Effect of Ti content in the photocatalytic behavior of Fe/TiO$_2$-SiO$_2$ systems

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In this work we report the synthesis of Fe/TiO$_2$-SiO$_2$ systems with different concentrations of TiO$_2$ in order to determine the influence of titanium content on the structural, textural, optical properties and their photocatalytic behavior. The materials were synthesized by the sol-gel method and their modification was carried out by incipient impregnation. All samples were characterized by means of X ray diffraction, N$_2$ physisorption (BET method), DR-UV-Vis and Raman spectroscopy. The modifications of the structural and optical properties are discussed on the basis of long-range order reduction, suggesting the formation of highly dispersed TiO$_2$ species. On the other hand, it was observed that the energy of the optical band gap decreases by introducing Fe. On the basis of these phenomena, the photocatalytic activity was measured, employing the degradation of orange II azo dye as a model reaction.

Keywords: Fe-TiO$_2$-SiO$_2$; photocatalysis; semiconductors.

1. Introduction

The control of pore size, distribution and structure of materials are important aspects to consider during research and development of new materials. These factors also play an important role in the production of adsorbents and catalysts, since they are intimately related to its catalytic activity. SiO$_2$-TiO$_2$ system has been studied extensively because of its multiple applications, such as the manufacture of special cements, paints and UV absorbers in creams and cosmetics for everyday use [1,2]. It has also been used in developing of refractory materials, glass with controlled refractive index and low expansion coefficient. Recent studies have found that catalytic systems including TiO$_2$ and TiO$_2$-SiO$_2$ show excellent results in oxidation and acid-base reactions [3-5].

In recent years, the wastewater discharged from the dye stuff manufacturing, printing and textile industries represent one of the most serious environmental problems, due to contain chemicals that exhibit mutagenic effects and toxic to human and aquatic life [6]. Unfortunately, azo-dyes compounds are not biodegradable and resist to conventional treatment. Heterogeneous photocatalysis is emerging as promising technologies to wastewater treatment due to it is not selective and therefore it is capable of destroy a wide variety of organic contaminants. In this process, a semiconductor is activated by UV or Visible radiation (with the adequate frequency) to photogenerate electron-hole pairs and HO• radicals, which are very strong oxidants. There are several studies where it has investigated the removal of organic pollutants on semiconductor TiO$_2$, TiO$_2$-SiO$_2$ or Fe$_2$O$_3$ catalysts [7-12]. However, there is no information on the use of TiO$_2$-SiO$_2$ system modified with Fe. This study shows the effect of Ti content and the unique structure and electronic properties that confer Fe doping TiO$_2$-SiO$_2$ system on the photodegradation of Orange II textile azo-dye.

2. Experimental

2.1. Material Synthesis

In order to have a reference, TiO$_2$ was synthesized by the following procedure: a homogeneous mixture of titanium isopropoxide in i-propanol was hydrolyzed at room temperature in the presence of HNO$_3$. After gelation, the sample was aged for 24 h, then dried at 120°C and calcined at 450°C under flowing air during 4 h.

To synthesize TiO$_2$-SiO$_2$ system, a mixture of titanium isopropoxide (in the necessary amounts to obtain materials with: 5, 10, 15, 25, 40, 60, 70 and 80 wt % of TiO$_2$) and tetraethyl ortho-silicate in i-propanol was hydrolyzed and aged to obtain the corresponding gels. The samples thus ob-
tained were dried for 24 hours at 120°C, to be finally calcined at 450°C for 4 hours in air stream.

The TiO₂-SiO₂ (with different Ti/Si mol ratio) powders were modified with a 1 % wt of Fe by means of a wet impregnation method at 25°C, employing a FeSO₄·7H₂O aqueous solution. After impregnation the materials were dried overnight at 120°C and subsequently calcined for 4 hours at 450°C in an air flow.

2.2. Characterization

The structural characterization of all synthesized materials was carried out by powder XRD using a Philips X’Pert diffractometer, operating in 2θ mode, samples were analyzed in the range of 5 to 80, 2θ degrees using a Cu tube Kα radiation (35 kV, 25 mA) at 2° s⁻¹ scan rate and wavelength λ= 0.15405 nm. The textural properties were determined by nitrogen physisorption at 77 K, employing the BET method in a Micromeritics ASAP 2020 apparatus. Before analysis the samples were out-gassed at 100°C for 12 h.

The optical properties of materials were determined using an UV-Vis (Varian Cary I double-beam) spectrophotometer operating in the diffuse reflectance mode. The absorption coefficient F (R∞) was obtained from diffuse reflectance data through the Kubelka-Munk equation. In order to determine the vibrational modes of Fe/TiO₂-SiO₂ systems and confirm their structural changes, dispersive Raman spectroscopy was used (Thermo-Nicolet Almega model, equipped with a laser source in the visible region 532 nm, using potential of 15000 V, 25 mA). The textural properties were determined by XRD analysis using an X’Pert pro MPD diffractometer, operating in the phi-2θ mode, samples were analyzed with a scan rate of 0.05° per second in the range of 5 to 80°. The structural characterization of all synthesized materials was performed using a Philips X’Pert diffractometer, operating in the phi-2θ mode, samples were analyzed with a scan rate of 0.05° per second in the range of 5 to 80°.

2.3. Photocatalytic Test

All experiments were carried out in a batch glass reactor of 100 mL, equipped with magnetic stirring, cooling jacket and Lummi UV lamp 7 W. The reactions were performed at room temperature (25°C) using an aqueous solution of Orange II dye with an initial concentration of 17.51 ppm and 2 mL of aqueous solution. After impregnation the materials were dried overnight at 120°C and subsequently calcined for 4 hours at 450°C in an air flow.

3. Results and Discussion

3.1. Textural Properties

The composition and results of the textural, structural and band gap energy (Eg) of the Fe/TiO₂-SiO₂ systems are shown in Table I.

From this Table, it was noticed that the incorporation of SiO₂ increases the specific area of synthesized materials and the higher value of specific area is developed by the sample with 25 % of TiO₂, this behavior may be associated to formation of SiO₂ tetrahedral species, which has the ability to form polymeric arrangements, leaving voids during thermal treatment (calcinations), and permit the expansion of the TiO₂ structure. For this reason, there are observed important variations in textural, structural and electronic properties depending in TiO₂ content.

According to the IUPAC classifications, the isotherms obtained for all Fe/TiO₂-SiO₂ systems are identified as type IV, which are characteristic of mesoporous solids. In Figure 1 are illustrated the adsorption-desorption isotherms, additionally it was found that the sample Fe/TiO₂-SiO₂ with 5% of TiO₂ have a hysteresis loop type H3, where it presents a limited adsorption at high values of p/p₀ so it is suggested that the system consists of aggregates of plate-like particles, resulting in slit-shaped pores.

The hysteresis loop of the sample Fe/TiO₂-SiO₂-25 is of type H1, this type has been associated with porous materials consisting with uniform and compact clusters arranged fairly regular and very narrow pore distribution.

On the other hand, the materials with 40 and 55 TiO₂ content have a loop of type H4, associated with narrow pores as slit and a significant microporosity. Adsorption isotherms for samples with 62, 70 and 80% of TiO₂ presents a hysteresis loop of type H2, which corresponds to a homogeneous distribution with a high porous degree of interconnection. These results show that the TiO₂ content has an important influence on the size, shape and porosity distribution, which depends largely on the arrangement or symmetry long-range (crys-

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>TiO₂ (W %)</th>
<th>SiO₂ (W %)</th>
<th>Surface Area m²/g</th>
<th>Pore Volume cm³/g</th>
<th>Pore Size (Å)</th>
<th>Eg(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>100</td>
<td>-</td>
<td>65</td>
<td>0.098753</td>
<td>56.2617</td>
<td>3.21</td>
</tr>
<tr>
<td>Fe/Si-Ti 80</td>
<td>80</td>
<td>20</td>
<td>205.749</td>
<td>0.155089</td>
<td>30.1511</td>
<td>2.87</td>
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<tr>
<td>Fe/Si-Ti 70</td>
<td>70</td>
<td>30</td>
<td>150.023</td>
<td>0.114958</td>
<td>30.6509</td>
<td>2.92</td>
</tr>
<tr>
<td>Fe/Si-Ti 62</td>
<td>62</td>
<td>38</td>
<td>318.777</td>
<td>0.288629</td>
<td>36.217</td>
<td>3.03</td>
</tr>
<tr>
<td>Fe/Si-Ti 55</td>
<td>55</td>
<td>45</td>
<td>201.881</td>
<td>0.114288</td>
<td>22.6447</td>
<td>2.94</td>
</tr>
<tr>
<td>Fe/Si-Ti 40</td>
<td>40</td>
<td>60</td>
<td>237.460</td>
<td>0.126721</td>
<td>21.3461</td>
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</tr>
<tr>
<td>Fe/Si-Ti 25</td>
<td>25</td>
<td>75</td>
<td>440.534</td>
<td>0.645548</td>
<td>18.6161</td>
<td>3.27</td>
</tr>
<tr>
<td>Fe/Si-Ti 5</td>
<td>5</td>
<td>95</td>
<td>27.560</td>
<td>0.072325</td>
<td>104.9692</td>
<td>3.31</td>
</tr>
</tbody>
</table>

talline structure) formed during the synthesis stage. Additionally, it was revealed that the surface area also depends on the size of crystals and how these are added, because a smaller particle size or crystal, generate a more number of defects and therefore the specific surface area increases.

3.2. Structural Characterization

Figure 2 shows the X-ray diffraction patterns of samples Fe/TiO$_2$-SiO$_2$. From these results we can see that samples with lower silicon content (rich in TiO$_2$), have very intense reflection at 2$\theta$ 25 degrees, which are characteristics of titanium oxide in anatase phase, it is important to notice that there are no reflections corresponding to rutile or brookite phases.

These intense and narrow peaks reveal the presence of TiO$_2$ crystals larger than 20 nm. Besides, the increase in silica content produce wide and low intensity reflections in the same positions, indicating that there is a loss of long-range ordering. This behavior can be attributed to the formation of nanocrystalline materials (less than 5 nm) of TiO$_2$, which are highly dispersed on silicon oxide surface due to the latter has an amorphous structure. Additionally, it was found, that the sample with 5% of TiO$_2$ content was completely amorphous (spectrum is not showed).

3.3. Optical Characteristics

The calculation of the optical band gap energy (E$_g$) of synthesized materials was obtained from extrapolation of the linear region of the Kubelka-Munk transformation of the UV-Vis absorption spectra (F(R) = 0), as shown in Fig. 3. As it is known, the absorption edge is the necessary energy to promote an electron from the HOMO (highest occupied molecular orbital) or valence band to a LUMO (lowest unoccupied molecular orbital) or conduction band. In Table I are summarized the values of E$_g$ obtained for all systems, finding that the TiO$_2$-SiO$_2$ systems with lower TiO$_2$ content show the highest E$_g$ values, this situation was expected, since the SiO$_2$ is an insulating material. Furthermore, we find that samples with low TiO$_2$ content (Fe/TiO$_2$-SiO$_2$ 25 and Fe/TiO$_2$-SiO$_2$ 5 E$_g$ = 3.27 and 3.31 eV respectively) present a band gap energy higher than the bulk Degussa P-25 TiO$_2$ (3.2 eV), this increase can be attributed to quantum confinement effect (decrease in crystallite size observed by XRD analysis).

For the samples modified with Fe it was observed a significant decrease in the E$_g$ (red shift), attributed to the formation of new electronic states located in the interband, which favors the electronic transitions and the generation of charge
EFFECT OF Ti CONTENT IN THE PHOTOCATALYTIC BEHAVIOR OF Fe/TiO$_2$-SiO$_2$ SYSTEMS

4. Conclusions

Titanium content in the synthesized materials plays a significant role both in the crystal structure in the shape and distribution of pores, as well as electronic and photocatalytic behavior. The photoactivity should be associated with the Eg and the amount of surface species from Ti-O-Fe and Ti-O-Ti bonds and Fe$_2$O$_3$ nanoparticles. The addition of Fe leads to a decrease in edge energy and the generation of internal electronic inter-band states (red shift), allowing the possibility to apply this systems for photovoltaic processes or photocatalysis using visible irradiation to remove different organic pollutants as Orange II azo-dye.

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