificial template accelerated hydrolysis. The synthesis employs a highly polar ZnO template supported on the surface of a stainless steel wire mesh (SSWM) that allows the material to be produced in a monolithic configuration. The resulting material has a large surface area of around 100 m\(^2\) g\(^{-1}\) and is obtained in a yield of up to 40 wt.% on the SSWM in the synthesis conditions employed in this work. Characterization of the material by TPR, XRD and XPS revealed that the solid solution is composed of an oxygen defective bulk and a partially oxidized surface. As part of this study, the \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{O} \) solid solution has been tested for the first time as a catalyst, displaying high activity in both the methanol steam reforming and the methanol decomposition reactions. At temperatures below 400°C the catalyst is not very selective in the methanol steam reforming reaction, and produces large amounts of CO. However at more elevated temperatures the water gas shift reaction improves the hydrogen yield and the carbon selectivity towards CO\(_2\), especially over higher contact times. Despite some catalyst deactivation due to coke deposition, methanol decomposition occurs with high conversion degrees and hydrogen yields in the temperature range of 250-350°C.

**Keywords:**
Zinc Oxide
\( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{O} \)
Sacrificial Template
Methanol steam reforming
Methanol decomposition

1. **Introduction**

Nowadays the number of catalysts being designed and developed by research groups at public institutions and private companies is so high that it is becoming more and more difficult to find new active formulae that have never been tested before in a catalytic process. What is more, the simpler the chemical formulation of the catalyst is (mono or bimetallic oxides), the harder the task. One of the formulations that has not yet been tested is the solid solution \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{O} \). The ability of zinc to dissolve in the NiO rocksalt lattice was recognized long ago [1, 2]. ZnO has a propensity to lose...
surface oxygen when heated in air, leaving excess zinc atoms behind that diffuse into interstitial positions of the lattice in order to preserve the electrostatic balance \[2\]. Conversely, when heated in air NiO takes up excess oxygen, as a result of which cation vacancies appear by the migration of nickel ions to the surface \[2\]. When both oxides are heated together, these complementary trends explain why zinc atoms dissolve into the NiO crystal. The solubility limit below which the rocksalt crystal structure of NiO is preserved lies in the range 0.3-0.4 (Zn/(Zn+Ni) molar ratio) \[1, 2\]. For higher fractions of zinc the wurtzite structure of ZnO appears on the XRD plots \[3\]. Auger parameter analysis indicates that the zinc has the octahedral coordination typical of a rocksalt structure \[3\]. This coordination is unusual for Zn\(^{2+}\), which prefers a tetrahedral coordination, as in the wurtzite structure of ZnO. The presence of Zn in the crystal lattice of NiO can be expected to affect its magnetic and electronic properties. NiO is antiferromagnetic and the interstitial presence of Zn atoms provokes a decrease in the Néel temperature, from 523 K (NiO) to 312 K (Ni\(_{0.7}\)Zn\(_{0.3}\)O) \[4\]. Similarly, the catalytic properties of Ni\(_{0.7}\)Zn\(_{0.3}\)O might also be expected to differ from those of NiO.

In line with this reasoning it seems clear that Ni\(_{0.7}\)Zn\(_{0.3}\)O must be prepared through a thermal process under air in order to create the necessary vacancies to provoke the migration of zinc cations towards the crystal structure of NiO (pulsed laser deposition also allows films of Ni\(_{0.7}\)Zn\(_{0.3}\)O to be grown \[5\]). A temperature of at least 500°C is thought to be required for the incorporation of zinc into the rocksalt structure of NiO \[6\]. This specificity is a drawback for the synthesis of materials with a high surface area, a property that is generally desired when designing catalysts, and may explain why this material has never been tested as a catalyst. CVD \[7\], solvothermal alcoholysis \[8, 9\] or co-precipitation \[10\] allows the formation of nickel-doped ZnO (Zn\(_x\),Ni\(_{1-x}\)O) as nanowire arrays, but with low contents of nickel (x≤-0.2) and the retention of the wurtzite structure of ZnO. Equimolar ZnO-NiO mixtures in which both phases are preserved in the final nanocomposite have also been prepared by co-precipitation/co-gel formation techniques, and tested for the photocatalytic decolourization of dyes \[11\].

However, to date no low temperature synthesis method of a Ni\(_{0.7}\)Zn\(_{0.3}\)O solid solution has been reported in the literature and this material has never been tested as a catalyst. To the best of our knowledge, this solid solution has only been tested for its photoluminescence \[12\] or electroluminiscence \[5\] properties.
In this work we report for the first time the room temperature synthesis of a high surface area Ni$_{0.7}$Zn$_{0.3}$O solid solution by sacrificial template accelerated hydrolysis (STAH). The catalyst was synthesized on the surface of a stainless steel wire mesh of micrometer dimensions. Stainless steel wire mesh (SSWM)-supported metal oxide catalysts have been demonstrated in recent years by our group to be very promising structured catalytic systems [13-18]. We recently demonstrated the potential of the STAH technique to produce high surface area metal oxides using highly polar ZnO templates [19]. In that work we reported that weakly acidic cations (pKa values below around -9.5, such as Ni$^{2+}$) could only produce mixed oxides when deposited over a polar ZnO template, unlike the pure NiO obtained with non-polar ZnO nanowires [20, 21]. As will be discussed below it is the difference in local Zn$^{2+}$ concentrations that appears to be the key to obtaining different products with both templates. The combination of a cheap and versatile support, such as SSWM, with a simple synthesis method, such as STAH, may lead to a process that is expected to be easily scalable and cost competitive for commercial applications.

To our knowledge the solid solution Ni$_{0.7}$Zn$_{0.3}$O has never been tested in any catalytic process. In this study we analyzed it for the production of hydrogen via methanol steam reforming and methanol decomposition. These endothermic reactions are both possible routes for producing hydrogen on board fuel cell-based electric cars. Compared to methanol decomposition, methanol steam reforming requires a substantially higher amount of heat to vaporize the reactants, conduct the reaction, and compensate for heat loss from the reactor and the effluent streams. It is therefore more applicable in large scale systems, where volumetric heat loss is lower than in small scale devices [22]. For the decomposition of methanol, the heat for the reaction can be obtained by burning the carbon monoxide released, either in a preferential oxidation step or after it has been separated from the hydrogen stream in a catalytic membrane reactor [22]. Decomposed methanol can also be used as a source of synthesis gas for a number of chemical processes. The SSWM-supported metal oxide catalysts are ideal for use in micro-reactors for the generation of hydrogen by methanol decomposition, as has recently been reported with cobalt-based catalysts [14]. Nickel-based catalysts have also been successfully tested in this reaction [23-26]. In this work we show that a high surface area nickel-zinc solid solution may also be an interesting contender for onboard hydrogen production.
2. Experimental

2.1. Material preparation

All chemical reagents were of analytical grade and so were not subjected to additional purification. All of the aqueous solutions were prepared with deionised water. The support was a SSWM [with a 30 μm wire diameter and a 40 μm screen opening] provided by CISA Cedacería Industrial (www.cisa.net). The SSWM supported polar ZnO with a yield of ~20 wt.% was synthesized as described in \[18, 19\]. In this standard procedure, zinc acetate dihydrate was dissolved together with urea in deionized water. A Zn$^{2+}$ concentration of 0.05M was used in the aqueous solution, with an urea/Zn$^{2+}$ molar ratio of 20. The pH of the solution was adjusted to 4.88 by using acetic acid. The wire mesh was placed in a Teflon autoclave (100 mL) filled with the growth solution. The autoclave was sealed and hydrothermal ZnO growth was allowed to proceed at 80°C for 23 h in a constant-temperature water bath. The ZnO coated-wire mesh was then taken out of the solution, thoroughly washed with deionised water and vacuum-dried at 60°C. Finally the sample was calcined at 210°C for 0.5 h in air.

In order to obtain samples with different ZnO yields, the standard method was modified by introducing changes in the synthesis temperature (60-90°C) and in the Zn$^{2+}$ concentration (0.025-0.2M). Three templates were selected for the synthesis of SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O catalysts; SSWM-Z20, SSWM-Z35 and SSWM-Z40, acronyms used to designate SSWM supported polar ZnO templates with approximately 20, 35 and 40 wt.% of ZnO, respectively. The ZnO yield was determined by weighing the samples.

To prepare the SSWM-supported nickel/zinc solid solution, the as synthesized SSWM supported ZnO templates with different ZnO yields were immersed in plastic flasks containing 50 mL water solutions of nickel nitrate. The closed flasks were subjected to shaking at RT in an orbital shaker for different periods of time. Subsequently, the samples were taken out of the flasks and washed with deionized water, vacuum-dried at 60°C for 30 min and calcined in air at 300°C for 2 hours. The calcination temperature was selected on the basis of the TGA analysis of a synthesized Ni/Zn sample. Both the nickel to zinc molar ratio in the flasks ($R_{\text{Ni/Zn}}$ from 2 to 20) and the substitution time ($t_{S}$ from 1 to 5 days) were varied in order to explore the effect of these variables on the final degree of nickel substitution. This optimization procedure was performed using the SSWM-Z20 template.
In some specific cases the ZnO phase remaining after the synthesis procedure was removed from the sample by washing it in a sodium hydroxide water solution (2M) for 24 hours.

2.2. Characterization

The chemical composition of the metal oxides was evaluated by means of atomic absorption spectroscopy (AAS, Shimadzu AA-6300). The morphology of the samples was studied by a scanning electron microscope (SEM, FEI Quanta FEG 650 model) and a transmission electron microscope (TEM, JEM -2100F) fitted with a detector for the EDS analysis. The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA using Cu Kα radiation (λ = 0.15406 nm). The crystal size values were estimated from the XRD pattern by means of Scherrer’s equation (dXRD). Instrumental contribution to line broadening was taken into account. The BET specific surface area of the samples was evaluated by means of N₂ adsorption isotherms (-196°C) obtained on a Micromeritics ASAP 2020 analyser. The BET surface area was deduced from an analysis of the isotherms in the relative pressure range of 0.04 to 0.20.

Ex-situ X-ray photoelectron spectroscopy (XPS) was carried out on a Specs spectrometer, using Mg-Kα or Al-Kα (30 eV) radiation emitted from a double anode at 50 W. The binding energies of the resulting spectra were corrected using the binding energy of adventitious carbon (284.6 eV) in the C1s region. The backgrounds were subtracted by means of Shirley baselines. All the analyzed regions were deconvolved by using mixed Gaussian-Lorentzian functions (90:10).

TPR analyses were performed in a chemisorption analyzer (Autochem II) equipped with a TCD detector. For each analysis the sample (8-10 mg of metal oxide) was first heated up to 400°C in Argon, and then cooled down to 50°C and treated with a 50 mL min⁻¹ stream of 10% H₂ in Argon from 50°C to 600°C at a rate of 5°C min⁻¹.

2.3. Catalytic activity tests

Catalytic activity tests for methanol steam reforming (MSR) and methanol decomposition (MD) were performed in a six-flow parallel microrreactor system that allows up to six samples to be simultaneously tested by means of an automatic
multiposition valve. Each catalyst consisted of a 5×1 cm² strip that was rolled up to form a 1 cm high cylindrical piece. A roll of catalyst was then inserted into each of the six stainless-steel reactors (¼” outer diameter). For both reactions the gas hourly space velocity was maintained in the range of 16,500 - 17,500 h⁻¹, the variations being due to small changes in the flow rates of the streams entering each reactor. Weight hourly space velocities (g CH₃OH g⁻¹ cat⁻¹ h⁻¹), on a metal oxide mass basis, varied in the range 2.6 - 11.4 h⁻¹, depending on the reaction tested and on the amount of catalyst loaded onto the metal wire mesh.

Each reactor was fed with a stream of 7 vol.% CH₃OH + 8 vol.% H₂O (MSR) or 10 vol.% CH₃OH (MD) plus 10 vol.% Ar and He to balance. The samples were first heated in a flow of He at 300°C during the calibration step, which lasted around 5 hours. Then the catalysts were subjected to the following isothermal steps: 300-350-400-450-350-300°C (MSR, 15-hour steps) or 225-250-275-300-325-300-275-250-225°C (MD, 10-hour steps). The transition ramp between each temperature step was performed under a helium atmosphere. The products were analyzed online by mass spectrometry (Omnistar 300O). CH₃OH, H₂, CO, CO₂, CH₄, H₂O and O₂ were quantitatively analyzed with the help of previous calibration steps, whereas the evolution of formaldehyde, dimethyl ether (DME) and methyl-formate (MF) was tracked from the changes in the mass intensities of fragments 60 (MF), 46 (DME) and the ratio of the intensities of the fragments 30 to 31 (formaldehyde). This procedure allowed an accurate assessment of the carbon-products formed during the reaction different from CO, CO₂ and CH₄.

The methanol conversion parameter (X_MeOH; %) represents the percentage of methanol converted during the process taking into account the difference between the total flow rates at the outlet and the inlet of the reactor (F_out and F_in, respectively, in mL min⁻¹):

\[
X_{\text{MeOH}} = 100 \times \left(1 - \frac{F_{\text{MeOH}}^{\text{out}}}{F_{\text{MeOH}}^{\text{in}}} \right)
\]

(1)

where \(C_{\text{MeOH}}^{\text{in}}\) and \(C_{\text{MeOH}}^{\text{out}}\) are the concentrations of methanol (vol.%) in the inlet and in the outlet gas stream, respectively. \(F_{\text{out}}^{\text{out}} / F_{\text{in}}^{\text{in}}\) can be evaluated as follows:

\[
\frac{F_{\text{out}}^{\text{out}}}{F_{\text{in}}^{\text{in}}} = \frac{A_2B_2 - A_1B_1}{A_2B_2 - A_1B_3}
\]

(2)
or, alternatively, for the case discussed below, as follows:

\[
\frac{F_{\text{out}}}{F_{\text{in}}} = \frac{A_1}{A_3} = \frac{B_1}{B_3}
\]

where parameters \(A\) and \(B\) are evaluated from the following expressions:

\[
A_1 = C_{\text{MeOH}}^{\text{in}} \tag{4}
\]

\[
A_2 = -\nu \tag{5}
\]

\[
A_3 = C_{\text{MeOH}}^{\text{out}} + C_{\text{CO}}^{\text{out}} + C_{\text{CO}_2}^{\text{out}} + C_{\text{CH}_4}^{\text{out}} \tag{6}
\]

\[
B_1 = C_{\text{MeOH}}^{\text{in}} + C_{\text{H}_2\text{O}}^{\text{in}} \tag{7}
\]

\[
B_2 = -\rho \tag{8}
\]

\[
B_3 = C_{\text{MeOH}}^{\text{out}} + C_{\text{H}_2\text{O}}^{\text{out}} + 2C_{\text{CO}_2}^{\text{out}} + C_{\text{CO}}^{\text{out}} \tag{9}
\]

In these equations, \(C_{i}^{\text{out}}\) (i: CO, CO\(_2\), CH\(_4\), H\(_2\)O) corresponds to the outlet concentration of i species, while \(C_{i}^{\text{in}}\) corresponds to its concentration (vol. \%) in the inlet gas stream. Parameters \(\nu\) and \(\rho\) are the number of carbon and oxygen atoms, respectively, of a carbon-containing molecule \(C_{\nu}\text{H}_{\mu}\text{O}_{\rho}\) that may be formed during the process, apart from CO, CO\(_2\) or CH\(_4\), assuming that only one type of molecule will be formed. Thus, if this molecule is formed, \(F_{\text{out}}/F_{\text{in}}\) must be calculated by means of equation (2), whereas, in the absence of this molecule, any of the equations in (3) may be used. The concentration of this molecule (the presence of which can be detected by the mass spectrometer but not quantitatively evaluated) can be determined by means of the following equation:

\[
C_{C_{\nu}\text{H}_{\mu}\text{O}_{\rho}}^{\text{out}} = \frac{A_1B_3 - A_3B_1}{A_1B_2 - A_2B_1} \tag{10}
\]

In this way, both the variation in the flow rate as a consequence of the reaction (the importance of which was underlined in a previous work [27] and the formation of a species not quantified but detected by the analytical system can be considered when calculating of the methanol conversion via equation (1).

The hydrogen yield, which depends on the type of reaction being analysed, can be evaluated from:
\[
X_{H_2} = 100 \times \frac{F_{H_2}^{\text{out}}}{\alpha F_{\text{MeOH}}^{\text{in}}} \tag{11}
\]

where \(F_{H_2}^{\text{out}}\) is the hydrogen flow rate at the outlet of the reactor and parameter \(\alpha\) takes the value of 3 in the MSR reaction \((\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2)\) and 2 in the MD reaction \((\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2)\).

Finally, carbon selectivity towards the different carbon-containing species \(\left(C_{\text{out}}^{\text{C}_i} = C_{\text{out}}^{\text{CO}}, C_{\text{out}}^{\text{CO}_2}, C_{\text{out}}^{\text{CH}_4} \text{ or } \nu C_{\text{out}}^{\text{C}_i\text{H}_j\text{O}_k}\right)\) can be evaluated as follows:

\[
S_{\text{C}_i}^C = 100 \times \frac{C_{\text{out}}^{\text{C}_i}}{C_{\text{out}}^{\text{CO}} + C_{\text{out}}^{\text{CO}_2} + C_{\text{out}}^{\text{CH}_4} + \nu C_{\text{out}}^{\text{C}_i\text{H}_j\text{O}_k}} \tag{12}
\]

\[
S_{\text{CO}_2}^C = 100 \times \frac{C_{\text{out}}^{\text{CO}_2}}{C_{\text{out}}^{\text{CO}} + C_{\text{out}}^{\text{CO}_2} + C_{\text{out}}^{\text{CH}_4} + \nu C_{\text{out}}^{\text{C}_i\text{H}_j\text{O}_k}} \tag{13}
\]

\[
S_{\text{CH}_4}^C = 100 \times \frac{C_{\text{out}}^{\text{CH}_4}}{C_{\text{out}}^{\text{CO}} + C_{\text{out}}^{\text{CO}_2} + C_{\text{out}}^{\text{CH}_4} + \nu C_{\text{out}}^{\text{C}_i\text{H}_j\text{O}_k}} \tag{14}
\]

\[
S_{\text{C}_i\text{H}_j\text{O}_k}^C = 100 \times \frac{\nu C_{\text{out}}^{\text{C}_i\text{H}_j\text{O}_k}}{C_{\text{out}}^{\text{CO}} + C_{\text{out}}^{\text{CO}_2} + C_{\text{out}}^{\text{CH}_4} + \nu C_{\text{out}}^{\text{C}_i\text{H}_j\text{O}_k}} \tag{15}
\]

The thermal conversion of methanol in the analyzed temperature range was not detected in any of the experiments performed without a catalyst. To compare the catalytic activities obtained in this work with those reported elsewhere, we employed a simple first order reaction rate equation, which for an integral reactor yields the following expression for the catalytic rate constant of methanol decomposition:

\[
k_{\text{md}} = - \frac{n_{\text{MeOH}}^{\text{in}}}{w_{\text{cat}} \times P_{\text{MeOH}}^{\text{in}}} \times \ln \left( \frac{X_{\text{MeOH}}}{100} \right) \tag{16}
\]

where \(n_{\text{MeOH}}^{\text{in}}\) is the inlet molar flow rate of methanol \((\text{mol s}^{-1})\), \(w_{\text{cat}}\) is the catalyst weight \((\text{g})\) (excluding the SSWM support) and \(P_{\text{MeOH}}^{\text{in}}\) is the inlet partial pressure of methanol \((\text{Pa})\).
SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O catalysts for hydrogen production

3. Discussion of results

3.1. Optimization of the ZnO yield in the templates

The SSWM-ZnO template prepared according to the standard procedure described in the Experimental section is composed of arrays of ZnO nanosheets forming a layer with a thickness of ~13 µm that covers the SSWM surface (SEM images in Figure 1), show good adhesion to the support and have a large proportion of polar surfaces [19]. The ZnO on the SSWM has a yield of ~20 wt.%, a BET specific surface area of between 60 and 80 m$^2$ g$^{-1}$ (on a ZnO mass basis) and a crystal size of $d_{XRD}$=~13 nm. A preliminary step for maximizing the ZnO yield in the SSWM-ZnO supported template was performed by varying the synthesis temperature and the precursor (zinc acetate) concentration.

![Figure 1](image.png)

**Figure 1.** Variation of the ZnO yield (a) with the synthesis temperature (a) and the concentration of Zn$^{2+}$ in the synthesis solution used for the fabrication of the SSWM-supported ZnO template. Insets: SEM images of the sample prepared at 80°C and [Zn$^{2+}$]=0.05 M.
Figure 1a shows the optimum synthesis temperature to be 80°C, as in the original procedure described in the Experimental section. At this temperature, an increase in the precursor concentration produced a concomitant increase in the ZnO yield, up to values of over 40 wt.% within the concentration range analysed (Fig. 1b). The specific surface area of ZnO in the materials obtained was maintained regardless of the value of the ZnO yield. The templates outlined in Fig. 1b were selected for preparing catalysts with different loads of Ni$_{0.7}$Zn$_{0.3}$O on the SSWM support, that would allow the WHSV values to be changed during the catalytic tests while the gas hourly space velocity was kept constant.

3.2. Synthesis and characterization of the SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O

Since all the preparations were performed at room temperature and ambient pressure, the main substitution parameters used when applying the STAH method with the polar SSWM-Z2O template were (i) the aqueous nickel ion to zinc molar ratio ($R_{Ni/Zn}$) and (ii) the substitution time ($t_s$).

![Figure 2](image_url)

**Figure 2.** Effect of a) substitution time ($t_s$) and b) $R_{Ni/Zn}$ on the degree of nickel substitution. c) Variation of the specific surface area with the degree of nickel substitution.
Using nickel acetate solutions our objective was to prepare the pure metal oxide, as we did with iron, titanium, cerium and copper oxides in [19]. Figure 2a shows the substitution degrees (Ni/(Ni+Zn) molar ratio in the obtained samples) for a value of \( R_{\text{Ni/Zn}} = 7 \) and different substitution times (1 to 10 days). It can be seen from this figure that the maximum exchangeable ratio is approximately 0.6. It was expected that higher values of \( R_{\text{Ni/Zn}} \) in the synthesis solution would increase this ratio but, as can be seen in Fig. 2b, the limit of 0.6 is still maintained. Even an increase of the synthesis temperature to 90°C failed to yield the expected increase in the substitution degree. To check whether the remaining zinc was in the form of zincite or not, the sample represented by the circle enclosed in the dashed box of Fig. 2b was washed with a solution of NaOH (2M). As a result the Ni/(Zn+Ni) molar ratio increased but only from 0.61 to 0.68 (triangle enclosed in the dashed box of Fig. 2b) indicating that the zinc present in the original sample was hardly in the form of soluble zincite.

The XRD diffraction patterns of the sample, before and after washing, are displayed in Figure 3, the upper plot corresponding to the unwashed sample (a macroscopic image of which is shown in the inset).

![Figure 3](image)

**Figure 3.** XRD spectra of a) an as-prepared SSWM-supported \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{O} \) sample and b) the same sample after being washed with NaOH (2M). Inset in Fig. 3a: Photograph of the original sample showing its flexibility.
The spectrum is made up of three phases: a small fraction of zincite (PDF# 01-075-0576), a major fraction of Ni$_{0.7}$Zn$_{0.3}$O (PDF# 01-075-0272) and the support (SSWM). As expected, in the washed sample the spectrum of zincite is absent. In view of this result and the Ni/(Zn+Ni) molar ratios of both samples (0.61 and 0.68), it can be concluded that the original sample was composed of around 90 mol% Ni$_{0.7}$Zn$_{0.3}$O and 10 mol% ZnO. The yield of metal oxides in the washed sample decreased from ~21 wt.% (original sample) to ~15 wt.%, which means that the disappearance of ZnO was accompanied by the loss of some Ni$_{0.7}$Zn$_{0.3}$O. This suggests that at least a part of the unreacted ZnO in the original sample became bonded to the SSWM, serving as a link between the mesh and part of the Ni$_{0.7}$Zn$_{0.3}$O phase.

Figure 4 shows the TPR profile of the washed sample. Three main peaks were obtained by applying a deconvolution procedure, with maxima at 167, 285 and 347°C. The low temperature peak can be attributed to non-stoichiometric oxygen on the surface (Ni$^{3+}$ ions) [28, 29], the peak at 285°C to easily reducible surface Ni$^{2+}$ (that which was originally present and that which originated from the reduction of Ni$^{3+}$) and the high temperature peak is ascribed to bulk Ni$^{2+}$[30]. Zn$^{2+}$ is not reducible in this temperature range, as confirmed by the TPR analysis of the SSWM-Z20 template.

![Figure 4. TPR profile of a NaOH-washed SSWM-supported Ni$_{0.7}$ZnO$_{0.3}$O sample](image-url)

The peak distribution shown in Figure 4 corresponds to the reduction of a species with the chemical formula Zn$^{2+}_{0.3}$Ni$^{2+}_{0.283}$Ni$^{3+}_{0.249}$O$_{1.084}$ with a relative error of ~3\% for the total hydrogen consumption. This means that around 60\% of the...
nickel atoms are located on the external surface of the sample, which is consistent with the low crystal size value obtained by applying Scherrer’s equation to the spectra shown in Figure 3 (d_XRD = 8 nm) and with the high values of specific surface area in Figure 2c. As occurred with most of the metal oxides synthesized in a previous work [19], the specific surface area increases with the degree of nickel substitution up to values of around 100 m² g⁻¹ for the fully developed solid solution.

XPS was also used to gain a better insight into the structure of the solid solution. Figure 5 shows the Ni2p3/2 spectra obtained for the washed sample by using Mg-Kα and Al-Kα radiation sources. The deconvolution parameters obtained for this and the rest of the XPS regions analyzed are indicated in Table 1.

Table 1. Deconvolution parameters for the XPS analysis of a NaOH-washed SSWM-supported Ni₀.7Zn₀.3O sample

<table>
<thead>
<tr>
<th>XPS region</th>
<th>Peak #</th>
<th>MG-Kα source</th>
<th>Mg-Kα source</th>
<th>Al-Kα source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni2p3/2</td>
<td>#1</td>
<td>852.9</td>
<td>0.09</td>
<td>853.3</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>854.3</td>
<td>0.49</td>
<td>854.7</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>856.2</td>
<td>0.05</td>
<td>856.5</td>
</tr>
<tr>
<td></td>
<td>#4</td>
<td>859.9</td>
<td>0.27</td>
<td>860.3</td>
</tr>
<tr>
<td></td>
<td>#5</td>
<td>862.8</td>
<td>0.11</td>
<td>863.2</td>
</tr>
<tr>
<td>O1s</td>
<td>#1</td>
<td>528.7</td>
<td>0.41</td>
<td>528.7</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>530.6</td>
<td>0.52</td>
<td>530.6</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>532.9</td>
<td>0.07</td>
<td>532.6</td>
</tr>
<tr>
<td>Zn2p3/2</td>
<td>#1</td>
<td>1020.2</td>
<td>0.52</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>1022.5</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>1035.1</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>Zn2p1/2</td>
<td>#4</td>
<td>1043.3</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>#5</td>
<td>1045.5</td>
<td>0.06</td>
<td>-</td>
</tr>
</tbody>
</table>

As can be seen, the main peaks are located at around 852.9-853.3 eV (#1), 854.3-854.7 eV (#2) and 856.2-856.5 eV (#3). Peak #2 at ~854.5 eV, which is close to what one would expect for NiO [29-31], is ascribed to octahedral Ni²⁺ forming part of the external surface of the particles. This is corroborated by the different area ratio
values for the main peaks (#1/#2) obtained with both X-ray sources (Figure 5). The lower relative area of peak #2 was obtained from the Al source, indicating that the species that gave rise to this peak was more concentrated on the external surface of the particles. Peak #3 at ~856.4 eV is attributed to the Ni\(^{3+}\) species [29, 32], which were also detected by TPR (Figure 4), while peaks #4 and #5 are satellite peaks.

![XPS spectra with two different radiation sources in the Ni2p3/2 region of a NaOH-washed SSWM-supported Ni\(_{0.7}\)ZnO\(_{0.3}\)O sample](image)

**Figure 5.** XPS spectra with two different radiation sources in the Ni2p3/2 region of a NaOH-washed SSWM-supported Ni\(_{0.7}\)ZnO\(_{0.3}\)O sample

The O1s spectra (Figure 6) corroborate the results reported above; peak #2 located at 530.6 eV is ascribed to oxygen linked to octahedral Ni\(^{2+}\) [32,33], which is more concentrated at the surface of the particles than inside the bulk (the #2/#1 peak area ratio decreases when using the Al radiation source), whereas peak #3 at ~536.7 eV is attributed to non-stoichiometric oxygen linked to Ni\(^{3+}\) cations [32, 33].
Figure 6. XPS spectra with two different radiation sources in the O1s region of a NaOH-washed SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O sample

Finally, the Zn2p spectrum (Figure 7) shows two main peaks at 1020.2 and 1043.3 eV (peaks #1 and #4) and two small peaks located at 1022.5 and 1044.5 eV (peaks #2 and #5 in Figure 7). Octahedral Zn$^{2+}$ in Ni$_{0.7}$Zn$_{0.3}$O obtained at high temperature has a binding energy in the Zn2p3/2 region of 1021.6 eV [3], for an assumed binding energy of the associated oxygen in the O1s region of 529.5 eV [3]. On the other hand, tetrahedral ZnO has binding energies of 1022.6 eV (Zn2p3/2), 1045.6 eV (Zn2p1/2) and 530.0 eV (O1s) [34]. It seems clear that the small peaks #2 and #5 (Figure 7) must be attributed to residual zincite (tetrahedral ZnO), but the low binding energy peaks cannot be ascribed to fully coordinated octahedral Zn$^{2+}$. 
A feature common to the spectra in Figures 5, 6 and 7, and rarely mentioned in the literature, is the presence of low binding energy peaks with no obvious assignation, i.e., those indicated by arrows in the figures. Peak #1 in the Ni2p3/2 spectra (852.9-853.3 eV) cannot be ascribed to metallic Ni, which has a lower binding energy [31, 35]. De Jesús et al. [36] detected this peak in nickel oxide films oxidized at room temperature while they were being subjected to argon ion bombardment. The O1s peak for the same sample was 529.1 eV [36], which is also very similar to peak #1 in the O1s spectra in Figure 6. These authors attributed the low binding energy peaks to the partial reduction of the nickel oxide as a consequence of argon ion...
SSWM-supported \( \text{Ni}_{0.7}\text{Zn}_{0.3}O \) catalysts for hydrogen production

bombardment. A similar observation was made by Li et al. [37] with respect to thin air annealed-ZnO films. When the samples experienced some reduction (loss of oxygen) they detected a clear decrease in binding energy in both the peak in the O1s region (from 530.8 to 529.9 eV) and the peak in the Zn2p3/2 region (from 1022.4 to 1021.5 eV) with respect to the unreduced sample. Remashan et al. [38], working with \( \text{N}_2\text{O} \) plasma-treated ZnO thin films observed low binding energy peaks in the O1s (529.5 eV) and Zn2p3/2 (1020.2 eV) regions, similar to peaks #1 in Figures 6 and 7, which, on the basis of previously published reports, they also attributed to a greater number of zinc atoms being bound to oxygen. These data support the hypothesis of a bulk rocksalt crystal structure with oxygen vacancies, in which most of the octahedral \( \text{Zn}^{2+} \) cations (peak #1 in Figure 7 holds most of the area of the Zn2p3/2 region) and part of the \( \text{Ni}^{2+} \) cations are in a slightly reduced state. An ideal representation of this structure is shown as an inset in Figure 7.

In the light of these new results, the empirical formula of the solid solution derived from the TPR results must now be changed slightly to:

\[
\text{Zn}^{2+}{}_{0.30}{}_{(\text{bulk})} + \text{Ni}^{2+}{}_{0.30}{}_{(\text{surf})} + 0.25 \text{Ni}^{3+}{}_{(\text{surf})} + 0.25 \text{Ni}^{2+} + 0.185 \text{O} \]

in which approximately the same number of zinc and nickel cations are affected by the oxygen vacancies in the rocksalt crystal structure.

The morphology, particle size and chemical make-up of the as-prepared solid solution were studied by SEM and EDS-assisted TEM analysis, the results of which are shown in Figure 8. A comparison of Figs. 1a and 8a reveals that the macroscopic morphology of the ZnO template is approximately unchanged after the synthesis. The mixed oxide is arranged in arrays of thin sheets of homogenous length in the 5-7 \( \mu \text{m} \) range. TEM images of the solid solution are shown in Figs. 8b and 8c. The sample is formed by three-dimensionally interconnected nanograins of size \( \sim 7 \) nm which give rise to a high porosity in the macroscopic nanosheets. This result is in good agreement with the crystal size evaluated by XRD (\( d_{\text{XRD}} = 8 \) nm). The lattice spacing observed in Figure 8c is approximately 2.1 Å, which corresponds to the (200) plane of the rocksalt crystal structure in NiO.

The composition of the mixed oxide was analysed using a dispersive X-ray spectroscopy (EDS) line scan profile of Ni, Zn and O (Figure 8b). The parallel location of nickel and zinc throughout the nanoparticle demonstrates that there is a homogenous distribution of Ni and Zn with a \( \text{Ni}/(\text{Zn}+\text{Ni}) \) atom ratio that is in fair agreement with that of the AAS analysis.
The exact mechanism by which the solid solution is formed by room temperature sacrificial template accelerated hydrolysis is unclear. The hydrolysis of nickel ions provides nickel hydroxide complexes and H\(^+\) in the surroundings of the ZnO template, which is simultaneously etched by the protons to form Zn\(^{2+}\). This consumption of H\(^+\) accelerates the hydrolysis process of the Ni\(^{2+}\), leading to an enhancement of the etching process of ZnO. As a result, nickel hydroxide complexes precipitate onto the ZnO scaffold, to form the early rigid framework of the nanosheets. We suggest that a combination of a low hydrolysis rate (nickel is a weakly acidic cation) and the high local concentration of Zn\(^{2+}\) originating from the dissolution of the highly polar ZnO template allows the nickel hydroxides being formed to trap the Zn\(^{2+}\) ions within their crystal structure. This phenomenon does not take place when non-polar ZnO nanowires are used [20, 21], probably due to a much lower local Zn\(^{2+}\) concentration. Progressive hydrolysis and the dissolution of the template eventually result in the high surface area Ni\(_{0.7}\)Zn\(_{0.3}\)O nanosheet-based architectures displayed in Figure 8a.
### 3.3. Catalytic production of hydrogen from methanol

For the catalytic tests three different catalysts were used: SSWM-Ni20, SSWM-Ni35 and SSWM-Ni40. These samples were prepared by applying sacrificial template synthesis at RT from SSWM-Z20, SSWM-Z35 and SSWM-Z40, respectively, for t=1 day and R_{Ni/Zn}=7, with Ni_{0.7}Zn_{0.3}O yields of 20.2, 35.2 and 41 wt.%, respectively. In all the experiments the same gas hourly space velocity (GHSV) was kept constant. Because three catalysts with different active phase yields were used, it was possible to study the effect of the changes in weight hourly space velocity (WHSV) on the reactions. The pure SSWM-supported ZnO catalyst was found to be almost inactive in the tested processes. As an example, the reaction rate constant for methanol decomposition of SSWM-supported ZnO was found to be two orders of magnitude lower than that of the Ni_{0.7}Zn_{0.3}O-based catalysts.

![Graph](image)

**Figure 9.** Variation of reaction temperature, methanol conversion and hydrogen yield with time for the SSWM-Ni35 catalyst tested in the methanol steam reforming reaction (MSR) and in the methanol decomposition reaction (MD)
Figure 9 offers the variation of reaction temperature, methanol conversion (eq. 1) and hydrogen yield (eq. 11) with time for the SSWM-Ni35 catalyst tested in the methanol steam reforming reaction (MSR) and in the methanol decomposition reaction (MD). The same experimental sequence was used for testing the rest of catalysts. The conversion points displayed in the ensuing figures are those corresponding to the end of each isothermal stage (i.e., diamonds in the MSR curves of Figure 9). The catalyst shows a good stability in the steam reforming reaction and a certain degree of deactivation in the methanol decomposition reaction, the cause of which will be discussed below.

![Figure 9](image-url)

**Figure 10.** Variation of methanol conversion and hydrogen yield with temperature for the catalysts tested in the methanol steam reforming reaction. The arrows indicate the direction of the experimental sequence.

Figure 10 shows the results of methanol conversion and hydrogen yield in the MSR reaction for the SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O catalysts with different yields (SSWM-Z20, SSWM-Z35 and SSWM-Z40) after 15 hours of reaction at the given temperatures (i.e., diamonds in Figure 9). The arrows indicate the direction of the
SSWM-supported Ni$_{0.7}$Zn$_{0.3}$O catalysts for hydrogen production

experimental sequence. It can be seen that, when the temperature is increased, there is a marked increment in methanol conversion between 300 and 350°C, as a consequence of the reduction of nickel oxide. At temperatures over 350°C there is a complete conversion of methanol which is maintained when the temperature is reduced again to ~300°C for the lowest WHSV values (SSWM-Ni35 and SSWM-Ni40). The hydrogen yield, which, as expected, is dependent to some extent on the WHSV, shows values somewhat below those of the methanol conversion, although it reaches values close to 90% at temperatures of around 400°C. The cause for this discrepancy between hydrogen yield and methanol conversion is the carbon selectivity. As can be seen in Figure 1, the carbon selectivity towards CO (methanol decomposition reaction: CH$_3$OH→CO +2H$_2$) is high at temperatures below 400°C, but it decreases in favour of the carbon selectivity towards CO$_2$ at increasing reaction temperatures and decreasing WHSV values.

Thus the methanol decomposition reaction is favoured over the water gas shift reaction (CO+H$_2$O→CO$_2$+H$_2$) at high values of weight hourly space velocity and low temperatures. This suggests that the steam reforming process needs longer contact times and/or higher steam pressures for the water gas shift reaction to proceed to the right, which causes the H$_2$ yield and the carbon selectivity towards CO$_2$ to increase. The longer contact time can be tested by increasing the gas hourly space velocity. This can be easily done in view of the modularity of the monolithic SSWM-supported catalysts. At temperatures over 400°C the carbon selectivity towards CO seems to have a bottom limit of around 42% at the GHSV tested in this work, probably due to thermodynamic constrains. Therefore, the temperature zone between 350 and 400°C seems in principle to be the most appropriate range for investigating the effect of the GHSV and/or the steam pressure on the carbon selectivity towards CO$_2$, considering that at higher temperatures carbon selectivity towards methane, though low, starts to become noticeable, especially at the lowest WGSV, something which was recognized long ago in methanol decomposition reactions over nickel-based catalysts [39]. However, this issue will be addressed in more detail in a future work on a micro-reactor specifically designed for this type of monolithic catalysts. The analytical system also detected some traces of dimethyl ether that decreased with a rise in temperature. Application of equation (10) yielded concentration values for this compound very close to zero.
Figure 11. Variation of carbon selectivity towards CO, CO$_2$ and CH$_4$ with temperature for the catalysts tested in the methanol steam reforming reaction. The arrows indicate the direction of the experimental sequence.
It is evident from the results discussed above that the tested catalysts are active in the methanol decomposition reaction over the temperature range analyzed. This reaction was studied in separate experiments, as pointed out in the Experimental section, the results of which are shown in Figures 12 and 13.

**Figure 12.** Variation of a) methanol conversion and hydrogen yield and b), c), d) carbon selectivity towards CO$_2$ with temperature for the catalysts tested in the methanol decomposition reaction. The arrows indicate the direction of the experimental sequence.

Figure 12a shows the variation in methanol conversion and hydrogen yield for the different catalysts after 10 hours of reaction at the given temperatures. Both curves are similar, which is a clear indication of the high carbon selectivity towards carbon monoxide, over 97% for all catalysts in the range of temperatures analyzed. At the
highest temperatures a small amount of methane was detected ($S_{\text{CH}_4}<2\%$), as a result of the methanation reaction ($\text{CO}+3\text{H}_2\leftrightarrow\text{CH}_4+\text{H}_2\text{O}$) [40]. At some low temperatures the hydrogen yield was slightly higher than the methanol conversion, due to the experimental error of the analytical method. As expected, the methanol conversion increases at lower values of WHSV. In all the experiments, the values of methanol conversion collected at increasing temperatures are higher than those obtained in the subsequent sequence at decreasing temperatures, as exemplified by the data for SSWM-Ni40 in Figure 12a. A similar trend was observed for the hydrogen yield in the methanol steam reforming reaction (Figure 10), once the onset of nickel reduction was surpassed ($T>330^\circ\text{C}$); in this case it is probably due to a higher reduction degree of the catalyst surface leading to an increase in the carbon selectivity to CO in the sequence at decreasing temperatures (Figure 11) and not to catalyst deactivation. As can be seen in Figure 12a, the onset of nickel oxide reduction occurs at a rather lower temperature in the absence of steam ($\sim 250^\circ\text{C}$). The lower conversion degrees in the sequence of decreasing temperatures are due in this case to gradual deactivation of the catalysts during the experimental sequence (MD curves in Figure 9) as a consequence of coke deposits. This is inferred from the low, though conspicuous, values of carbon selectivity towards $\text{CO}_2$, plotted in Figures 12b to 12d for values of methanol conversion of over 15%. $\text{CO}_2$ is formed on reduced nickel centres via the Boudouard equilibrium ($2\text{CO}\leftrightarrow\text{C}+\text{CO}_2$) [40]. As can be observed in the figures, the amount of $\text{CO}_2$ released increases with the temperature and as the reaction proceeds, the latter being a consequence of the greater availability of reduced nickel centres.

To calculate the methanol decomposition constant, the more conservative values of the sequence at decreasing temperatures were used. Figure 13 shows an Arrhenius plot with the $k_{\text{md}}$ values obtained for the different catalysts (eq. 16). This is an intrinsic constant that should be independent of the active phase yield or WGHV. However, Figure 13 shows that there is a slight dependence of catalytic performance on these variables. The reason for this dependence is the different degrees of catalyst deactivation due to coke deposition for different values of WGHV. EDX analyses of the surface of the catalysts after a complete reaction sequence show an increase in carbon content for increasing values of WHSV (inset in Figure 13), which explains the higher deactivation degree of SSWM-Ni20 compared to the other catalysts. This indicates that a higher contact time enhances the durability of the catalysts. The absolute values of $k_{\text{md}}$ (4.6-10.7 x 10$^{-10}$ mol g$^{-1}$ Pa$^{-1}$) reported in Figure 13, although affected to some extent by partial catalyst deactivation, when included into the
SSWM-supported $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ catalysts for hydrogen production

ranking scale established by Marbán et al. [14] show these catalysts to be among the most active ever synthesized for methanol decomposition.

Figure 13. Arrhenius plot of the methanol decomposition constant (eq. 13) for the catalysts tested. Inset: variation of the surface carbon content with the weight hourly space velocity after a complete experimental sequence of methanol decomposition.

4. Conclusions

We have demonstrated in this work the feasibility of synthesizing a high surface area $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ solid solution by means of a room-temperature process, sacrificial template accelerated hydrolysis. The key to achieving this result was the use of a highly polar ZnO template supported on the surface of a stainless steel wire mesh (SSWM), which allowed the material to be produced in a monolithic configuration. The catalyst was produced with a high surface area of around 100 m$^2$ g$^{-1}$ and in a considerable yield over the SSWM (up to 40 wt.% in the synthesis conditions employed in this work). The characterization of the material by TPR, XRD and XPS revealed that it was composed of an oxygen-defective solid solution with an empirical formula of the type $\text{Zn}^{(2-\delta)+}_{0.30}\text{Ni}^{(2-\delta)+}_{0.28}\text{Ni}^{2+}_{0.25}\text{Ni}^{3+}_{0.17}\text{O}^{1.085-0.15}_{0.14}$. The catalyst
was not very selective in the methanol steam reforming reaction, as it produced large amounts of CO at temperatures below 400°C. However, at more elevated temperatures the water gas shift reaction improved the hydrogen yield and the carbon selectivity towards CO$_2$, especially over higher contact times. Methanol decomposition took place with high conversion degrees and hydrogen yields in the temperature range 250-350°C. In spite of some catalyst deactivation due to coke deposition, which was more noticeable at the highest weight hourly space velocity, this catalyst has been demonstrated to be among the most active catalysts ever reported in the literature.

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SSWM-supported $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ catalysts for hydrogen production


GENERAL CONCLUSIONS
In this PhD Thesis, we have examined and designed different procedures to synthesize nanostructured metal oxides supported on stainless steel wire meshes (SSWM), and have tested the materials as monolithic catalysts for environmental and energy applications. These include the degradation of organic pollutants in water and the production of hydrogen from methanol. The most important conclusions derived from this work are summarized below:

1. With regard to the synthesis of ZnO nanostructures supported on SSWM substrates:
   a) A number of facile and one-step hydrothermal procedures have been successfully applied for the growth of ZnO nanostructures on stainless steel wire meshes.
   b) The surface polarity and shape of the SSWM-supported ZnO nanostructures can be tuned by adjusting the synthesis parameters \(i.e.\) synthesis temperature, synthesis time, addition of additives, etc.). In this way, it is possible to direct the growth of ZnO crystals either towards the \(c\)-axis, that entails the formation of less polar ZnO nanorods \((d_{\text{XRD}} \sim 30-45 \text{ nm})\) with a low geometric surface area, or towards the \(a\)-axis resulting in highly polar ZnO nanosheets \((d_{\text{XRD}} \sim 14 \text{ nm})\) with a high specific surface area \((80 \text{ m}^2 \text{ g}^{-1})\).

2. With regard to the photocatalytic degradation of methylene blue using SSWM-supported ZnO photocatalysts:
   a) A mathematical technique based on the deconvolution of the UV-Vis absorption curves was developed in order to determine the true methylene blue concentration during the photocatalytic tests. This technique allows the contribution of the reaction intermediates (azure A, azure B and azure C) to the spectra to be taken into account, without the need for actually measuring them.
b) The photocatalytic activity of SSWM-supported ZnO catalysts is independent of certain structural characteristics such as crystal size, specific surface area or ratio.

c) For ZnO particles of length >1500 nm, photocatalytic activity increases with the number of polar surfaces of the crystals.

d) The photocatalytic activity of the SSWM-supported ZnO catalysts is inversely related to the length of the ZnO nanostructures.

e) The SSWM-supported ZnO catalyst consisting of parallel arrays of nanorods of ~700 nm length and ~100 nm width exhibits an outstanding photocatalytic activity which is higher than that of commercial P25 TiO₂ particles.

3. With regard to the photocorrosion of SSWM-supported ZnO:

a) Doping of ZnO with Ag atoms enhances its photocatalytic activity but does not prevent the extensive loss of catalyst mass after a few reaction cycles as a consequence of photocorrosion.

b) Coating the catalysts with a thin layer of polysiloxane (surface Si/Zn atom ratio = 1) prevents photocorrosion and stabilizes the catalytic activity.

4. With regard to the synthesis of SSWM-supported metal oxides via sacrificial template accelerated hydrolysis (STAH):

a) High surface area nanostructures of a variety of metal oxides (CuO, α-Fe₂O₃, TiO₂, CeO₂, Cd₂Zn₁₋ₓO and Ni₀.₇Zn₀.₃O) supported on SSWM have been successfully produced by STAH using a novel template consisting of highly polar high surface area ZnO nanosheets supported on SSWM.

b) The metal oxides display much higher specific surface area values (37-275 m² g⁻¹) than those synthesized by the standard STAH technique using ZnO nanorods as template.
c) The metal oxides are obtained with a high purity (95-98 mol%) in a high yield with respect to the SSWM support (up to 40 wt.%) and exhibit a good adhesion to the support.

5. With regard to the applications of SSWM-supported metal oxides synthesized via STAH:

a) A structured Fenton-like catalyst made up of high surface area α-Fe₂O₃ (220 m² g⁻¹) has been successfully used for the continuous degradation of methylene blue in aqueous solution. A conversion of over 80% was obtained for a residence time of τ ~6.5 min. The catalyst shows an outstanding stability during several reaction cycles and it is more active than other high-performing catalysts described in the literature.

b) With regard to the photocatalytic degradation of methylene blue using SSWM-supported CdₓZn₁₋ₓO as photocatalyst:

- The amount of Cd incorporated into the ZnO structure (x≤0.2) can be controlled by tuning the synthesis variables (Cd/Zn molar ratio in the synthesis solution, synthesis time, temperature and addition of sodium citrate).

- This catalyst is a CdₓZn₁₋ₓO solid solution (~37 m² g⁻¹) in which cadmium is replacing part of the zinc atoms in the hexagonal structure of ZnO. There is a profile of the Cd concentration in the substituted ZnO layer, by which the stoichiometric formula changes gradually from ZnO in the bulk to CdO on the surface in the case of the catalyst with the highest degree of substitution (x=0.2).

- The catalyst exhibits a significant photocatalytic activity and a high stability under ultraviolet irradiation, which indicates that the addition of small amounts of Cd to ZnO (x=0.05) notably reduces the photocorrorion of ZnO.
The Cd-substituted catalysts display a slightly higher catalytic activity than the pure ZnO catalysts under visible irradiation.

c) With regard to the photocatalytic degradation of methylene blue using SSWM-supported TiO$_2$ as photocatalyst:

- The calcination temperature of the catalysts significantly affects the composition, crystallinity, the textural properties and the photocatalytic activity of the catalysts.
- At 250°C the catalyst, which is mainly composed of anatase and amorphous TiO$_2$ and, to a lesser extent, a ZnO-TiO$_2$ rutile-like solid solution, the amount of which decreases with the increase in the calcination temperature, has a high specific surface area (275 m$^2$ g$^{-1}$) and shows a remarkable catalytic activity for the photodegradation of methylene blue in aqueous solution.
- At 375°C the anatase crystal size has grown considerably and both the specific surface area and the catalytic activity have experienced a parallel decrease.
- In the 375-450°C range the transformation of amorphous TiO$_2$ into small anatase crystals causes a decrease in anatase crystal size and a marked increase in catalytic activity, which reaches its highest value at 450°C. From this temperature to 600°C the catalytic activity undergoes a gradual reduction as a consequence of the loss of active centers due to sintering. Beyond 600°C the reduction in catalytic activity is more severe as a consequence of the onset of rutile formation.
- The most active catalyst prepared in this work shows twice as much catalytic activity as the reference catalyst P25 TiO$_2$.

d) With regard to the production of hydrogen from methanol by using a novel Ni$_{0.7}$Zn$_{0.3}$O catalyst supported on SSWM substrates:
General Conclusions

- A high surface area Ni$_{0.7}$Zn$_{0.3}$O solid solution (100 m$^2$/g) supported on a SSWM substrate has been synthesized at room temperature for the first time.

- The material is an oxygen-defective solid solution with a slightly distorted rocksalt crystal structure and with an empirical formula of the type Zn$^{(2-\sigma)^+}_{0.30}$Ni$^{(2-\delta)^+}_{0.28}$[bulk]$_{0.25}$Ni$^{3+}_{0.25}$O$_{1.085-0.15\sigma-0.145\delta}$.

- The material has been tested as catalyst for the first time. It was applied in the steam reforming of methanol (MSR) and the methanol decomposition (MD) reaction to produce hydrogen.

- Once reduced, the catalyst displays a remarkable catalytic activity for MSR in the 300-450°C range, achieving methanol conversions of nearly 100%. However the catalyst is not very selective in this temperature range as it produces high amounts of CO.

- This material is a very active and selective catalyst for the MD reaction in the 250-350°C temperature range, although it undergoes a slight catalyst deactivation due to the formation of coke deposits. The catalyst has been proven to be one of the most active catalysts ever reported in the literature for this process.
CONCLUSIONES GENERALES
En esta Tesis Doctoral se han analizado y diseñado distintos procedimientos para la síntesis de óxidos metálicos nanoestructurados soportados en mallas de acero inoxidable, utilizando los materiales obtenidos como catalizadores monolíticos para aplicaciones medioambientales y energéticas. Estas incluyen la degradación de contaminantes orgánicos en agua y la producción de hidrógeno a partir de metanol. Las conclusiones más importantes derivadas de este trabajo se muestran a continuación:

1. En lo que se refiere a la síntesis de nanoestructuras de ZnO soportadas en mallas metálicas:
   a) Se han utilizado con éxito diversos procedimientos hidrotermales sencillos que permiten sintetizar las nanoestructuras de ZnO sobre las mallas.
   b) Mediante el control de los parámetros de síntesis (temperatura y tiempo de síntesis así como la presencia de aditivos) es posible obtener nanoestructuras de ZnO de diferentes morfologías y con diferente proporción de planos polares. De este modo se puede favorecer el crecimiento bien en la dirección del eje c, que implica la formación de nanovarillas de ZnO poco polares ($d_{XRD} \sim 30-45$ nm) con baja superficie, o bien en la dirección del eje $a$, dando lugar a la formación de nanohojas de ZnO con elevada proporción de planos polares ($d_{XRD} \sim 14$ nm) y elevada superficie específica ($80 \text{ m}^2 \text{ g}^{-1}$).

2. En lo que respecta a la degradación fotocatalítica de azul de metileno utilizando fotocatalizadores de ZnO soportados en mallas metálicas:
   a) Se ha desarrollado un procedimiento matemático para determinar la concentración real de azul de metileno durante los ensayos de fotodegradación. La técnica diseñada para el análisis de las curvas de absorción UV-Vis permite tener en cuenta la contribución al espectro de diversos intermedios de reacción que (azar A, azur B y azur C) sin tener que medirlos analíticamente.
b) Se ha demostrado que la actividad fotocatalítica de los catalizadores de ZnO soportados en mallas metálicas es independiente de ciertas características estructurales del material, como tamaño de cristal o superficie específica.

c) Para partículas de ZnO de tamaño superior a 1500 nm, la actividad fotocatalítica aumenta con la proporción de superficies polares en los cristales.

d) La actividad fotocatalítica de ZnO soportado en mallas es inversamente proporcional a la longitud de las nanoestructuras de ZnO.

e) El catalizador de ZnO soportado en malla constituido por nanovarillas paralelas de aproximadamente 700 nm de longitud y unos 100 nm de espesor presenta una elevada actividad catalítica, superior a la del catalizador P25 TiO₂ comercial.

3. Respecto a la fotocorrosión de ZnO soportado en mallas metálicas
   a) El dopaje de ZnO con átomos de Ag mejora la actividad fotocatalítica del catalizador pero no evita la pérdida masiva del mismo tras unas pocas etapas de reacción debido al fenómeno de fotocorrosión.
   b) El recubrimiento del catalizador con una fina capa de polisiloxano (concentración superficial atómica Si/Zn=1) evita la fotocorrosión y estabiliza la actividad catalítica.

4. En lo que se refiere a la síntesis de óxidos metálicos soportados en mallas vía STAH.
   a) Se han obtenido óxidos metálicos nanoestructurados (CuO, α-Fe₂O₃, TiO₂, CeO₂, Cd₂Zn1₋xO y Ni₀.₇Zn₀.₃O) soportados aplicando el método STAH sobre un molde de sacrificio novedoso que consiste en nanohojas de ZnO de elevada superficie y altamente polares soportadas sobre una malla flexible de acero inoxidable.
   b) Los óxidos metálicos sintetizados en este trabajo presentan áreas superficiales mucho mayores (37-275 m²g⁻¹) que otros materiales
Conclusiones Generales

obtenidos por el método STAH convencional que utiliza nanovarillas de ZnO no polar como molde.

c) Este procedimiento permite obtener óxidos metálicos de alta pureza (95-98 mol%) con elevado rendimiento respecto a la malla que actúa como soporte (hasta 40% peso) y que muestran buena adherencia al soporte.

5. En cuanto a las aplicaciones de los óxidos metálicos sintetizados mediante el método STAH:

a) Se ha sintetizado un catalizador estructurado compuesto por α-Fe₂O₃ de elevada superficie (220 m² g⁻¹) que ha sido utilizado con éxito en un proceso tipo Fenton para la degradación en continuo de azul de metileno en solución acuosa (con conversiones del 80% para tiempos de residencia de 6.5 minutos) con buena estabilidad durante varios ciclos de reacción y elevada actividad comparada con la de los catalizadores descritos en la literatura.

b) En lo que respecta a la degradación fotocatalítica de azul de metileno con CdₓZn₁₋ₓO como fotocatalizador:

- La cantidad de Cd incorporado en la estructura del ZnO (x≤0.2) puede ser controlada mediante el ajuste de las variables de síntesis (proporción molar de Cd/Zn en la mezcla de síntesis, tiempo y temperatura de síntesis, adición de citrato de sodio).

- El catalizador es una solución sólida CdₓZn₁₋ₓO (~37 m² g⁻¹) en la que el cadmio se encuentra reemplazando parte de los átomos de zinc en la estructura hexagonal del ZnO. Existe un perfil de concentración de Cd en la capa de ZnO sustituido de forma que la fórmula estequiométrica varía gradualmente desde ZnO en el seno del catalizador hasta CdO en la superficie, para el catalizador con mayor grado de sustitución (x=0.2).
• El catalizador muestra una buena actividad fotocatalítica y elevada estabilidad bajo irradiación ultravioleta, lo que muestra que la adición de pequeñas cantidades de Cd al ZnO ($x=0.05$) reduce considerablemente la fotocorrosión del ZnO.

• Los catalizadores con Cd muestran una actividad catalítica en el visible ligeramente superior a la exhibida por el ZnO.

c) Referido a la degradación fotocatalítica de azul de metileno con catalizadores de TiO$_2$ soportados en mallas:

• La temperatura de calcinación de los catalizadores afecta significativamente a la composición, cristalinidad, propiedades texturales y actividad fotocatalítica de los catalizadores.

• A 250°C el catalizador está principalmente compuesto de anatasa y TiO$_2$ amorfo, con la presencia de una pequeña cantidad de una solución sólida de ZnO-TiO$_2$ con estructura similar al rutilo, y presenta una elevada superficie específica (275 m$^2$·g$^{-1}$) y alta actividad en la degradación de azul de metileno en presencia de radiación UV.

• A 375°C el tamaño de cristal de la fase anatasa aumenta lo que produce una disminución de la superficie y de la actividad catalítica del catalizador.

• A temperaturas comprendidas entre 375 y 450°C se produce la transformación del TiO$_2$ amorfo en pequeños cristales de anatasa, dando lugar a una disminución en el tamaño medio de los cristales de anatasa y un importante aumento en la actividad catalítica, que alcanza su valor máximo para la temperatura de calcinación de 450°C. El aumento posterior de la temperatura hasta 600°C produce la disminución de la actividad catalítica debido a la sinterización de los centros activos. A temperaturas superiores a 600°C la disminución de la actividad catalítica es más significativa debido a la transformación de la anatasa en rutilo.
El catalizador más activo de este trabajo duplica la actividad catalítica del fotocatalizador de referencia P25 TiO₂.

d) En lo que respecta a la producción de hidrógeno a partir de metanol utilizando los catalizadores de Ni₀.₇Zn₀.₃O soportados en mallas de acero:

- Ha sido posible sintetizar a temperatura ambiente una solución sólida Ni₀.₇Zn₀.₃O de alta superficie específica (100 m² g⁻¹) sobre la malla de acero.

- El catalizador es una solución sólida con defecto de oxígeno, que presenta la estructura cúbica de la sal de roca ligeramente distorsionada, cuya fórmula empírica es:

  \[\text{Zn}^{(2-\sigma)^+}_{0.30}\text{Ni}^{(2-\delta)^+}_{0.28}\text{Ni}^{2+}_{0.25}\text{Ni}^{3+}_{0.17}\text{O}_{1.085-0.15\sigma-0.14\delta}\]

- El óxido Ni₀.₇ZnO₀.₃O soportado sobre malla ha sido utilizado por primera vez como catalizador en la producción de hidrógeno a partir de metanol. Se ha comprobado que este catalizador muestra una actividad elevada en el proceso de reformado con vapor de agua en el rango 300-450°C, con conversiones cercanas al 100%. Sin embargo la selectividad del catalizador es baja, dando lugar a elevadas cantidades de CO.

- El catalizador Ni₀.₇ZnO₀.₃O es muy activo y selectivo en la reacción de descomposición de metanol en el rango 250-350°C, si bien se produce una ligera desactivación debido a la formación de depósitos de coque. Aun así, este catalizador destaca entre los más activos para este proceso.


Nanostructured metal oxides supported on SSWM


Nanostructured metal oxides supported on SSWM


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Nanostructured metal oxides supported on SSWM


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