



Characterization of SiO₂-TiO₂ and Photocatalytic Degradation of Methyl Orange

LINA ZHOU¹, XIAOFANG HAN¹, WENJIE ZHANG^{1,*} and HONGBO HE^{2,*}

¹School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, P.R. China

²Institute of Applied Ecology, The Chinese Academy of Sciences, Shenyang 110016, P.R. China

*Corresponding authors: Tel: +86 24 24680345; E-mail: wjzhang@aliyun.com; hehongbo@iae.ac.cn

Received: 29 June 2013;

Accepted: 5 November 2013;

Published online: 23 June 2014;

AJC-15356

A SiO₂-TiO₂ composite photocatalyst was prepared through sol-gel method for photocatalytic degradation of methyl orange. The material is composed of anatase TiO₂ and most probably amorphous SiO₂. The crystallite size of the TiO₂ (101) plane is 14.39 nm. The surface of the sample is fairly rough. Some particles in the size smaller than 1000 nm scatter on the surface. The pore size of the material is mainly below 15 nm and the pore diameter mainly distributes in the range from 2 nm to 11 nm. Adsorption only contributes a small part, less than 1.36 %, to the total decoloration of methyl orange on the TiO₂-SiO₂ material. The degradation of methyl orange continues with increasing irradiation time. Degradation rates after 0.5 and 2 h are 31.1 % and 92.9 %. The two main absorption peaks of methyl orange at 468 nm and 270 nm decline with increasing reaction time.

Keywords: TiO₂, SiO₂, Photocatalysis, Methyl orange.

INTRODUCTION

The treatment of organic pollutants in the environment is always research focus among which photocatalytic oxidation has grown to be an interesting method^{1,2}. The widely studied TiO₂ is believed to be a satisfactory material because of its high activity and other advantages³⁻⁶. In order to promote the activity of pure TiO₂, composite materials were prepared including the composition of TiO₂ and other oxides, such as SiO₂⁷, ZrO₂⁸, WO₃⁹, Cu₂O¹⁰ and Ta₂O₅¹¹. We firstly published a paper recently in reporting one-step sol-gel method to prepare porous TiO₂-Al₂O₃ composite photocatalyst¹².

In this paper, a SiO₂-TiO₂ photocatalyst was prepared through sol-gel method for photocatalytic degradation of methyl orange. The materials were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), frontier transform infrared spectrophotometer (FT-IR) and N₂-adsorption and desorption techniques. Photocatalytic activity of the materials was also investigated for degradation of methyl orange.

EXPERIMENTAL

The SiO₂-TiO₂ catalyst was prepared according to a sol-gel process by the following method. Tetrabutyl titanate [Ti(OBu)₄, 2 mL] and ethyl silicate (0.0075 mL) were slowly added to ethanol under continuous magnetic stirring to obtain a mixed slurry. Another ethanol-water solution was added to

the mixed slurry to hydrolyze tetrabutyl titanate and ethyl silicate after the mixture was stirred for 1 h. The molar Si/Ti ratio in the final precursor was 0.003 and V[Ti(OC₂H₅)₄]: V(C₂H₅OH): V(H₂O): V(HCl) = 1: 5: 0.5: 0.05. The resulting slurry was still under continuous magnetic stirring until it became a gel. The gel was dried at 80 °C for 8 h and calcined at 500 °C for 3 h. Finally, the catalysts were grinded into fine powders and stored in the dark.

Characterization: Scanning electron microscope (SEM) image was taken on a HTACHI S-3400N scanning electron microanalyzer. The sample for SEM imaging was coated with a thin layer of gold film to avoid charging. The crystalline phase of the photocatalyst was measured by X-ray diffraction (XRD) with D/max-rB diffractometer using a CuK_α radiation. FT-IR spectrum of the sample was recorded using a FT-IR spectrometer in the wavenumber range of 4000-400 cm⁻¹. The N₂-adsorption and desorption of the sample was measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. Specific surface area and pore size distribution were calculated from the N₂ desorption isotherms, according to Brunauer-emmett-teller (BET) equation and Barrett-joyner-halenda (BJH) method, respectively.

Photocatalytic activity: Photocatalytic activity of the photocatalyst was evaluated by measuring degradation rate of aqueous methyl orange under UV irradiation. In each experiment, 0.03 g of the photocatalyst was put into 50 mL of 10 mg/L aqueous solution of methyl orange in a 200 mL beaker.

A 20 W UV lamp was suspended 11 cm above the solution. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 1100 mW/cm². In prior to turn on the lamp, the solution was magnetically stirred for 30 min to ensure adsorption equilibrium. Methyl orange concentration was measured by a spectrophotometer (Shanghai spectrum instruments 721E) at its maximum adsorption wavelength of 466 nm. The suspensions were filtered through a Millipore filter (pore size 0.45 mm) before measuring. Irradiation time in the subsequent experiments was 0.5 h except for the prolonged examination.

RESULTS AND DISCUSSION

Transition metal doping and composite photocatalyst have been used to enhance the activity of TiO₂ containing materials. Sol-gel is a widely applied method used for preparation of nano-sized TiO₂ photocatalyst. The introducing of SiO₂ can effectively enhance crystalline structure of TiO₂, inhibit phase transform from anatase to rutile and therefore promote photocatalytic activity.

Fig. 1 shows XRD pattern of TiO₂-SiO₂ composite material which was calcinated at 500 °C for 3 h. The diffraction peaks of (101), (004) and (200) planes are in accordance to standard anatase TiO₂. There is no apparent diffraction peak corresponding to rutile TiO₂ or brookite TiO₂. Meanwhile, there is no diffraction peak corresponding to crystalline SiO₂. The material is composed of anatase TiO₂ and most probably amorphous SiO₂. The crystallite size of the (101) plane is 14.39 nm, calculating using Scherrer formula.

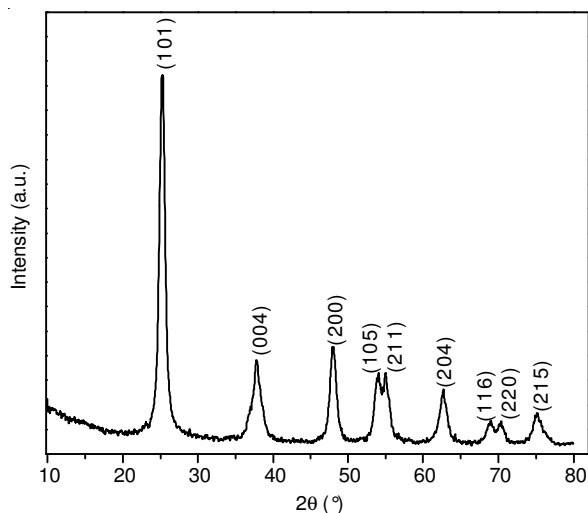


Fig. 1. XRD pattern of TiO₂-SiO₂ composite material

SEM image of TiO₂-SiO₂ composite material is shown in Fig. 2. The surface of the sample is fairly rough. Some particles in the size smaller than 1000 nm scatter on the surface. These small particles might be produced during grinding and be adsorbed on the surface.

FT-IR spectrum of TiO₂-SiO₂ composite material is shown in Fig. 3. The low-frequency absorption band at 466 cm⁻¹ is attributed to the Ti-O-Ti vibration of the samples. The band at 1625 cm⁻¹ corresponds to the bending vibration of O-H and the band around 3416 cm⁻¹ is assigned to the surface adsorbed water and hydroxyl groups. That means some H₂O molecules

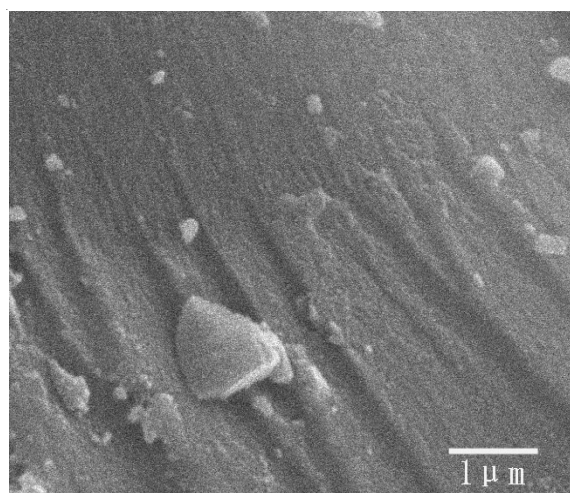


Fig. 2. SEM image of TiO₂-SiO₂ composite material

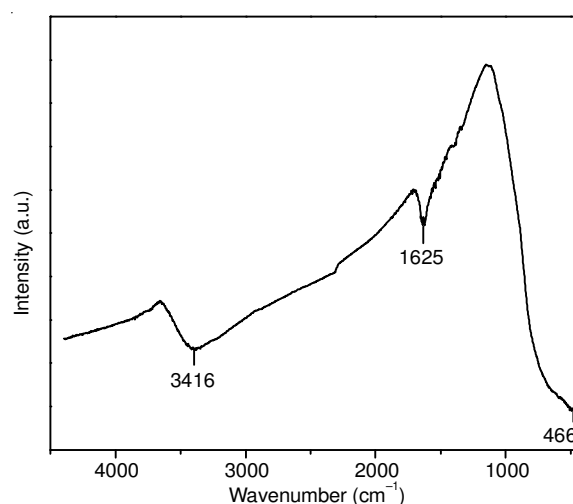


Fig. 3. FT-IR spectrum of TiO₂-SiO₂ composite material

are adsorbed on the surface. No clear evidence of Si-O-Si or Si-O-Ti vibration is found in the FT-IR spectra because of the very low concentration of SiO₂ in TiO₂ matrix.

Fig. 4 presents N₂ desorption isotherm and pore size distribution of TiO₂-SiO₂ composite. With the increase of relative pressure P/P₀ in Fig. 4a, the adsorption of N₂ on the material amplifies apparently. When the relative pressure P/P₀ is between 0.7 and 0.9, the increment of adsorption is significant because of capillary condensation of nitrogen molecules in the pores of the material. Fig. 4b clarifies the mesoporous structures of the material. The pore size of the material is mainly below 15 nm and the pore diameter mainly distributes in the range from 2 nm to 11 nm. The material has the maximum pore volume of 0.02935 cm³ g⁻¹ when pore size is 4.628 nm. The average pore diameter is 13.02 nm and the total pore volume is 0.2004 cm³ g⁻¹ along with specific surface area of 61.56 m² g⁻¹, as calculated using BJH and BET methods.

The degradation of methyl orange and adsorption on the TiO₂-SiO₂ under UV irradiation are shown in Fig. 5. Under magnetic stirring, adsorption reaches its equilibrium in less than 0.5 h. No variation occurs with further increase of adsorption time. Meanwhile, adsorption only contributes a small part, less than 1.36 %, to the total decoloration of methyl orange on the TiO₂-SiO₂ material. The degradation of methyl orange

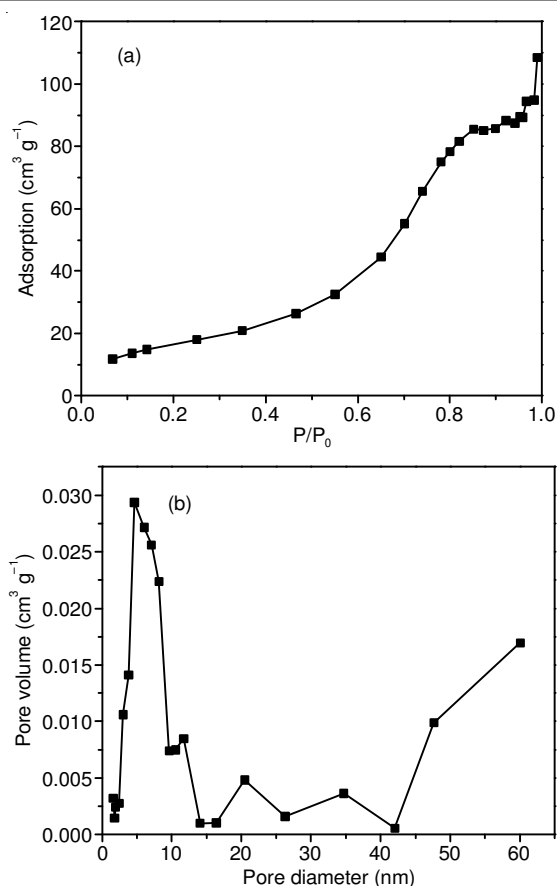


Fig. 4. N₂ desorption isotherm (a) and pore size distribution (b) of TiO₂-SiO₂ composite

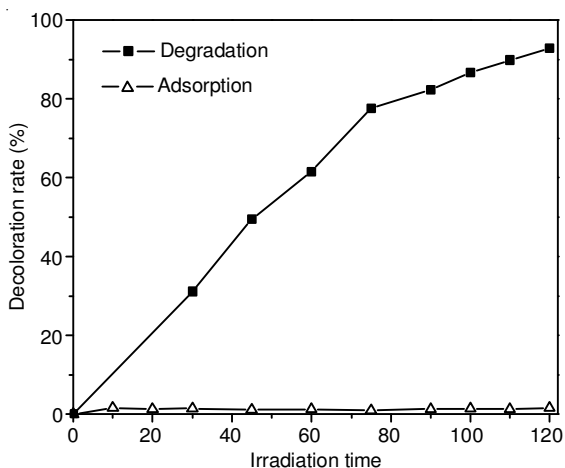


Fig. 5. Effect of irradiation time on decoloration rate of methyl orange

continues with increasing irradiation time. Degradation rates after 0.5 and 2 h are 31.1% and 92.9%, respectively. The 100% decoloration of the dye can be expected with prolonged irradiation time.

UV-visible absorbance curves of methyl orange solution after different irradiation time are shown in Fig. 6. The two main absorption peaks of methyl orange at 468 nm and 270 nm decline with increasing reaction time. The absorbance of the peak at 468 nm nearly disappears after 4 h of irradiation. The azo structure in the dye is fully degraded during photocatalytic oxidation process.

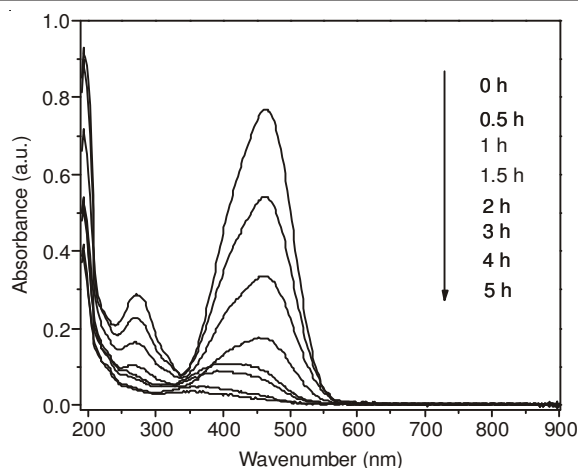


Fig. 6. UV-visible curves of methyl orange after different irradiation time

Conclusion

A SiO₂-TiO₂ photocatalyst was prepared through sol-gel method for photocatalytic degradation of methyl orange. The material is composed of anatase TiO₂ and amorphous SiO₂. No clear evidence of Si-O-Si or Si-O-Ti vibration is found in the FT-IR spectra because of the low concentration of SiO₂ in TiO₂ matrix. The average pore diameter is 13.02 nm and the total pore volume is 0.2004 cm³ g⁻¹ along with specific surface area of 61.56 m² g⁻¹. Methyl orange degradation continues with increasing irradiation time. The azo structure in the dye is fully degraded during photocatalytic oxidation process.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 41271251) and the Open Research fund of Key Laboratory of Wastewater Treatment Technology of Liaoning Province, Shenyang Ligong University.

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