Photocatalytic activity of mesoporous α -Fe₂O₃ synthesized via soft chemistry and hard template methods for degradation of azo dye Orange II

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Abstract

The photocatalytic activities of two samples of α -Fe₂O₃ nanoparticles have been evaluated. One sample has been synthesized by a precipitation method with oxalic acid (soft method), and the other sample has been produced with the aid of a hard template (nanocasting with silica). The photodegradation of azo dye Orange II (**OII**), a model water pollutant, has been used as a benchmark reaction. It has been found that the synthetic method has a deep effect on the photocatalytic activity of the tested hematites, since sample created with the soft method is notably more photoactive than the one made with nanocasting procedure ($k = 8.9 \cdot 10^{-3} \text{ min}^{-1}$ vs $k = 1.6 \cdot 10^{-3} \text{ min}^{-1}$ respectively) when irradiated with UV light. Similar higher activity of the soft method sample has been found when visible light was used as excitation source ($k = 8.3 \cdot 10^{-3} \text{ min}^{-1}$ vs $k = 0.4 \cdot 10^{-3} \text{ min}^{-1}$ respectively). The enhanced surface adsorption of **OII** on the sample prepared via the soft methodology, which is ten times higher than the adsorption on sample prepared via the nanocasting path, could explain the better photocatalytic performance of the former material.

Keywords: α -Fe₂O₃; photocatalysis; azo dye Orange II; nanocasting; soft template.

Introduction

Nanoparticles have been used extensively as catalysts in an overwhelming number of reactions [1]. In the photocatalytic context, semiconductor nanoparticles of TiO_2 , ZnO and Fe_2O_3 have been used to carry out light induced transformations [2,3]. Photodegradation of pollutants is one of the most frequent applications of such nanoparticles [4,5,6]. In the case of Fe_2O_3 , a growing number of synthetic preparations have led to the development of materials with varied photocatalytic activities. A recent publication by the group of Chun reviews this area [7]. This oxide can be found in different crystalline structures such as wüstite (FeO), magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). This last form is the most stable, it is very cheap, as it is widely available in Nature, and has the valuable property of being an n-type semiconductor with a bandgap of ca. 2.2 eV [8] which has boosted the development of practical applications (from gas sensing [9] to energy capture [10] or water splitting [11]). Unlike other semiconductors used in photocatalysis absorbing mostly in the UV region of the solar spectrum, like TiO_2 and ZnO , hematite absorbs light up to 600 nm which makes this oxide a very attractive alternative to harness the light of the Sun [7].

We have described recently two types of hematite samples, prepared by soft chemistry (oxalic acid route) and hard template (nanocasting route with a silica template) [12]. The first procedure led to the formation of a mesoporous catalyst formed by aggregation of nanocrystals. The second method produced a mesoporous material with crystalline walls. The total oxidation of two volatile organic compounds (VOCs) like propane and toluene was studied and it was found that both iron oxides are effective for the removal of such VOCs and that the preparation methodology has a deep influence on the reaction mechanism. As a continuation of that work, and considering the promising properties of hematite in combination with light, we decided to compare the two types

of hematites above described (soft chemistry vs. hard template) in the photocatalytic context. For this study we employed a well-known water pollutant like azo dye Orange II (**OII**) (or Acid Orange 7) as target (Figure 1), since this molecule has been object of photodegradation by a number of semiconducting materials [13,14,15,16,17] including iron oxides [18,19,20,21,22]. It must be remarked that both the pollution of air by VOCs and the contamination of waters by textile dyes are two challenging environmental problems faced by current industrial societies and hence the importance of developing multi-purpose catalytic materials based on readily available sources like Fe_2O_3 .

Figure 1. Formula of Orange II.

Experimental

Materials and methods

Orange II was obtained from Sigma-Aldrich and was used as received. Water used in all the assays was ultrapure milli-Q grade. Irradiations with UV light were performed with a medium pressure Hg vapour lamp (125 W) inserted in an immersion photochemical reactor consisting of a double jacketed quartz well, refrigerated with circulating water, placed 3 cm away from the reaction flask. Irradiations with visible light were performed using two LED lamps (11W each, Lexman, $\lambda = 400\text{-}700$ nm emission output, Lexman

dimensions: 17 x 3,5 x 3,5 cm) placed 3 cm away from the reaction flask. The spectral output for this irradiation setup [23] involves the following main lines: 253.7 nm, 265.2 nm, 280.4 nm, 289.4 nm, 296.7 nm, 302.5 nm, 313.0 nm, 366.0 nm [24]. The irradiance of this setup was measured with a Delta Ohm HD 2302.0 photoradiometer (400-1.050 nm) resulting an average value of 156 W/m^2 . Dark adsorptions of the dye and kinetic measurements of the photoreactions were performed spectrophotometrically using a Hewlett-Packard 8453 apparatus. All the measurements were done at 20°C (at such temperature the concentration of dissolved oxygen is $2.9 \cdot 10^{-4} \text{ M}$, according to the literature [24]).

Preparation of photocatalysts

Samples **S** (for soft) and **H** (for hard) of hematite $\alpha\text{-Fe}_2\text{O}_3$ were synthesized via the soft chemistry (oxalic acid) and hard template (nanocasting) methods, respectively. The mesoporous catalyst via the soft template, **S**, was prepared by mixing in water iron nitrate and oxalic acid (molar ratio= 1:5) and heating at 80°C until water is evaporated. The paste was introduced in a furnace and left overnight at 120°C. Finally the solid was calcined in air for 2 h at 300°C and then for 2h at 500°C. The catalyst **H**, was prepared by a nanocasting route using mesoporous silica with a KIT-6 structure as a hard template. The replica of iron oxide was synthesized by dispersing the KIT-6 in EtOH with Fe-nitrate and calcined in air at 500°C. Then, the silica template was removed by using a NaOH solution. A detailed description of the synthetic procedures and a comprehensive chemical characterization has been given elsewhere [12]. For comparative purposes a sample of commercial origin from Panreac (named **R** for reference) was included in the study.

Catalyst characterisation

Fe₂O₃ samples were characterized by N₂ adsorption at -196 °C, using a Micromeritics ASAP 2020 apparatus. Samples were degassed at 150 °C prior to analysis. From these data, the following textural parameters were calculated: multipoint Brunauer–Emmet–Teller (BET) surface area (SBET) was estimated over the relative pressure range from 0.05 to 0.25 and both mesopore volume (VT) and mean pore size (d) were calculated applying the Barrett–Joyner–Halenda (BJH) method to the adsorption branch of the isotherm. Structural and morphological characterization of the catalysts was carried out by Transmission Electron Microscopy (TEM), high resolution TEM (HRTEM) and selected Area electron diffraction (SAED) by using a FEI Field Emission Gun (FEG) TECNAI G2 F20 S-TWIN microscope operated at 200 kV. Powder X-Ray diffraction (XRD) was used to identify the crystalline phases present in the samples. A Bruker D8 Advance diffractometer with a monochromatic Cu K α X-ray source, operated at 40 kV and 40 mA, was used. The experimental patterns were calibrated against a silicon standard and the crystalline phases were identified by matching the experimental patterns to the JCPDS powder diffraction file database. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Axis ultra DLD photoelectron spectrometer using a non-monochromatized Mg K α X-ray source ($h\nu$ = 1253.6 eV). An analyser pass energy of 50 eV was used for survey scans and 20 eV for detailed scans. Binding energies were referenced to the C1s peak from adventitious carbonaceous contamination, assumed to have a binding energy of 284.8 eV. XPS data were analysed using Casa XPS software. All the peaks of the corrected spectra were fitted with a Gaussian–Lorentzian shape function to peak fit the data. Iterations were performed using the Marquardt method. Relative standard deviations were always lower than 1.5%. Diffuse reflectance UV–Vis spectra were collected on a UV-2600 Shimadzu equipped with a “Praying Mantis” attachment from Harrick. The sample cell was

equipped with a heater unit, a thermocouple, and a gas flow system for in situ measurements. The samples were dehydrated in situ in dry air at 150°C for 30 min.

Photocatalytic procedures

Samples of **S**, **H** or **R** (15 mg) were suspended in 50 mL of milli-Q water containing $2.2 \cdot 10^{-5}$ M of the dye Orange II. No modification of pH was done in order to avoid external influence on the systems object of study. Also no additives such as hydrogen peroxide or anions were added, for the same reason. In the future, a comprehensive study could be done considering the effect of additional parameters on the photochemical performance of these oxides. The only two variables considered in this study are the synthetic procedure (oxalic or nanocasting route) and the excitation source (UV or visible light). Thus, the suspensions of hematite samples in the presence of **OII** were first allowed to equilibrate overnight and then it was calculated the degree of adsorption of the dye on the surface of the catalyst by means of absorption spectroscopy. The equilibrated suspensions were irradiated using either UV (Hg vapour lamp) or visible light (LED lamps). Aliquots (1 mL) of the irradiated samples were removed from the flask, filtered and analysed by UV-vis spectrophotometry. The kinetics of the photodegradation of **OII** was monitored at 0, 15, 30, 45 and 60 min. The absorption at the maxima (485 nm) was fitted to a pseudo first order kinetic model (equation 1). In equation 1 c is the concentration of **OII** at a certain time, c_0 is the initial concentration of **OII**, t is the irradiation time and k is the observed kinetic constant. Taking into account the low concentrations used it has been considered that the ratio of absorbances (A/A_0 , initial A_0 and at a certain time A) is equal to the ratio of concentrations during the experiment ($c/c_0 = A/A_0$).

$$\text{Eq.1} \quad \ln c/c_0 = \ln A/A_0 = -k \cdot t$$

Results and discussion

Irradiations of suspensions of hematite samples prepared by the soft (**S**) and hard (**H**) methods led to dramatically different results. Also a third sample (**R**) from a commercial source and non-nanometric in nature was used as reference for comparative purposes. The oxide prepared via the oxalic acid method (**S**) resulted much more photoactive for the photodegradation of **OII** than the one prepared via the silica template procedure (**H**). As it can be seen in Figure 2a, the bleaching of the absorption of **OII** under UV irradiation (mainly 254 nm) in the presence of **S** is much faster than the reaction in the presence of **H** under the same irradiation conditions (Figure 2b). Reference sample **R** showed negligible photochemical activity (Figure 2c). The kinetic analysis of the data afforded the following degradation pseudo first order constants: $k_{UV}(S) = 8.9 \cdot 10^{-3} \text{ min}^{-1}$, $k_{UV}(H) = 1.6 \cdot 10^{-3} \text{ min}^{-1}$, $k_{UV}(R) < 10^{-4} \text{ min}^{-1}$. On the other hand, when visible light (400-600 nm) was employed, the kinetics were very similar, with **S** being the unique material showing photocatalytic activity (Figures 2d, 2e and 2f). In this case the kinetic constants were $k_{Vis}(S) = 8.3 \cdot 10^{-3} \text{ min}^{-1}$, $k_{Vis}(H) = 0.4 \cdot 10^{-3} \text{ min}^{-1}$, $k_{Vis}(R) < 10^{-4} \text{ min}^{-1}$. In Figure 3 all the kinetic data are compiled for a better comparison.

Figure 2. Light-induced bleaching of **OII** ($2.2 \cdot 10^{-5} \text{M}$) in the presence of $\alpha\text{-Fe}_2\text{O}_3$: sample **S** (a, d); sample **H** (b, e); sample **R** (c, f). Excitation source is UV light (a, b and c) or visible light (d, e, f).

Figure 3. Kinetics of the light-induced bleaching of **OII** ($2.2 \cdot 10^{-5} \text{M}$) in the presence of $\alpha\text{-Fe}_2\text{O}_3$. UV light irradiation of samples **S**, **H** and **R** corresponds to S.UV, H.UV and R.UV, respectively; Visible light irradiation of samples **S**, **H** and **R** corresponds to S.VIS, H.VIS and R.VIS, respectively.

The observed behaviour highlights the importance of the preparation method in the catalytic activity of the material. Previously it was shown that hematite prepared via the soft method (**S**) was more efficient for the total oxidation of propane than the material prepared by nanocasting (**H**). The opposite was found for the oxidation of toluene,

being **H** more effective than **S**. Now it has been found that the difference is even more dramatic from the photocatalytic point of view, since **S** is at least six times more photoactive than **H**, and the activity of **R** is negligible.

The photocatalytic activity of **S** is comparable to the reported behaviour of other iron oxides. Comparison of kinetic values obtained using different experimental setups is always approximate, but at least afford a qualitative view about the performance of the material. Thus, our α -Fe₂O₃ prepared by the oxalic acid method is able to degrade **OII** at a rate of $8.9 \cdot 10^{-3} \text{ min}^{-1}$ under UV light excitation and $8.3 \cdot 10^{-3} \text{ min}^{-1}$ under visible light excitation and these values lie within the same range of activities described by the group of Xu for the degradation of **OII** using several iron oxides and hydroxides (between 1 and $10 \cdot 10^{-3} \text{ min}^{-1}$ depending on the reaction conditions [20]). **OII** has been also photodegraded using other catalytic materials, for instance TiO₂ nanoparticles [14] ($k_{\text{UV}} = 1.67 \cdot 10^{-2} \text{ min}^{-1}$, $k_{\text{vis}} = 8.5 \cdot 10^{-3} \text{ min}^{-1}$), CdS nanoparticles [15] ($k_{\text{UV}} = k_{\text{vis}} = 10^{-2} \text{ min}^{-1}$) and TiO₂ nanotubes [16] ($k_{\text{UV}} = 1.58 \cdot 10^{-2} \text{ min}^{-1}$). It must be remarked that our result could be improved if adjusting some parameters, not taken into account in this preliminary investigation, which have been demonstrated to have a deep impact on the photocatalytic activity such as pH, addition of H₂O₂ or additives like silver or fluoride [20].

In order to explain the differences in photoactivity of the tested samples it must be pointed out that the dark adsorption of the dye in the surface of the catalyst is notably different. Thus, **S** is capable to adsorb up to 50.2 μmol of **OII** per g of iron oxide, whereas **H** adsorbs only 5.0 $\mu\text{mol/g}$ and **R** less than 1.0 $\mu\text{mol/g}$. The adsorption capacity of hematite synthesized with the soft chemistry methodology lies within the range of loadings reported for other iron oxide materials (ca. 10-100 $\mu\text{mol/g}$ depending on the preparation method) [20,21,22]. This differential adsorption could be the ultimate

reason for the observed photoactivity. It could be hypothesized, in principle, that there is a correlation between adsorption capacity and specific surfaces areas, but this correlation does not exist since the most active material **S** has a specific surface intermediate ($71 \text{ m}^2/\text{g}$) between **H** ($208 \text{ m}^2/\text{g}$) and **R** ($3.3 \text{ m}^2/\text{g}$). See Table 1 for a compilation of data.

Table 1. Chemical characterization and photocatalytic activity of hematite samples **S**, **H** and **R**.

Sample	Si/Fe ^(a)	S_{BET} ^(b) (m^2/g)	V_{BJH} ^(c) (cm^3/g)	d_{BJH} ^(d) (nm)	E_g ^(e) (eV)	$Q^{24\text{h}}$ ^(f) ($\infty\text{mol/g}$)	k_{UV} ^(g) / 10^{-3} (min^{-1})	k_{VIS} ^(h) / 10^{-3} (min^{-1})
S	<0.001	71	0.20	17	2.19	50.2	8.9	8.3
H	0.1	208	0.38	10	2.32	5.0	1.6	0.4
R	<0.001	3.3	0.01	n.d. ⁽ⁱ⁾	2.23	<1.0	<0.1	<0.1
Control ^(j)	-	-	-	-	-	-	<0.1	<0.1

(a) Ratio Si/Fe determined by XPS; (b) specific surface area; (c) mesopore volume calculated by the BJH method; (d) mean pore size calculated by the BJH method; (e) Energy gap (DR-UV); (f) Adsorption capacity of OII after 24h; (g) observed kinetic constant upon irradiation with UV light (R^2 for S.UV=0.9807; R^2 for S.Vis=0.9880) ; (h) observed kinetic constant upon irradiation with visible light (R^2 for H.UV=0.9625; R^2 for H.Vis=0.9567); (i) not determined; (j) control irradiation of OII without photocatalyst.

It has been reported that electrostatic attraction between negative azo dyes and several materials is the driving force for the adsorption process [18,19]. According to this fact, electrostatic attraction seems to be disfavoured in hematite **H**, despite its relevant surface area. It can be assumed that the presence of negative charges due to the existence of some remaining silica at the surface of the Fe_2O_3 nanoparticles, which has not been removed during the template etching step, could play some undesirable role. In line with this assumption, XPS data shows that a Si/Fe ratio of 0.1 is found for the **H** sample. Likewise, whilst the O1s spectrum only showed two surface oxygen species for **S** sample (Figure 4) at 529 eV and 531 eV, corresponding to Olatt (Fe–O–Fe lattice oxygen) and Oads species [22] (oxygen vacancies and also surface adsorbed oxygen, hydroxyl groups and carbonates), respectively; the **H** sample showed the presence of

two additional contributions at 530 and 532 eV, which can be related to oxygen binding with iron in different coordination or aggregation, or even to Fe–O–Si and Si–O–Si oxygen species [25], see Figure 4.

The materials were optically characterized by means of Diffuse Reflectance (DR) spectroscopy (not shown) and the energy gaps calculated from the DR spectra were not different enough to justify such a different photocatalytic activity ($E_g(\text{S}) = 2.19$ eV; $E_g(\text{H}) = 2.32$ eV and $E_g(\text{R}) = 2.23$ eV). All the values are in agreement with the literature value of 2.2 eV. It must be noted that the group of Xu [20,21] reported a careful study showing the influence of the sintering temperature on the photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ but did not found any correlation with the energy gaps (all with the 2.1-2.2 eV range).

Figure 4. O1s XPS spectra and TEM pictures of the S and H samples

Two mechanisms could be invoked, in principle, to explain the photodegradation of **OII**. One approach involves the well-known paradigm described in detail in the literature for semiconducting materials, i.e. the generation of an electron-hole (e^-/h^+) pair in the nanoparticle leading to the formation of reactive species such as hydroxyl radical ($\cdot\text{OH}$) or superoxide radical anion (O_2^-) [7]. In this case the formation of superoxide is very unlikely to occur since, as Kormann et al. have shown [26] the oxygen molecule is not reduced on hematite particles due to energetic reasons. There is another more plausible mechanistic explanation involving the molecule of **OII** adsorbed on the surface of the oxide: excitation and photodegradation of a ligand(dye)-to-metal charge transfer (LMCT) within a surface complex of **OII** and iron oxide has been demonstrated by the group of Kiwi [18,19]. This explanation is in accordance with the enhanced photoactivity of iron oxide **S** here described, i.e. the only sample of $\alpha\text{-Fe}_2\text{O}_3$ capable of strong dye adsorption.

Conclusion

In summary, it has been shown that the synthetic method to obtain $\alpha\text{-Fe}_2\text{O}_3$ is a key factor to produce materials with photocatalytic properties. The soft chemistry procedure involving precipitation with oxalic acid yields a photocatalyst capable to remove the pollutant Orange II from aqueous solutions using UV or visible light, at a rate of $8.9 \cdot 10^{-3} \text{ min}^{-1}$ and $8.3 \cdot 10^{-3} \text{ min}^{-1}$, respectively. On the contrary, the methodology employing a silica hard template (nanocasting) yields a material with much less photocatalytic activity. Surface adsorption on the photocatalyst has been identified as key factor to account for the differences. This study confirms the importance of the synthetic conditions for the preparation of photocatalysts with optimal properties. Hematite

prepared via soft chemistry methodology can be considered as a dual catalyst useful for environmental remediation, either thermally for VOCs like propane or toluene, as reported earlier, or photochemically for azo dyes like Orange II.

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Conflict of Interest Statement

All the authors declare there is not any competing financial interest.

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