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

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Abstract

In this work, high surface area stainless steel wire mesh-supported $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ catalysts ($x=0.01-0.20$) were successfully synthesised and tested for the photodegradation of methylene blue 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 , $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ solid solution, sacrificial template, photocatalysis, methylene blue

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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 TiO₂ [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:

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

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 TiO₂/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_xZn_{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 powdered 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], polyethylene 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. Materials and Methods

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 ($R_{\text{Cd/Zn}}$ 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 K α radiation ($\lambda = 0.15406$ 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-K α or Al-K α (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 C1s 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 re-introduced 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:

$$C_C = \frac{w_C}{V_0 (1 - bt)} \quad (3)$$

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

$$-\frac{dC_{MB}}{dt} = k C_C C_{MB}^n \quad (4)$$

where C_{MB} is the methylene blue concentration at a given time t , k is the reaction rate constant ($\text{mg}_{MB}^{1-n} \cdot \text{mg}_C^{-1} \cdot \text{L}^n \cdot \text{min}^{-1}$) 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:

$$C_{MB} = C_{MB,0} \exp \left\{ -k C_{C,0} \left(\frac{1}{b} \right) \ln \left[\frac{1}{1 - bt} \right] \right\} \quad (5)$$

whereas for $n \neq 1$:

$$C_{MB} = \left\{ C_{MB,0}^{1-n} - (1-n) k C_{C,0} \left(\frac{1}{b} \right) \ln \left[\frac{1}{1 - bt} \right] \right\}^{-\frac{1}{n-1}} \quad (6)$$

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:

$$A_C = \frac{1}{t_{0.5} C_{C,0}} \quad (7)$$

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 $n=1$:

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

whereas for $n \neq 1$:

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

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}):

$$\frac{1}{t_{0.5}^*} = A_c \cdot 333 \cdot \frac{C_{C,0}}{C_{C,0}^0} \quad (10)$$

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 ($80 \text{ m}^2 \text{ g}^{-1}$ for samples calcined at 210°C and $36 \text{ m}^2 \text{ g}^{-1}$ 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 (TiO_2 , CuO , CeO_2 , $\alpha\text{-Fe}_2\text{O}_3$) 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 pK_a 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 pK_a 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 (t_s) of 1 to 3 days. Figure 1 shows that, with this method, low substitution degrees ($\leq 6 \text{ mol.}\%$) were obtained for values of Cd to Zn molar ratios ($R_{\text{Cd/Zn}}$) 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 $R_{\text{Cd/Zn}}=5$ (Figure 1). Higher values of $R_{\text{Cd/Zn}}$ 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 approx.. 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 ($t_s=1$ day, $T=25^\circ\text{C}$), 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 $\text{m}^2 \text{g}^{-1}$ respectively, and remained practically unchanged from that of the ZnO-support calcined at 350°C (36 $\text{m}^2 \text{g}^{-1}$).

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. 2 b) 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.

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 $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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 $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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 $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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 .

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 $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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 $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, an illustration of which is provided in Figure 5. In this mechanism, the hydrolysis of a cadmium ion (or citrate-complexed cadmium ion) generates the intermediate species $\text{Cd}(\text{OH})^+$ and a proton in the vicinity of the highly polar ZnO template. ZnO is simultaneously etched by the proton to form $\text{Zn}(\text{OH})^+$. The $\text{Cd}(\text{OH})^+$ species reacts inside the crystal network position that is abandoned by the outgoing $\text{Zn}(\text{OH})^+$, 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 $\text{Zn}(\text{OH})^+ + \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O}$. 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 (Figure 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 $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{O}$, 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-K α radiation source to 7.1 mol% with a Al-K α radiation source. Both types of radiation interact with the outermost layers of the sample, though Al-K α 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 6 shows the DRS spectra corresponding to the SSWM-supported ZnO (calcined at 210°C) and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ materials. Considering the narrow band gap of the CdO materials, the optical absorbance region of SSWM-supported $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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 a greater photocatalytic efficiency could be achieved with $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ than with pure ZnO in the visible region.

Additional evidence of the red shift of Cd-doped samples is provided in Figure 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 3.13 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 $Cd_xZn_{1-x}O$ solid solution ($E_g=2.81$ eV).

3.2 Photocatalytic activity and photostability of SSWM-supported $Cd_xZn_{1-x}O$ 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 radiation there is a reorganization of the structure that causes the incorporation of CdO phase into the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ phase.

Figure 10 shows SEM images of the SSWM-supported $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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). Table 1 also includes, for comparison reasons, the intrinsic catalytic activity values of TiO_2 P25 and nanoparticulate ZnO obtained from the supported samples. It can be observed that the unsupported particles exhibit almost twice the activity of the supported catalysts.

3.3 Photocatalytic activity and photostability of SSWM-supported $\text{Cd}_x\text{Zn}_{1-x}$ 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. 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. It can be observed again that the unsupported samples almost double the intrinsic catalytic activity of the supported samples due to the better distribution of light (quantum yield) in the powder system. Under the experimental conditions of this work TiO_2 P25

exhibits catalytic activity as can be seen in Table 1, although it is lower than that of the ZnO particles obtained from the SSWM.

3.4 Conclusions

High surface area stainless steel wire mesh-supported $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ 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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Captions to Figures

Figure 1. Effect of $R_{\text{Cd/Zn}}$ on the degree of cadmium substitution

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

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

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

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

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

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

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

Figure 10. SEM images of SSWM-supported $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ samples with 0.0 (calcined at 210°C) and 5.3 mol% Cd before reaction (stage #0) and after 7 reaction stages (#7)

Figure 11. Methylene blue concentration decay curves under visible irradiation for SSWM-supported $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ catalysts

Tables

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

mol% Cd (#stage)	$1/t^*_{0.5} \times 10^2$ (min ⁻¹)		$A_C \times 10^4$ (mg _C ⁻¹ ·L·min ⁻¹)		ZnO losses (baseline corrected) (wt.%)	
	UV	Visible	UV	Visible	UV	Visible
0.0 (#1) ^a	6.69	0.35 (0.35) ^c	2.03	0.10	56.0	-0.1
0.0 (#7) ^a	0.61		0.94		77.6	
0.0 (#1) ^b		0.36 (0.36) ^c		0.11		-0.1
1.1 (#1)	1.69	0.42 (0.42) ^c	0.50	0.12	8.2	0.9
1.1 (#7)	0.99		0.30		18.3	
5.3 (#1)	1.92	0.38 (0.40) ^c	0.57	0.11	2.1	-0.1
5.3 (#7)	1.98		0.65		7.9	
20.3 (#1)	0.57	0.39 (0.49) ^c	0.17	0.12	0.0	-0.4
20.3 (#7)	0.72		0.24		3.6	
P25	19.28	0.70	5.79	0.21	-	-
ZnO NP ^d	12.72	0.77	3.82	0.23	-	-

^a Material calcined at 210°C.

^b Material calcined at 310°C

^c In brackets: values on a ZnO mass basis

^d Nanoparticulate ZnO scratched from the supported catalysts

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11