

## Effects of Calcination Time on Structure and Activity of Porous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Photocatalyst

WENJIE ZHANG<sup>1,\*</sup>, HONGLIANG XIN<sup>1</sup>, RUYUAN LI<sup>1</sup> and HONGBO HE<sup>2</sup>

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

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

\*Corresponding author: Tel: +86 24 83978969; E-mail: metalzhang@yahoo.com.cn

(Received: 19 March 2012;

Accepted: 14 January 2013)

AJC-12691

A novel porous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite nano-material was prepared by sol-gel preparation method. The materials prepared after different calcination times were all composed of anatase TiO<sub>2</sub> and amorphous Al<sub>2</sub>O<sub>3</sub>. Crystallite sizes of anatase TiO<sub>2</sub> were 10.06, 10.55 and 11.13 nm for the samples calcinated for 1, 2 and 3 h, respectively. The surfaces of the materials were very rough with long grooves on the surface. BET specific area, pore volume and average pore size of the materials varied with calcination time. The sample calcinated for 2.5 h had the maximum specific area of 128.9 m<sup>2</sup> g<sup>-1</sup>. The sample calcinated for 3 h showed the maximum photocatalytic activity and adsorption capacity. The average pore size for the material was 14.56 nm and the total pore volume was 0.3945 cm<sup>3</sup> g<sup>-1</sup> for the sample calcinated for 3 h. After 90 min of reaction, degradation rate of methyl orange on the material was 77.0 % and the total dye decoloration rate was 95.1 %.

**Key Words:** TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Photocatalytic, Calcination.

### INTRODUCTION

Photocatalytic oxidation has grown to be very impressive technique in dealing with environmental pollutions<sup>1-3</sup>. A number of published literatures have reported the satisfactory future both on fundamental theory and applicable research in this field. The development of new photocatalytic materials with high activity is always the research focus in this field. There are two ways to improve the photocatalytic activity of TiO<sub>2</sub> based materials. One is doping with other elements, such as noble metals<sup>4,5</sup>, heavy metals<sup>6,7</sup> and rare earth elements<sup>8,9</sup>. Another way is to prepare TiO<sub>2</sub> based composite photocatalytic materials, such as TiO<sub>2</sub>-SiO<sub>2</sub><sup>10</sup> and SnO<sub>2</sub>/TiO<sub>2</sub><sup>11</sup>.

The preparation of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite was not reported in the previously published literatures. In our recent work, the combination of TiO<sub>2</sub> and HZSM-5 zeolite showed much improved photocatalytic activity on methyl orange degradation<sup>12</sup>. Here came the idea that combination of TiO<sub>2</sub> with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> might have satisfactory results since the HZSM-5 is composed of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The functions of SiO<sub>2</sub> to the influences on TiO<sub>2</sub> were discussed in other paper<sup>13</sup>.

In this article, a novel porous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite nano-material was prepared by sol-gel preparation method. Precursors were composed of tetrabutyl titanate and aluminum isopropoxide. The composite materials were produced after calcination at 500 °C for different time. The samples were characterized by XRD, SEM and specific surface areas and

pore size distribution. The influences of calcination time on photocatalytic degradation of methyl orange on the TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite were investigated.

### EXPERIMENTAL

**Sol-gel preparation:** A given mass of tetrabutyl titanate, aluminum isopropoxide [n(Ti)/n(Al) = 12], polyethylene glycol (PEG1000) and concentrated hydrochloric acid were added into absolute ethanol under magnetic stirring. Another mixture of deionized water and absolute ethanol was dropped into the former solution at a constant speed. The volume ratio of constituents in the final solution was V[Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]: V(C<sub>2</sub>H<sub>5</sub>OH):V(HCl):V(H<sub>2</sub>O) = 1:5:0.05:0.5. The solution was kept under stirring until the sol and gel formed. The gel was left for 12 h at ambient temperature and dried at 80 °C for 8 h. After that, the samples were grinded and calcinated at 500 °C for different time. The prepared materials were grinded again before use.

**Characterization:** Scanning electron microscope (SEM) images were taken on a HTACHI S-3400N scanning electron microanalyzer. The samples for SEM imaging were coated with a thin layer of gold film to avoid charging. The crystalline phases of the photocatalysts were measured by X-ray diffraction (XRD) with D/max-rB diffractometer using a CuK<sub>α</sub> radiation. The N<sub>2</sub>-adsorption and desorption of the sample was measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. Specific surface areas and pore size

distribution were calculated from the  $N_2$  desorption isotherms, according to Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively.

**Photocatalytic activity:** The photocatalytic activity of  $TiO_2-Al_2O_3$  composite was evaluated by degradation of methyl orange solution under UV light irradiation. The adsorption and photocatalytic activity of the samples were investigated by measuring the decoloration rate of methyl orange (MO) in a lab-scale photocatalytic reactor. The reactor consisted of a 250 mL beaker and a UV lamp hanging over the beaker. The 20 W UV-light lamp with main irradiation wavelength at 253.7 nm was used as a light source to trigger the photocatalytic reaction and the average light intensity was about  $1100 \mu W/cm^2$ . The concentration of methyl orange was calculated by Lambert-Beer law using 721E spectrophotometer. The absorbency of methyl orange was measured at 468 nm corresponding to the maximum absorption wavelength.

The mixed solution of methyl orange and photocatalyst ( $V = 50$  mL,  $C_{MO} = 10$  mg/L) was put into a beaker. Before photocatalytic reaction, the adsorption of methyl orange on photocatalyst was measured in the suspension. The solution was allowed to reach an adsorption-desorption equilibrium under 0.5 h of magnetic stirring in the dark. After that, 5 mL of suspension was taken out of the reactor and was filtered through a Millipore filter (pore size  $0.45 \mu m$ ) to remove the catalyst. The filtrated solution was measured for its absorbency. After that, the remaining methyl orange and photocatalyst suspension was put under UV light irradiation. After a distinct time, 5 mL of suspension solution was removed and filtrated to measure the change of methyl orange concentration. If not indicated, the irradiation time in the subsequent experiments was set to 0.5 h.

## RESULTS AND DISCUSSION

Sol-gel is a widely applied method used for preparation of nano-sized  $TiO_2$  photocatalyst. In order to improve the properties of the photocatalyst, some kinds of techniques such as transition metal doping and composite photocatalyst have been used to enhance the activity of the materials. Porous materials are regarded as one of the promising choice in improving performance on pollutant treatment. Mesoporous and macroporous materials accompanied with large specific surface area are considered to have advanced photocatalytic oxidation efficiency. In order to prepare suitable porous material for the above mentioned purpose, template is always needed in the preparation process as pore formation director. In this paper, polyethylene glycol (PEG1000) was chosen as the template to prepare porous  $TiO_2-Al_2O_3$  composite.

Fig. 1 shows the XRD patterns of porous  $TiO_2-Al_2O_3$  composite materials calcinated at  $500^\circ C$  for different times. It can be seen from the patterns that, all the samples presented anatase  $TiO_2$  crystalline structure. In the current preparation conditions, there was no rutile  $TiO_2$  phase appearing in the patterns. Meanwhile, there were no noticeable diffraction peaks of any of crystalline phases of  $Al_2O_3$ . It indicates that  $Al_2O_3$  was in amorphous phase in the materials. The materials prepared under different calcination times were all composed of anatase  $TiO_2$  and amorphous  $Al_2O_3$ . Since  $n(Ti)/n(Al)$  ratio

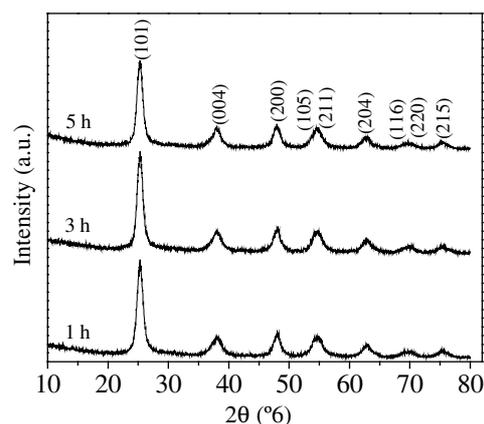


Fig. 1. XRD patterns of porous  $TiO_2-Al_2O_3$  composites calcinated at  $500^\circ C$  for different times

in the materials was 12, anatase  $TiO_2$  matrix composed the main skeleton of the materials and amorphous  $Al_2O_3$  was mixed with  $TiO_2$  crystallite.

Long time calcination can benefit crystalline formation of the material. As calculated from Scherrer formula on (101) plane of the XRD patterns, crystallite sizes of anatase  $TiO_2$  were 10.06, 10.55 and 11.13 nm for the samples calcinated for 1, 2 and 3 h, respectively. The prolonged calcination time can lead to a slight grow up of  $TiO_2$  crystals. However, the crystallite size difference was not large since the diffraction peaks did not have much variation in peak intensity and width. On the other hand, the existence of  $Al_2O_3$  would also prohibit crystalline formation of  $TiO_2$ . Crystallite sizes of anatase  $TiO_2$  were around 10 nm, a size range near nano size that does not usually appear at high temperature calcination.

Fig. 2 shows the SEM images of porous  $TiO_2-Al_2O_3$  composite materials calcinated at  $500^\circ C$  for different times. Surface morphology is a very important technique to study adsorption and photocatalytic activity of the materials. The surfaces of the materials were very rough with long grooves on the surface. The materials were composed of large amorphous like matrix, along with some small particles laying on the surface.

BET specific surface area and average pore size of porous  $TiO_2-Al_2O_3$  composite materials calcinated at  $500^\circ C$  for different times are listed in Table-1. The results reveal that BET specific area, pore volume and average pore size of the materials varied with calcination time. The sample calcinated for 2.5 h had the maximum specific area of  $128.9 m^2 g^{-1}$ . High pore volume and average pore size were possessed by the samples calcinated for 1 and 3 h. Taking the specific surface area for consideration, the data increased at first with increasing calcination time and then declined after even longer time calcination. The reasons are that, short time calcination could not remove organic substances in the materials thoroughly and left a certain content of organic substances existing on the surface of the materials, acting as reducing the surface area. On the other hand, too long time calcination would destroy the porous structure of the material, leading to reduced surface area. The materials had large specific surface area with average pore size between 10-16 nm. It can be expected that the materials might have high adsorption capacity.

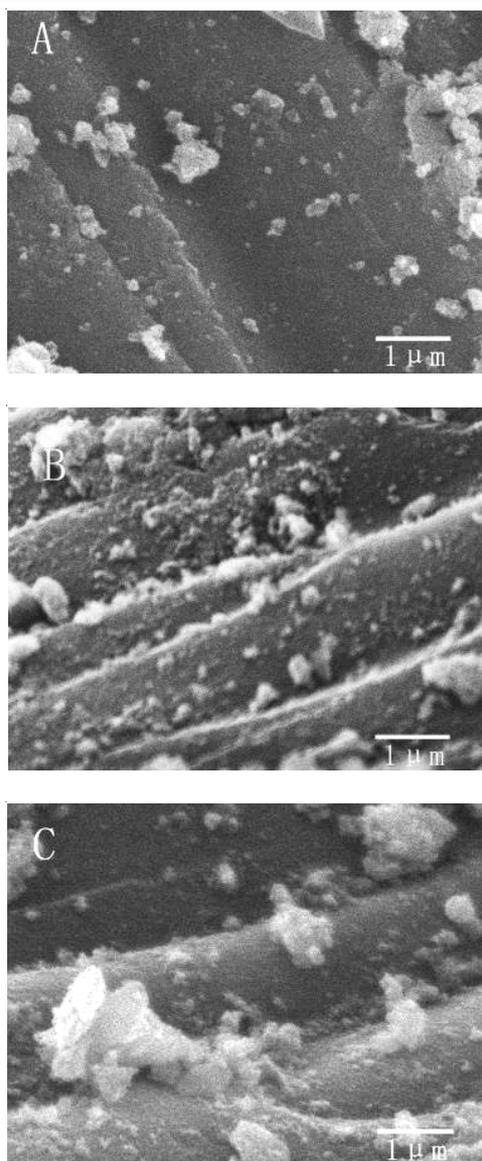


Fig. 2. SEM images of porous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composites calcinated at 500 °C for different times. (A) 1 h, (B) 3 h, (C) 5 h

TABLE-1  
BET SPECIFIC SURFACE AREA AND AVERAGE PORE SIZE OF POROUS TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> COMPOSITES CALCINATED AT 500 °C FOR DIFFERENT TIMES

Time (h)	BET specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
1.0	94.8	0.39	16.6
2.0	124.2	0.33	10.6
2.5	128.9	0.38	11.7
3.0	128.4	0.39	14.6
3.5	115.8	0.39	13.3

Fig. 3 presents effect of calcination time on photocatalytic activity and adsorption of porous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite materials. While being calcinated at 500 °C, photocatalytic activities of the materials increased at first and then dropped down with increasing calcination time. The sample calcinated for 3 h showed the maximum activity of 35 %. Methyl orange adsorption on the materials showed the same trend as photocatalytic degradation. The sample calcinated for 3 h had the maximum adsorption capacity as well. Short time calcination

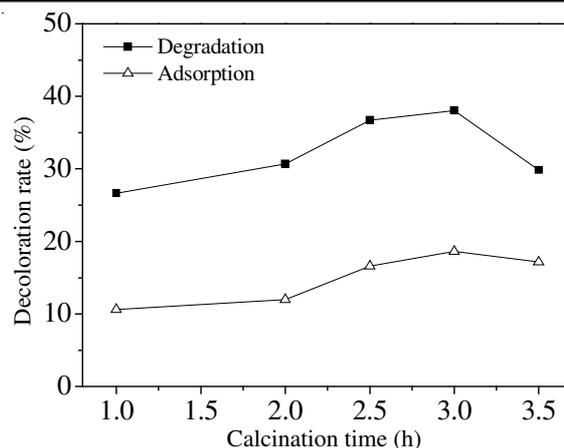


Fig. 3. Effects of calcination time on photocatalytic activity and adsorption of porous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composites

could not remove organic substances in the materials thoroughly and left a certain content of organic substances existing on the surface of the materials, acting as blocking active centers on the surface. On the other hand, too long time of calcination would destroy the porous structure of the material, leading to reduced active centers on the surface.

Fig. 4 shows the pore size distribution of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite calcinated at 500 °C for 3 h. The pore size distribution is not even in the whole pore size range. When pore size is 7.1 nm, the maximum pore volume of the material is 0.066 cm<sup>3</sup> g<sup>-1</sup>. The average pore size for the material is 14.6 nm and the total pore volume is 0.39 cm<sup>3</sup> g<sup>-1</sup>, as calculated from BJH method.

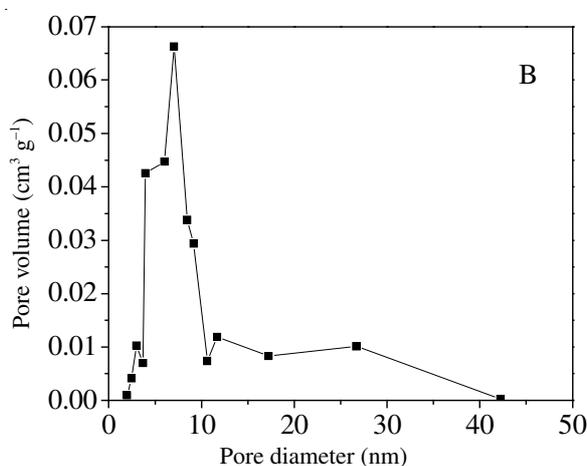


Fig. 4. Pore size distribution of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite calcinated at 500 °C for 3 h

In order to obtain porous structure, suitable template needs to be used to bond with precursors in sol-gel system. There are some chemical compounds that have been used as templates, such as surfactants and copolymers. Polyethylene glycol [H-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-OH] is one of nonionic templates and dissolves easily in polar solvents. In sol-gel system, three-dimensional structure of precursor is formed preferably by crosslink action among hydrolyzates and polyethylene glycol. Porous materials with arranged structure can be prepared by removing polyethylene glycol template through thermal treatment subsequently.

The pore size of the material distributes in a comparatively narrow range around 7 nm. Therefore, the material represents the characters of mesoporous structure. The material is regarded to have good adsorption capacity due to the high total pore volume. Since adsorption of organic pollutants on the material is the initial step for photocatalytic oxidation, the material having high pore volume and suitable pore size distribution is believed to have good performance during photocatalytic degradation process.

The activity of the  $\text{TiO}_2\text{-Al}_2\text{O}_3$  composite calcinated at 500 °C for 3 h is shown in Fig. 5. Methyl orange decoloration is composed of two parts, adsorption of the dye on photocatalyst and photocatalytic degradation of the dye under UV light irradiation on the photocatalyst. Adsorption of the dye can reach a maximum value after the system reaches its adsorption equilibrium and cannot increase further with reaction time. On the other hand, photocatalytic degradation of the dye increases with irradiation time. Methyl orange adsorption on the material reached its equilibrium value after 0.5 h, where 18.6 % of the initial methyl orange molecules were adsorbed on the photocatalyst. Photocatalytic degradation of methyl orange continued constantly with prolonged irradiation time. After 90 min of reaction, methyl orange degradation rate on the material was 77.0 % and the total dye decoloration rate was 95.1 %, containing both adsorption and photocatalytic degradation.

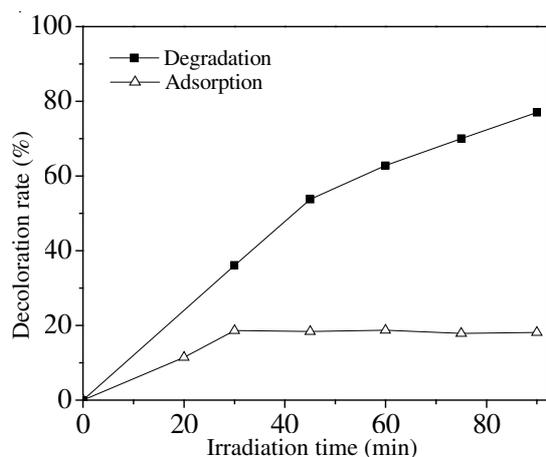


Fig. 5. Effects of irradiation time on activity of the  $\text{TiO}_2\text{-Al}_2\text{O}_3$  composite calcinated at 500 °C for 3 h

## Conclusion

Porous  $\text{TiO}_2\text{-Al}_2\text{O}_3$  composite nano-materials were prepared by sol-gel preparation method. The materials had large specific surface area with average pore size between 10-16 nm. BET specific area, pore volume and average pore size of the materials varied with calcination time. While being calcinated at 500 °C, photocatalytic activities of the materials increased at first and then dropped down with the increasing calcination time. The pore size of the material distributes in a comparatively narrow range around 7 nm. Therefore, the material represents the characters of mesoporous structure. Photocatalytic degradation of methyl orange continued constantly with prolonged irradiation time. After 90 min of reaction, methyl orange degradation rate on the material was 77.0 % and the total dye decoloration rate was 95.1 %.

## ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 41071161), National Key Basic Research Foundation of China (2011CB403202) and Liaoning Science and Technology Project (2010229002).

## REFERENCES

- M.R. Hoffmann, S.T. Martin, W. Choi and W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
- A. Fujishima, T.N. Rao and D.A. Tryk, *J. Photochem. Photobiol. C*, **1**, 1 (2000).
- M.I. Litter, *Appl. Catal. B*, **23**, 89 (1999).
- Q.Y. Li, K. Wang, S.L. Zhang, M. Zhang, J.J. Yang and Z.S. Jin, *J. Mol. Catal. A*, **258**, 83 (2006).
- H.M. Sung-Suh, J.R. Choi, H.J. Hah, S.M. Koo and Y.C. Bae, *J. Photochem. Photobiol. A*, **163**, 37 (2004).
- W.C. Hung, Y.C. Chen, H. Chu and T.K. Tseng, *Appl. Surf. Sci.*, **255**, 2205 (2008).
- R. Khan and T.J. Kim, *J. Hazard. Mater.*, **163**, 1179 (2009).
- Y.N. Huo, J. Zhu, J.X. Li, G.S. Li and H.X. Li, *J. Mol. Catal. A*, **27**, 237 (2007).
- M.T.S. Adrián, G.S. Cláudia, D. Goran and L.F. Joaquim, *Catal. Today*, **44**, 13 (2009).
- S. Qourzal, N. Barka, M. Tamimi, A. Assabbane, A. Nounah, A. Ihlal and A. Ait-Ichou, *Mater. Sci. Eng. C*, **29**, 1616 (2009).
- S.F. Chen, L. Chen, S. Gao and G.Y. Cao, *Mater. Chem. Phys.*, **98**, 116 (2006).
- W.J. Zhang, K.L. Wang, Y. Yu and H.B. He, *Chem. Eng. J.*, **163**, 62 (2010).
- H. Li, Q. Li and W.J. Zhang, *Adv. Mater. Res.*, **214**, 40 (2011).