Journal of Molecular Catalysis A: Chemical 180 (2002) 193–200

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Occurrence and prevention of photodissolution at the phase junction of magnetite and titanium dioxide

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Received 23 August 2001; accepted 30 October 2001

Abstract

A stable magnetic photocatalyst was prepared by coating a magnetic core with a layer of photoactive titanium dioxide. A direct deposition of titanium dioxide onto the surface of magnetic iron oxide particles proved ineffective in producing a stable magnetic photocatalyst, with high levels of photodissolution being observed with these samples. This observed photodissolution is believed to be due to the dissolution of the iron oxide phase, induced by the photoactive the titanium dioxide layer due to electronic interactions at the phase junction in these magnetic photocatalysts. The introduction of an intermediate passive SiO_2 layer between the titanium dioxide phase and the iron oxide phase inhibited the direct electrical contact and hence prevented the photodissolution of the iron oxide phase. The magnetic photocatalyst is for use in slurry-type reactors from which the catalyst can be easily recovered by the application of an external magnetic field. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photodissolution; Magnetic photocatalyst; Titanium dioxide; Iron oxide

1. Introduction

Titanium dioxide mediated photocatalytic oxidation offers potentially a facile and cheap method for removing inorganic and organic pollutants from waste waters. It has been an area of intense interest for the past two decades, particularly for removing organic compounds as they can be completely mineralised under photocatalytic oxidation. The photocatalyst has been used either as a suspension or immobilised onto inert substrates such as glass or sand for destroying a plethora of hazardous chemicals in waters. Whilst it obviates the need for separating the photocatalyst from the water after treatment, the immobilised phase system has the disadvantages of low mass transfer and the occasional need for physically coating the surface after prolonged use. For large scale of water treatment, photocatalytic systems using suspension would offer significant advantages if a way could be found for the easy removal of the photocatalyst after treatment.

For the past few years, we have been working on the synthesis of stable magnetic titanium dioxide photocatalyst particles. The impetus for this is that

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PII: S1381-1169(01)00429-0

the photocatalyst, used as a suspension, can be easily separated after treatment. The photocatalyst, once separated, can be reused because of its regenerative property under photocatalytic reaction.

This communication reports a photodissolution phenomenon, we found in coating an anatase form of titanium dioxide directly onto magnetite. Electronic interactions are postulated here to occur between the titanium dioxide coating and the iron oxide core. To overcome this, a passivation layer is required. A stable form of magnetic titanium dioxide has now been patented by this group.

2. Experimental

The preparation of the magnetic photocatalyst particles entailed the coating of a magnetic iron oxide core with a layer of photoactive titanium dioxide. These samples are referred to as TiO_2/Fe_3O_4. The coating process was carried out using the sol–gel technique involving the hydrolysis of titanium butoxide (TBOT) onto the surface of 4–10 nm magnetite seed particles (with a surface area of $86\,m^2/g$). A more detailed description of the preparation technique is given in earlier published work [1]. The preparation of the modified photocatalyst particles has been described in detail elsewhere [2]. The modification involved introducing an intermediate passive SiO_2 layer between the iron oxide core and the photoactive titanium dioxide layer. This was achieved by firstly encapsulating the magnetite particles within a silica shell by following the method described by Philipse et al. [3]. These silica coated magnetite particles were subsequently used as seed particles, and coated with a layer of titanium dioxide by following the procedure earlier described. These samples are referred to as $TiO_2/SiO_2/Fe_3O_4$.

Single-phase TiO_2 particles were prepared following the procedure described above in the absence of the magnetite particles.

The deposited titanium dioxide was amorphous in nature and thus a heat treatment step was required in order to transform it into a crystalline phase (predominantly anatase). The heat treatment was carried out at 450 °C in a tubular furnace and applied for 3 h under an air atmosphere.

The photoactivity of a suspension of the prepared particles was assessed using a system consisting of a spiral, re-circulating photoreactor with a near-UV illumination source (wavelength ∼350 nm) and a conductivity monitor for measuring carbon dioxide. The photooxidation of 25 μg of carbon, added as sucrose, was used as the test reaction. A catalyst loading of 0.2 g/l was used. The pH of the catalyst suspension was adjusted to 3.5 by adding perchloric acid. The photoactivity of the prepared particles was compared to that of the commercially available photocatalyst, Degussa P25, under the same conditions.

The photodissolution tests were carried out by recovering the photocatalyst suspension after circulation through the reactor, in the presence of sucrose, under illumination for 30 min. The supernatant of the catalyst suspension was collected and filtered through a 0.2 μm micropore filter, and analysed for Fe ions using AAS.

3. Results

3.1. Particle preparation

The direct coating of titanium dioxide onto the surface of the magnetite particles resulted in the formation of an aggregate of magnetite particles surrounded by a matrix of titanium dioxide. These TiO_2/Fe_3O_4 particles are shown in Fig. 1. Fig. 1(a) is a STEM image, whereas Fig. 1(b) and (c) are X-ray-mapping images taken using an energy dispersive X-ray (EDX) spectrometer. These images show the distribution of the elements Ti and Fe in the sample.

The modified photocatalyst was made up of three components. A TEM micrograph of a typical sample of the modified photocatalyst ($TiO_2/SiO_2/Fe_3O_4$) is shown in Fig. 2. From this TEM micrograph, it can be seen that the thickness of the titania shell was approximately 100–150 nm. Since the deposition of the SiO_2 coating resulted in a cluster of the nanosized magnetite particles encapsulated in a silica matrix, it is difficult to estimate the thickness of the SiO_2 shell.

The magnetic properties of both the two component (TiO_2/Fe_3O_4) particles and the three component particles ($TiO_2/SiO_2/Fe_3O_4$) particles were still present after the heat treatment. However, due to a colour change of the samples from light brown to orange, it is assumed that the magnetite particles have been oxidised to maghemite during the heat treatment. A

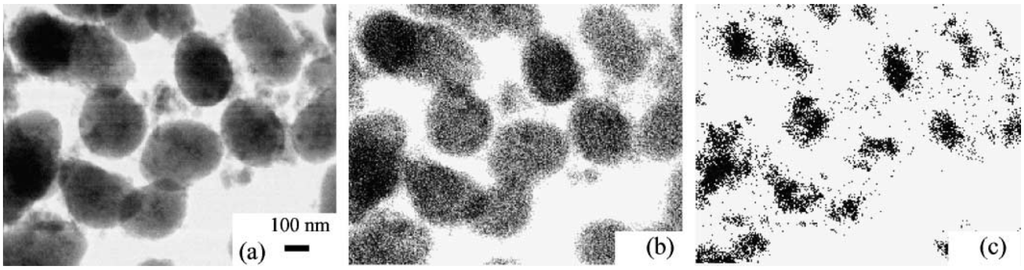

Fig. 1. (a) STEM image of TiO_2/Fe_3O_4 particles; (b) corresponding Ti X-ray map; (c) corresponding Fe X-ray map.

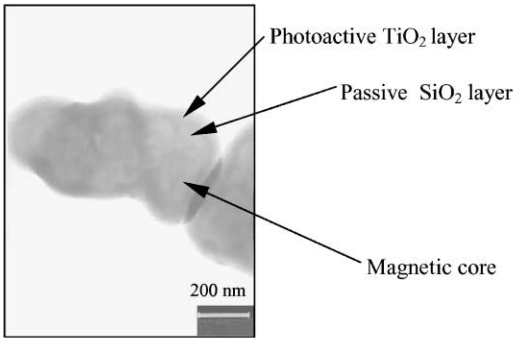

Fig. 2. TEM micrograph of the modified $Fe_3O_4/SiO_2/TiO_2$ photocatalyst.

qualitative XRD analysis confirmed that anatase was the main phase present in all the prepared samples.

3.2. Photoactivity

Fig. 3 shows the results of the photoactivity testing. This plot shows the amount of carbon dioxide generated as the reaction proceeded. A description of the samples tested is given in Table 1. These photoactivity results allowed two main observations to be made. Firstly, the activity of the particles consisting of titanium dioxide directly deposited onto an iron oxide core (sample A) was lower than that of single-phase TiO_2 samples (either prepared TiO_2 or Degussa). Secondly, a remarkable improvement in photoactivity was achieved with the modified photocatalyst (sample C), in which direct contact between the TiO_2 and the iron oxide phase was prevented.

3.3. Photodissolution

The stability of the magnetic particles (i.e. iron oxides) was studied by measuring the dissolution and photodissolution of the iron oxides. The results are summarised in Fig. 4. The results are presented as the percentage of the iron oxide dissolved, which is the ratio of the Fe ions in the solution to the amount of Fe present in the coated particles. A back calculation was performed based on the known catalyst composition and catalyst loading in suspension to derive the total amount of iron present in the catalyst suspension. Since some of the Fe ions would have remained adsorbed on the surface of the particles, the amount of Fe in the solution measured by AAS is in fact an estimate of the minimum amount dissolved. When the

Table 1
Samples used in photoactivity tests

Sample code	Sample details	Composition mass (%)	Mean diameter (nm)	Surface area (m^2/g)
P25	Degussa P25	100% TiO_2	249 ± 3	42 ± 1
Sample A	Coated colloidal magnetite, calcined at 450 °C for 3 h	81 ± 6% TiO_2, 19 ± 6% Fe_3O_4	411 ± 26	60 ± 1
Sample B	Single-phase TiO_2, calcined at 450 °C for 3 h	100% TiO_2	323 ± 29	38 ± 3
Sample C	Modified photocatalyst, calcined at 450 °C for 3 h	57 ± 5% TiO_2, 29 ± 5% Fe_3O_4 (the remainder is the passive component)	∼1000	29 ± 1

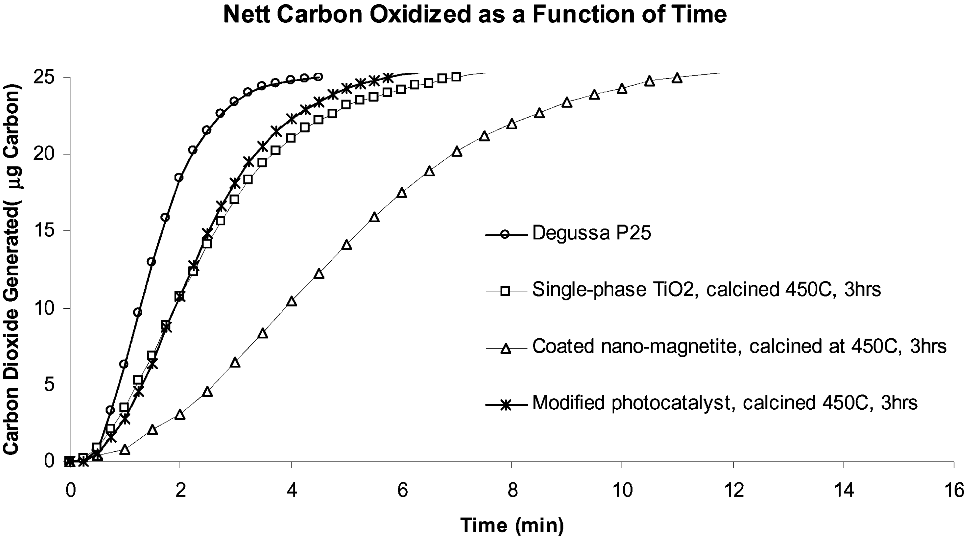

Fig. 3. Photoactivity results—a total of 25 µg of carbon was mineralised to CO_2.

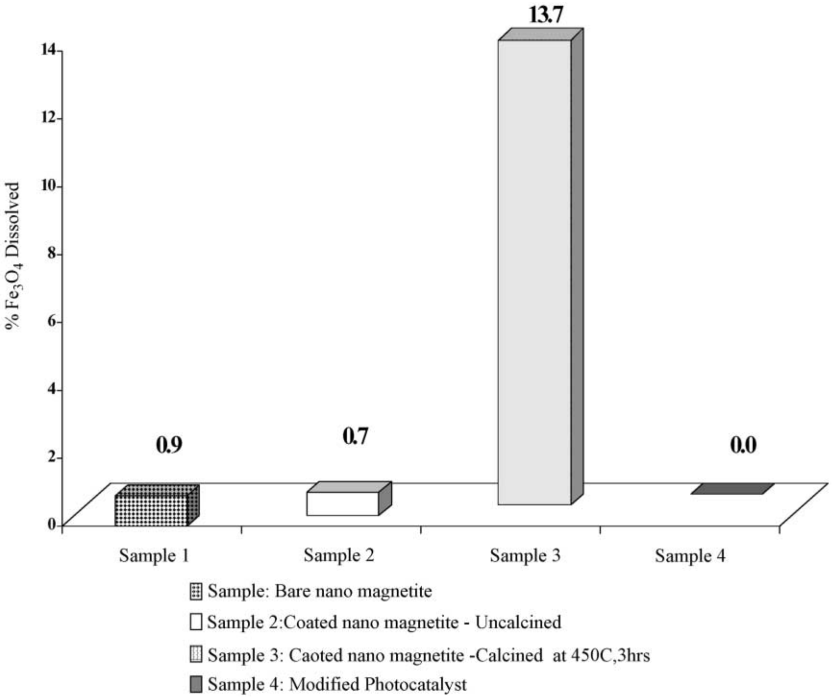

Fig. 4. Extent of photodissolution—quantitatively represented as the amount of Fe_3O_4 dissolved as a percentage of the amount present in the original sample.

photodissolution levels were severe (as observed in sample 3), physical evidence of photodissolution was provided by TEM examination, which revealed the "holes" in the photocatalyst particles (where the iron oxide core had been).

4. Discussion

As stated previously this research aims to produce a magnetic photocatalyst with enhanced separation properties from slurry photoreactor systems. The approach of coating a photoactive layer (titanium dioxide) directly onto the surface of a magnetic core (magnetite) failed to achieve the goal of preparing this novel photocatalyst with the desired properties of being photoactive, magnetic and stable. The results showed that the direct contact between the titanium dioxide phase and the iron oxide phase was responsible for both the low photoactivity and the photodissolution of the prepared photocatalyst.

This conclusion was made from the observed low photoactivity of sample A in Fig. 3 (and sample 3 in Fig. 4) when compared to that achieved with single-phase TiO_2, as well as the observed high levels of photodissolution this sample suffered from upon illumination with near UV light. The remarkable improvement in photoactivity and the negligible levels of photodissolution, which were observed once the direct contact between the TiO_2 and the iron oxide phases was prevented as in sample C in Fig. 3 (equivalent to sample 4 in Fig. 4), confirmed this postulation.

The low photoactivity of iron oxide/titania systems (in particular hematite/titania systems) has been observed by a number of workers [4–7]. In these systems it was shown that the electronic interactions between these two semiconductors were the major contributing factor for the reduced photoactivity. These observations can be extended to explain the TiO_2/magnetite and TiO_2/maghemite systems. It is important to note that while the titanium dioxide layer in the coated particles underwent a phase transformation during the heat treatment, the iron oxide core was also oxidised (due to the porosity of the coating). Thus depending on the different calcination conditions, the iron oxide will be present as magnetite, maghemite or hematite or a mixture of these phases.

Table 2
Conduction band potentials, valence band potentials, and band gap energies of titanium dioxide (TiO_2), magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) at pH 3.5

	TiO_2	Fe_3O_4	γ-Fe_2O_3	α-Fe_2O_3
Conduction band potential (V)	−0.04	0.17	0.29	0.21
Valence band potential (V)	3.16	0.27	2.59	2.42
Band gap energy (eV)	3.20	0.10	2.30	2.20

Electronic interactions occur at the point of contact of the different phases (heterojunction), leading to the transfer of charge carriers across this junction, when two or more semiconductors are in contact. The basic concept is that the photogenerated charge carriers in the excited semiconductor can be transferred to the second semiconductor if this is thermodynamically feasible.

When examining the relative positions of the valence band and the conduction bands in Table 2, it is evident that it is in fact thermodynamically feasible for the generated electrons in titanium dioxide to be transferred to the lower lying conduction band of any the iron oxides phases present, while the photogenerated holes may also be transferred to the upper lying valence bands of the iron oxides. The narrower bandgap of the iron oxides is thought to lead to an increase in the incidence of electron-hole recombination, lowering the photoactivity, while the continuous hopping between Fe^{2+} and Fe^{3+} in the magnetite lattice has been reported to enhance electron–hole recombination [8]. The lower oxidising power and reducing power of the of the available electrons and holes once transferred to the iron oxide phase, as suggested by Litter and Navio [9], can also be translated into lower photoactivity.

The photodissolution of the iron oxide phase puts forward the possibility of the occurrence of competing reactions with the oxidation reaction of sucrose. The main competing reaction of concern is the oxidation of the dissolved Fe^{2+} back to Fe^{3+}. The possible occurrence of this back reaction has been suggested by a number of people and is thought to involve the Fe^{2+} competing with the sucrose molecule for the photogenerated holes (or $OH^{\bullet}$) [6,10–13]. These back reactions may hinder the oxidation of the organic (even though the photodissolution mechanism itself might in fact lead to an enhanced charge separation).

The photodissolution results enabled us to make a very important conclusion regarding the driving force behind the photodissolution observed. It is clear that the stability of the coated particles is highly dependent on the nature of the titanium dioxide. This conclusion was made upon comparison between the levels of photodissolution of uncoated magnetite samples (sample 1), coated-uncalcined samples (sample 2), and coated-calcined samples (sample 3). While both the bare magnetite particles and the uncalcined-coated samples exhibited minimal photodissolution, the coated-calcined samples, made up of iron oxide in direct contact with a crystalline titanium dioxide phase, showed very high photodissolution levels.

The narrow band gap of magnetite (0.1 eV) [14] and the existence of a favourable environment for electron-hole recombination in its lattice [8] might explain the low levels of photodissolution of the bare magnetite particles. The low photodissolution of the coated-uncalcined samples can be explained in terms of the amorphous nature of the titanium dioxide coating deposited during the coating step. These TiO_2 particles do not have a well-defined crystal structure, and, therefore, cannot be activated by UV light.

It is clear from our results that it is the heat treatment step which is leading to the formation of a system which is highly unstable. Three possible sources have been identified as being likely to be responsible for the high levels of photodissolution encountered in the heat-treated samples.

The first possible source is the photodissolution of Fe ions which had diffused into the TiO_2 coating during the heat treatment step. The second possible source is the photodissolution of interfacial Ti–Fe oxides compounds formed during the heat treatment step due to a reaction between the titanium dioxide and the iron oxide phases. Finally, the third possible source is the direct photodissolution of the iron oxide core itself.

Fe ion diffusion into the TiO_2 matrix during the heat treatment of TiO_2 and iron oxide phases in contact, leading to an Fe-doped TiO_2 lattice, has been reported often [16–18]. The dissolution of these Fe-doped TiO_2 systems upon illumination with UV light has also been frequently encountered [7,10,16–21]. As we had reported elsewhere [22], characterisation of the microstructure of the TiO_2/Fe_3O_4 particles we prepared, using an elemental X-ray mapping technique, was inconclusive regarding the diffusion of Fe ions into the titanium dioxide coating. However, from the photoactivity results as well as comparison with what has been reported in the literature regarding Fe-doped TiO_2 systems, there is strong evidence to suggest that Fe ion diffusion into the TiO_2 matrix had also occurred in our system during the heat treatment step. Therefore, the photodissolution of Fe ions from an Fe-doped TiO_2 matrix can be considered as a likely source of the photodissolution observed.

In the earlier publication [22], we also reported that we found no XRD evidence to suggest the presence of an interfacial Fe/Ti mixed oxide (such as pseudobrookite) in our system. Such compounds are produced by a reaction between TiO_2 and the iron oxide during excessive heat treatment [5,6,8,10,15,20,23]. Even if this phase were indeed present, its photodissolution is not expected to contribute greatly to the high levels of photodissolution observed in our systems, due to its high stability [9]. Thus the observed photodissolution cannot be attributed to the presence of such compounds.

We believe that the photodissolution is primarily due to the photodissolution of the core iron oxide phase itself. This is strongly supported by the TEM analysis of the heat-treated samples after the photodissolution had occurred. This analysis revealed the presence of ‘holes’ found in the particles where the iron oxide core had been but had dissolved after the UV illumination (Fig. 5). It is also believed that the observed photodissolution is in fact induced-photodissolution, occurring due to electronic interactions between the titanium dioxide coating and the iron oxide core. This is postulated to involve the photogenerated electrons in the titanium dioxide nanocrystals being transferred into the lower lying conduction band of the iron oxide core. It is these electrons which are leading to the dissolution of the iron oxide core with Fe^{2+} and Fe^{3+} ions being formed and migrating to the solution. The negligible photodissolution levels (below the detection limit of the AAS) of the modified photocatalyst (the three-layer composite) confirmed our postulation regarding the occurrence of this induced photodissolution. By placing an electronic barrier (the passive silica layer) between the titanium dioxide and the iron oxide phase, we were able to prevent the injection

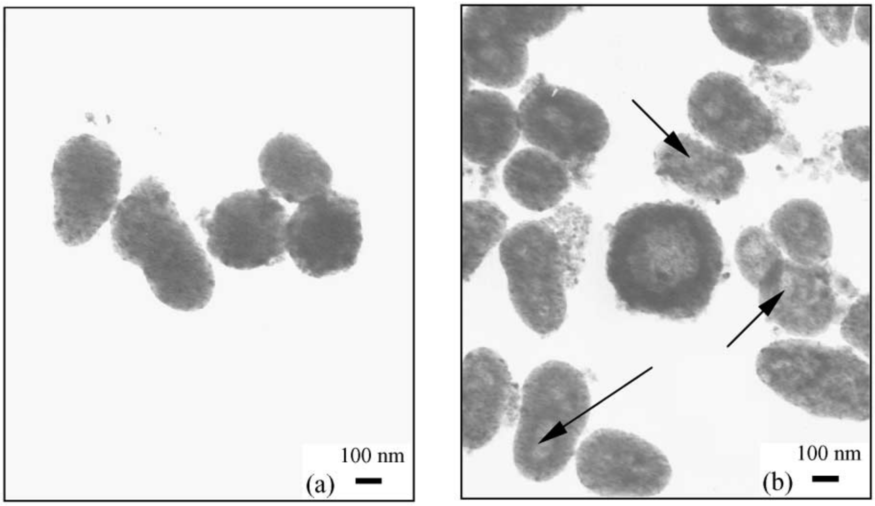

Fig. 5. TiO_2/Fe_3O_4 particles before (a) and after (b) the photoreaction. The arrows indicate the 'holes' observed in the catalyst particles after the photodissolution phenomenon.

of the reducing electrons into the iron oxide phase, thereby protecting it against photodissolution.

The remarkable improvement in the photoactivity observed in the modified sample can also be attributed to the presence of the silica layer. The silica layer is believed to have inhibited the diffusion of Fe ions into the TiO_2 coating, therefore, preventing any detrimental effects this can have on the performance of the TiO_2 photocatalyst [5,6,8,10,20,23,24]. By limiting the electronic interactions at the titania/iron oxide heterojunction, the silica layer is also believed to have prevented the iron oxide from acting as an electron-hole recombination centre. This also translates into a higher photoactivity.

5. Conclusions

Our initial investigation into the preparation of a magnetic photocatalyst by directly coating titanium dioxide onto the surface of magnetite particles proved unsuccessful in terms of producing a stable and active photocatalyst. Both the low activity and the alarming photodissolution were seen to be due to electronic interactions between two semiconductors in contact. By modifying the catalyst and introducing an intermediate passive SiO_2 layer between the two semiconductors, thus preventing any electronic interactions, a catalyst, which was stable, magnetic and photoactive, was produced. The catalyst has enhanced separation properties and can be easily recovered from a slurry with the application of an external magnetic field.

To possess high magnetic properties, the insulation layer and the photoactive layer (TiO_2) of the catalyst have to be as thin as possible. However, a minimum insulation thickness would exist, below which the protection from photodissolution will not suffice. At the same time, an optimum thickness of the photoactive layer will exist below which maximum photodegradation rates cannot be achieved. Hence, future work will involve optimising the activity, stability and the magnetic properties of this novel photocatalyst.

References

[1] D. Beydoun, R. Amal, G. Low, S. McEvoy, in: Proceedings of the World Congress on Particle Technology, Vol. 3, Brighton, UK, 6–9 July 1998, 1998, Paper No. 385.
[2] D. Beydoun, R. Amal, G. Low, S. McEvoy, Provisional Patent (1999) 9722.
[3] P. Philipse, M.P.B. van Bruggen, C. Pathmamanoharan, Langmuir 10 (1994) 92.
[4] R.I. Bickley, T. Gonzalez-Carreno, A.R. Gonzalez-Elipe, G. Munuera, L. Palmisano, J. Chem. Soc., Faraday Trans. 90 (15) (1994) 2257.
[5] J.A. Navio, M. Macias, M. Gonzalez-Catalan, A. Justo, J. Mater. Sci. 27 (1992) 3036.

[6] J. Navio, G. Colon, M. Trillas, J. Peral, X. Domenech, J.J. Testa, J. Padron, D. Rodriguez, M.I. Litter, Appl. Catal. B 16 (1998) 187.
[7] K.T. Ranjit, B. Viswanthan, J. Photochem. Photobio. A 108 (1997) 79.
[8] M. Buchler, P. Schmuki, H. Bohni, T. Stenberg, T. Mantyla, J. Electrochem. Soc. 145 (2) (1998) 378.
[9] M.I. Litter, J.A. Navio, J. Photochem. Photobio. A 84 (1994) 183.
[10] C. Pulgarin, J. Kiwi, Langmuir 11 (1995) 519.
[11] A. Ansari, J. Peral, X. Domenech, R. Rodriguez-Clemente, A. Roig, E. Molins, J. Photochem. Photobio. A 87 (1995) 121.
[12] A. Ansari, J. Peral, X. Domenech, R. Rodriquez-Clemente, Environ. Pollut. 95 (3) (1997) 283.
[13] E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domenech, J. Casado, Appl. Catal. B 16 (1998) 31.
[14] T.D. Waite, in: M.F. Hochella, A.F. White (Eds.), Reviews in Mineralogy, Vol. 23, Mineralogical Society of America, Washington, DC, 1990, p. 559.
[15] P. Madhusudhan Rao, B. Viswanathan, P.P. Viswanath, J. Mater. Sci. 30 (1995) 4980.
[16] H. Yuan, S. Tsujikawa, Zairyo-to-Kankyo 44 (1995) 534.
[17] J. Huang, T. Konishi, T. Shinohara, S. Tsujikawa, Zairyo-to-Kankyo 47 (1998) 193.
[18] J. Huang, T. Shinohara, S. Tsujikawa, Zairyo-to-Kankyo 46 (1997) 651.
[19] D.W. Bahnemann, D. Bockelemann, R. Goslich, M. Hilgendorff, D. Weichgrebe, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 301.
[20] A. Milis, J. Peral, X. Domenech, J. Mol. Catal. 87 (1994) 67.
[21] D. Bockelmann, M. Lindner, D. Bahnemann, in: E. Pelizzetti (Ed.), Fine Particles Science and Technology, Kluwer Academic Publishers, Dordrecht, 1996, p. 657.
[22] R.I. Bickley, T. Gonzalez-Carreno, L. Palmisano, R.J.D. Tilley, J.M. Williams, Mater. Chem. Phys. 51 (1997) 47.
[23] D. Beydoun, R. Amal, G. Low, S. McEvoy, J. Phys. Chem. B. 104 (18) (2000) 4387.
[24] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Gonzalez-Elipe, J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, Appl. Catal. B 7 (1995) 49.