Synthesis and characterization of Fe-doped TiO$_2$ photocatalyst by the sol–gel method

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Abstract

Thin layers of pure TiO$_2$ and TiO$_2$ doped by different amounts of Fe$_2$O$_3$ have been prepared by the sol–gel method with tetraisopropyl orthotitanate and Fe(NO$_3$)$_3$. Physico-chemical properties of catalysts were characterized by BET Adsorption, x-ray Diffraction (XRD), FE-SEM, as well as Raman and UV-Vis spectroscopy. The photocatalytic activity of the obtained materials was investigated in the reaction of complete oxidation of p-xylene in gas phase under the radiation of UV ($\lambda = 365$ nm) and LED ($\lambda = 470$ nm) lamps. It has been found that the particle size of all samples was distributed in the range 20–30 nm. The content of the rutile phase in Fe-doped TiO$_2$ samples varied in the range 6.8 to 41.8% depending on the Fe content. Iron oxide doped into TiO$_2$ enables the photon absorbing zone of TiO$_2$ to extend from UV towards visible waves as well as to reduce its band gap energy from 3.2 to 2.67 eV. Photocatalytic activities of the TiO$_2$ samples modified by Fe$^{3+}$ have been found to be higher than those of pure TiO$_2$ by about 2.5 times.

Keywords: Fe-doped TiO$_2$, photooxidation, p-xylene

Classification numbers: 5.00, 5.07

1. Introduction

As a conventional photocatalyst, TiO$_2$ is applied in many processes of pollutant treatment in waste water, as well as in air [1, 2]. Doping TiO$_2$ with transition metals such as Fe, V and Cu makes it active higher in photocatalytic conversions [3]–[6]. This is explained by the ability of the modified titania samples to reduce the band gap energy value and the recombination rate of the pair electron-photoinduced hole under sunlight radiation compared to that in the case of pure TiO$_2$ [7, 8]. It has been indicated that the movement of $\lambda$ towards the red light area decreased in the following order: V $>$ Cr $>$ Mn $>$ Fe $>$ Ni [9]. It has also been noticed that this movement increases slightly with the content of metals Mn, V, Fe and Cr in the modified samples [9, 10]. The purpose of this study is to use the sol–gel method [11, 12] for the synthesis of Fe-doped TiO$_2$ catalysts, to characterize their physico-chemical properties and to test their photocatalytic activity in degradation (complete oxidation) of p-xylene.

2. Experiment

The Fe-doped TiO$_2$ catalysts were prepared by the sol–gel method as below: Dissolve 3 ml of tetraisopropyl orthotitanate (TTIP) in 50 ml of mixture HNO$_3$-ethanol (pH = 3). The obtained solution must be clear and transparent. Make the sol by adding Fe(NO$_3$)$_3$ solution over 90 min. The content of Fe (Fe$_2$O$_3$/TiO$_2$) was adjusted to be 0.025, 0.05, 0.10, 0.50, 1.00 and 2.00 mol.% to obtain catalyst samples symbolized as 025FeTi, 050FeTi, 100FeTi, 500FeTi, 1000FeTi and 2000FeTi, respectively. The sol by adding Fe(NO$_3$)$_3$ solution over 90 min. The content of Fe (Fe$_2$O$_3$/TiO$_2$) was adjusted to be 0.025, 0.05, 0.10, 0.50, 1.00 and 2.00 mol.% to obtain catalyst samples symbolized as 025FeTi, 050FeTi, 100FeTi, 500FeTi, 1000FeTi and 2000FeTi, respectively. The sol was kept at room temperature until the complete hydrolysis of TTIP and gel has been formed (24 h). The obtained precipitates were filtered and washed...
with ethanol and distilled water. The samples were dried at 110 °C for one hour and then calcined and crystallized at 550 °C for 4 h.

Characterization of the catalyst samples was carried out by BET adsorption (CHEMBET 3000), XRD (x-ray Diffraction XD 5A, SHIMADZU), FE SEM (HITACHI S-4800), FT-Raman (Perkin-Elmer 2000), Absorption UV-Vis (Jasco V-550) and IR-Spectroscopy (VECTOR 22 BRUKER).

The photocatalytic activity of the samples was tested in the gas phase deep oxidation of p-xylene at 40 °C and the initial partial concentrations of reactants (C_o, mg L^{-1}) and total flow velocity (V, Liter h^{-1}), as described below for each series of experiments (in tables 2 and 3).

The doped-TiO_2 catalyst samples were made in the form of transparent thin film on Pyrex tube (area of 68 cm^2 and weight of 5 mg). The radiation sources were a UV lamp (λ = 365 nm, power of 8 W) and 80 pieces of LED (λ in the range 400–510 nm, total power 19.2 W).

The photocatalytic activity of the catalysts was evaluated by results obtained from analysis on the gas-chromatograph GC Agilent 6890 Plus, detector FID, capillary column HP-1 with methyl siloxane (30 m, 0.32 mm, 0.25 µm).

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

XRD spectra of the catalysts (figure 1) only show the characteristic peaks of TiO_2 in anatase (2θ = 25.3°) and rutile (2θ = 27.5°) phases without any characteristic peaks of Fe_2O_3. This result indicates that probably some Fe^{3+} ions replaced Ti^{4+} ions in the crystal framework of TiO_2.

The particle size values of the catalysts were calculated from the Scherrer equation. Data in table 1 show that the influence of iron oxide content on the ratio of anatase/rutile phases is complex. In the range 0.05 to 0.1 mol.% of Fe_2O_3 the percentage of rutile phase increased from 24.1 to 41%, but at higher values of iron oxide content the proportion of the rutile to anatase phase in the studied samples decreased regularly and reached the quantity of 18.2 mol.%, close to that in commercial TiO_2 Degussa P25. Also the iron oxide content influences the particle size and, as a rule, the specific surface area of the catalyst samples. Although the trend is not very clear, a general remark could be that the particle size decreased with the content of iron oxide, while the values of surface area varied in the opposite direction.

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**Table 1.** Characteristics of the obtained catalysts (particle size d, nm; specific surface area S_{BET}, m^2 g^{-1}, wavenumber of absorbed light \(\lambda_{max}\), nm; band gap energy \(E_{bg}\), eV).

| Catalyst       | TiO_2 | 0.025FeTi | 0.05FeTi | 0.10FeTi | 0.50FeTi | 1.00FeTi | 2.00FeTi |
|----------------|-------|-----------|----------|----------|----------|----------|----------|
| Fe_2O_3, mol.% | 0     | 0.025     | 0.05     | 0.10     | 0.50     | 1.00     | 2.00     |
| Anatase, mol.% | 93.2  | 75.9      | 58.3     | 58.9     | 81.0     | 80.4     | 81.8     |
| Rutile, mol.%  | 6.8   | 24.1      | 40.8     | 41.1     | 19.0     | 19.6     | 18.2     |
| d, nm          | 30.0  | 27.6      | 29.5     | 30.3     | 24.8     | 21.6     | 19.5     |
| S_{BET}, m^2 g^{-1} | 45.0  | 15.5      | 11.2     | 9.6      | 34.6     | 36.9     | 42.9     |
| \(\lambda_{max}\), nm | 387   | 425       | 424      | 423      | 442      | 449      | 464      |
| \(E_{bg}\), eV | 3.20  | 2.92      | 2.93     | 2.93     | 2.80     | 2.76     | 2.67     |
Figure 2. FE SEM images of Fe-doped TiO\textsubscript{2} catalysts: (a) 025FeTi, (b) 050FeTi, (c) 100FeTi, (d) 500FeTi, (e) 1000FeTi, (f) 2000FeTi.

Figure 3. Raman spectra of Fe-doped TiO\textsubscript{2} catalysts with different contents of Fe\textsubscript{2}O\textsubscript{3}.

Figure 4. UV-Vis spectra of Fe-doped TiO\textsubscript{2} catalysts with different Fe\textsubscript{2}O\textsubscript{3} content.

The FE SEM image of the sample 025FeTi catalyst (figure 2) shows a uniform particle size, but in the range 0.05 to 1.00 mol.% of iron oxide content one can observe a mixture of fine particles and bulk TiO\textsubscript{2}. In comparison, the image of sample 2000FeTi shows very fine and uniform particles of the TiO\textsubscript{2} crystals.

The Raman spectra of the Fe-doped TiO\textsubscript{2} catalysts (figure 3) show peaks at 407, 522, 648 and 853 cm\textsuperscript{-1} characterizing the absorption of anatase TiO\textsubscript{2} [13]. No characteristic peaks of Fe\textsubscript{2}O\textsubscript{3} have been observed. It is very probable that the presence of Fe\textsuperscript{3+} ions in the lattice resulted in the shift of absorption peaks characteristic of TiO\textsubscript{2} to the region of higher frequencies. This is explained by the decrease in particle size of the Fe-doped TiO\textsubscript{2} samples. The specific features of the Raman spectra of Fe-doped TiO\textsubscript{2} catalysts are the absence of the characteristic anatase peak at 144 cm\textsuperscript{-1} and the appearance of the new peak at 853 cm\textsuperscript{-1}. These facts confirm the idea about the penetration of Fe\textsuperscript{3+} ions into the framework of TiO\textsubscript{2} crystals.

The pure TiO\textsubscript{2} catalyst is characterized by the value of the band gap energy of anatase TiO\textsubscript{2} (\(E_{\text{bg}} = 3.20\) eV). The UV-Vis spectra of all the Fe-doped TiO\textsubscript{2} catalyst samples (figure 4) show the shift of the \(\lambda_{\text{max}}\) towards the red light zone and this shift depends on the iron content in the lattice. Concomitantly, the increase of iron content in the lattice resulted in a decrease of \(E_{\text{bg}}\). The 2000FeTi sample expressed the biggest shift, the value of \(\lambda_{\text{max}}\) reaching 464 nm and the value of \(E_{\text{bg}}\) decreasing to 2.63 eV. Also one can observe that the color of the catalyst samples changed from white to yellow with the increase of iron content in the lattice.

The IR spectra (figure 5) of all Fe-doped TiO\textsubscript{2} samples show peaks characteristic of OH at the surface (3225 cm\textsuperscript{-1}), molecular water (1621 cm\textsuperscript{-1}), Ti-O (653–550 cm\textsuperscript{-1}) and Ti-O-Ti (495–436 cm\textsuperscript{-1}) as in the case of pure TiO\textsubscript{2}. But it is interesting to note the appearance of a new peak at 2200 cm\textsuperscript{-1}, the absorption intensity of which regularly increases with iron content. The order is as follows: 2000FeTi > 1000FeTi > 500FeTi > 100FeTi > 050FeTi > 025FeTi. It is
Figure 5. IR-spectra of Fe doped-TiO$_2$ catalyst samples: (1) 025FeTi; (2) 050FeTi; (3) 100FeTi; (4) 500FeTi; (5) 1000FeTi and (6) 2000FeTi.

Table 2. Photocatalytic activity of TiO$_2$ and of the Fe doped-catalysts expressed in initial extents of p-xylene conversion ($X_o$) and productivity of p-xylene degradation for 60 min. ($P$) under UV and LED radiation at $T = 40 ^\circ C$; $V = 61 h^{-1}$; $C_{xylene} = 19 mg l^{-1}$; $C_{O_2} = 300 mg l^{-1}$; $C_{H_2O} = 11.5 mg l^{-1}$.

| Catalyst | TiO$_2$ | 025FeTi | 050FeTi | 100FeTi | 500FeTi | 1000FeTi | 2000FeTi |
|----------|---------|---------|---------|---------|---------|----------|----------|
| $X_o$, % | 41.7    | 14.3    | 93.3    | 26.3    | 40.6    | 65.5      | 100.0     | 42.4     | 58.7    | 55.0    | 43.3    |
| $P$, g/g | 8.10    | 1.88    | 5.59    | 3.62    | 3.48    | 3.02      | 5.34      | 2.74     | 4.09    | 2.52    | 5.64    |

$^a$3 pieces of UV-lamp, $\lambda = 365$ nm (total power 24 W).
$^b$80 pieces of LED, $\lambda = 470$ nm (total power 19.2 W).

very probable that this peak could be assigned to Ti-O-Fe vibration.

3.2. Photocatalytic activity of the catalysts in the gas phase degradation of p-xylene

From the data in table 2 it follows that practically all the Fe doped-TiO$_2$ samples expressed higher initial activities than that of pure TiO$_2$. This fact can be explained by the presence of Fe making the amount of active sites higher due to the formation of Fe—O—Ti bonds in the TiO$_2$ crystal lattice, as well as the consequent formation of defects on the catalyst surface that plays the role of a trap for preventing electron-hole recombination. Also the reduction of particle size and the increase of surface area should make the substrate adsorption stronger. An important effect of the modification of TiO$_2$ by iron oxide doping must be the reduction of its band gap energy value. Comparing the results obtained in two experiments under UV-lamp and LED lighting one can see that under LED radiation, in contrary with the case under UV lighting, the modified catalysts expressed much higher activity and productivity than pure TiO$_2$.

An experiment with sample 2000FeTi using a combined radiation source (UV + LED) has been carried out. The data in table 3 show the advantage of combined radiation; in this case one can observe sufficiently high values of xylene conversion as well as productivity in its complete oxidation.

Table 3. Conversion extent of p-xylene at different times ($X$) and productivity of p-xylene degradation ($P$) for 60 min on catalyst 2000FeTi under different radiation regimes$^a$.

| Reaction time, min | Conversion of p-xylene, X % | Productivity of p-xylene degradation, P, g/g catalyst |
|--------------------|------------------------------|---------------------------------------------------|
| 1                  | 31.2                         | 14.4                                              |
| 5                  | 38.0                         | 22.3                                              |
| 30                 | 33.1                         | 13.8                                              |
| 60                 | 24.8                         | 13.2                                              |
| $P$, g/g catalyst  | 4.72                         | 2.08                                              |

$^a$ $T = 40 ^\circ C$, $V = 121 h^{-1}$, $C_{xylene} = 6.33 mg l^{-1}$, $C_{O_2} = 300 mg l^{-1}$, $C_{H_2O} = 7.83 mg l^{-1}$.
$^b$3 pieces of UV-lamp.
$^c$80 pieces of LED.
$^d$1 piece of UV-lamp plus 80 pieces of LED.

4. Conclusion

Fe$^{3+}$ ions doped into TiO$_2$ have caused changes in phase composition and some properties of the catalyst such as phase composition, particle size and surface area, as well as broadening the light absorption zone towards the red region and reducing the band gap energy of the oxide. At low concentrations of iron oxide the percentage of the rutile phase increased and the particle size decreased with Fe$_2$O$_3$. The composition and particle size of catalyst samples containing 0.50 to 2.00 mol.% Fe$_2$O$_3$ have been shown to be similar to those of TiO$_2$ Degussa P25, but their photochemical properties...
are completely different; Fe$^{3+}$ ions reduced the value of the band gap energy of TiO$_2$, making the modified samples able to absorb light in the visible region. Under the radiation of LED lighting the ability to degrade p-xylene of the modified Fe-TiO$_2$ samples has been found to be 2–3 times higher than that of pure TiO$_2$. In the experiment using a combined system (UV+LED) of lighting it has been shown that this way of radiation should considerably increase the productivity of TiO$_2$ catalysts modified by Fe$_2$O$_3$ in p-xylene decomposition.

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