Preparation and characterization of Fe³⁺-doped TiO₂/diatomite composite

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Keywords: Diatomite; TiO₂; Iron ion doping; Photocatalyst;

Abstract. Fe^{3+} -doped TiO₂/diatomite composite photocatalyst were prepared by sol-gel method with titanium isopropoxide used as precursor material. The samples were characterized by SEM, XRD, XPS, BET surface area analysis and UV-Vis techniques. The results showed that the optimum concentration of Fe³⁺ in the composite catalyst was 0.2wt% when the quantity of TiO₂ loaded on the diatomite was 30.3wt%. Compared with the un-doped photocatalyst, the Fe³⁺-doped sample exhibited red shifts of absorption edge and significant enhancement of light absorption at 400~600 nm.

Introduction

 TiO_2 has been considered as one of the most promising photocatalysts ever since Honda and Fujishima [1] reported its photochemical properties. However, TiO_2 is not thermally stable and loses surface area readily when used as a high surface area powder. On the other hand, both the reaction mechanisms, under either UV or visible irradiation, indicated that preliminary adsorption of organic substrate on the TiO_2 surface exhibited an advantage for high efficient degradation. These have led to a number of attempts to anchor TiO_2 on high surface area supports, such as zeolites, activated carbon and clays, by a variety of chemical or physical methods, e. g., ionized cluster beam deposition, wet chemical methods, chemical vapor deposition and impregnation-desiccation [2]. Recently, one siliceous sedimentary rock, named diatomite, has received attention for its unique combination of physical and chemical properties. It was successfully used as adsorbent to remove various pollutants, and examined as perfect support for TiO₂ to prepare hierarchical structured catalysts [3].

The other disadvantage of TiO₂ is that it can only utilize a relative small part of the solar spectrum (UV light) for photocatalytic oxidation. Doping or combining of TiO₂ with various metal or non-metal ions was reported as a good tool to improve the photocatalytic properties and for enhancement of visible light response [4]. Amongst a variety of transitional metals, iron had been considered to be an appropriate candidate due to the fact that the radius of Fe³⁺ (0.79 A) is similar to that of Ti⁴⁺ (0.75 A), so that Fe³⁺ can be easily incorporated into the crystal lattice of TiO₂ [5].

Based on the above considerations, we prepared Fe^{3+} -doped TiO_2 /diatomite photocatalytic materials according to a sol-gel route in which diatomite particle was incorporated into the titanium isopropoxide sol during the course of the sol-gel process. The samples have been characterized by means of XRD, SEM, XPS, BET and UV-Vis technologies, and the optimum concentration of Fe³⁺ in the composite catalyst was studied.

Experimental

Materials and reagents. The following reagents were employed to prepare TiO_2 : titanium-(IV)-isopropoxide (97%) as TiO_2 source; hydrochloride acid (37%) as catalyst; Iron(III) nitrate (99%) as dopant source; ethyl alcohol (96%) as solvents. Diatomite was obtained from Sheng county in Zhejiang province of China. The sample was calcined at 500 °C to remove organic impurities before TiO_2 coated.

Preparation of Fe³⁺-doped TiO2/Diatomite. 10 mL of titanium isopropoxide was dissolved into 50 mL of anhydrous ethanol (solution A). Solution B consisted of 0.5 mL of HCl, 2 mL of distilled water and Fe(NO₃)₃· 9H₂O in the required stoichiometry. Then solution B was added drop-wise into solution A with stirring magnetically. After the drop, 5g of diatomite was added to the solution. The resultant mixture was stirred at room temperature for 30 min to hydrolysis until the transparent sol was obtained. The sol was then aged for 72 h until the formation of gel. Then dried and ground. At last, the powder was kept for 1 h under 500 °C in the oven.

Characterization. Surface morphologies of the samples were investigated using SEM (model SIRION-100, Fei Company, Holland). For the specific surface area and pore size evaluation, nitrogen gas adsorption method was used. N₂ gas adsorption–desorption isotherms were measured at -196 °C using a model Autosorb-1 nitrogen-adsorption apparatus (Quantachrome Corp., USA). The specific surface area, S_{BET} , was calculated based on the BET theory. Phases and crystallite sizes of the prepared samples were characterized by XRD technique. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK α radiation. The UV-Vis variations of the solution were analyzed by a Shimadzu UV-2550 spectrophotometer.

Results and discussion

SEM analysis. The diatomite used in this work was in the form of cylindraceous particle with bulk density of 616 g/L and median particle diameter of 10.25 μ m (Laser particle size). The oxide analysis in our previous study [6] showed that SiO₂ was the main component (67.3%) and the metal oxides (15.4% Al₂O₃, 7.07% Fe₂O₃, 3.97% K₂O, 3.87% ZnO, 1.36% TiO₂ and 1.05% CaO) were the minor constituents. Fig. 1 shows the SEM images of diatomite and Fe³⁺-TiO₂/diatomite. It clearly displayed the cylindrical figure and the special porous texture of diatomite, and the surface was completely modified after TiO₂ loaded. The quantity of TiO₂ loaded on the diatomite surface may mainly depend on the quantity of titanium isopropoxide used in the experiment and the nature of the surface. In this study, the loading on the surface of the diatomite was determined to be approximately 30.3% using the differential weight method.



Fig. 1 SEM images of (a) diatomite and (b) Fe^{3+} -TiO₂/diatomite.

Surface area study. Highly porous morphologies with improved surface area offer more adsorption sites for the dye molecules and enhance the reaction rate. Hence, determination of the specific surface area is often a prerequisite for studying and interpreting adsorption properties quantitatively [7]. In this work, the pore properties, i.e., S_{BET} , pore volume V, and average pore diameter R, of diatomite and Fe³⁺-doped TiO₂/diatomite powders were characterized by N₂ adsorption-desorption experiments. The results were listed in Table 1. It can be seen that the BET surface area and pore volume of Fe³⁺-doped TiO₂/diatomite were higher that that of the initial diatomite. This suggested that the prepared sample could show improved capability in adsorption and photocatalytic degradation. Jia et al [3] have prepared hierarchical porous TiO₂/diatomite materials by a layer-by-layer (LBL) assembly method, and also obtained a higher BET surface area and pore volume with diatomite.

I able 1 lexture properties from nitrogen adsorption analysis			
Sample	$S_{\rm BET} ({ m m}^2/{ m g})$	$V(\text{cm}^3/\text{g})$	<i>R</i> (nm)
Diatomite	50.63	0.1296	10.24
Fe ³⁺ -TiO ₂ /diatomite	74.95	0.1540	8.221

XRD analysis. TiO₂ materials exist in three different crystalline phases: anatase, rutile and brookite. Fig. 2 shows XRD patterns of undoped and Fe³⁺-doped TiO₂/diatomite. It can be seen that both 0% and 0.2% Fe-doped samples had the anatase phase, and other crystalline phases were not detected. The reason may be that Fe³⁺ ions substituted Ti⁴⁺ ions and inserted into the crystal lattice of TiO₂ when the amount of Fe³⁺ ions was low, since the radii of Ti⁴⁺ and Fe³⁺ ions were similar. When the Fe³⁺ dopant percentage were 0.5% and 1.0%, the peaks of anatase phase decreased, while the peaks of rutile and iron oxide increased. Thus, the excess of Fe³⁺ dopant in the composite could lead to the phase transformation. It could be concluded from this experiment that almost all of Fe³⁺ in 0.2% Fe³⁺-TiO₂/diatomite were trapped in the crystal lattice of TiO₂, whereas 0.5% and 1.0% Fe³⁺-TiO₂/diatomite contained segregated iron oxide in addition to Fe³⁺ doped TiO₂.



Fig. 2 XRD patterns of Fe doped TiO₂/diatomite. Fig. 3 UV–Vis spectrum of Fe-doped sample.

UV-Vis analysis. Fig. 3 displays the UV–Vis absorption spectrum of undoped and Fe³⁺-doped TiO₂ powders. Pure TiO₂ exhibited an absorption edge rising steeply toward the UV region below 400 nm, which could be attributed to the band-gap excitation of anatase (3.2 eV), without absorption in visible region (>400 nm). Compared with the undoped photocatalysts, Fe³⁺-doped TiO₂ samples exhibited red shifts of absorption edge and significant enhancement of light absorption at 400~600 nm, and this enhancement increased as the doped Fe³⁺ percentage increased, accompanying with the change of powder color from white to primrose yellow. This result satisfies the aim of the study which was to increase the visible light absorption of Fe³⁺-doped TiO₂/diatomite powders.

XPS analysis. Fig. 4 shows the XPS spectra of Fe^{3+} -doped TiO₂/diatomite particles. Peaks of Ti 2p, Si 2p and O 1s were clearly observed for the sample in the wide spectra (Fig. 4a). Weak signals of Fe 2p could only be detected in the partial range of the XPS spectra, and the signals were fluctuant greatly, due to the low doping level, as shown in Fig. 4b. The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spin-orbital splitting photoelectrons for Fe^{3+} -TiO₂/diatomite were observed at 458 and 464 eV, respectively, which was consistent with the values of Ti⁴⁺ in the TiO₂ lattices. The comparison between the Ti 2p spectra of undoped TiO₂ and the doped TiO₂/diatomite (Fig. 4c and 4d) indicated that the latter had small binding energy shifts (the Ti $2p_{1/2}$ peak had a greater shift than the Ti $2p_{3/2}$ peak). It might infer that the doped Fe ions might diffuse into TiO₂ lattices to form the Fe-O-Ti bond.



Fig. 4 XPS spectra of synthesized Fe^{3+} -TiO₂/diatomite particles: (a) full range, (b) Fe, (c) Fe^{3+} -doped Ti and (d) undoped Ti in TiO₂

Conclusions

In this paper, Fe^{3+} -doped TiO₂/diatomite composite photocatalyst were successfully fabricated and characterized. It showed that the light absorption for the Fe-doped sample moved to a longer wavelength, and the doped Fe ions might diffuse into TiO₂ lattices to form the Fe-O-Ti bond.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (51203140), Zhejiang Provincial Natural Science Foundation of China (Y5110173), Zhejiang Provincial Key Innovation Team of China (No. 2010R50038) and Talents Training Foundation of Zhejiang Science and Technology Association.

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10.4028/www.scientific.net/AMM.268-270

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10.4028/www.scientific.net/AMM.268-270.15

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