Al-B-TiO$_2$ Photocatalyst Prepared by Solvothermal Method

HONG LI[1], XIAOFANG HAN[1], WENJIE ZHANG[1,*] and HONGBO HE[2]

[1]School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, P.R. China
[2]Institute of Applied Ecology, The Chinese Academy of Sciences, Shenyang 110016, P.R. China

*Corresponding author: Tel: +86 13609880790; E-mail: metalzhang@yahoo.com.cn

Al-B-TiO$_2$ photocatalysts were prepared by solvothermal method using tetrabutyl titanate, tributyl borate and aluminum isopropoxide as the initial precursors at calcination temperature of 400 ℃ or 500 ℃. Boron doping content was fixed at 3 % in all the samples and aluminum content varied in different samples. The adsorption volume of N$_2$ on the material increased at higher N$_2$ relative pressure P/P$_o$. The pore sizes of the material distributed mainly in the range from 2-20 nm. The total pore volumes were 0.352 and 0.321 mL/g and BET specific surface areas were 113.24 and 78.6 m^2/g for the materials calcined at 400 and 500 ℃, respectively. The maximum degradation rate, 34.1 % degradation of the initial methyl orange, appeared on the sample containing 1 % Al at calcination temperature of 500 ℃.

Key Words: TiO$_2$, Photocatalytic, Solvothermal, Calcination.

INTRODUCTION

TiO$_2$ based composite materials have been studied since some researchers reported that this type of composite has better activity than pure TiO$_2$[1-3]. In many of the preparation method in synthesizing such kind of materials, doping technology is applied as an effective method to improve photocatalytic activity of TiO$_2$-based materials[4,5]. Boron has been studied to promote photogenerated charges separation in TiO$_2$ because boron doped TiO$_2$ attracted much attention. Zaleska[6] used a simple surface impregnation method to prepare boron modified TiO$_2$ and boron as a B-O-Ti species existed in the surface of TiO$_2$ grains. Al can be the other choice because Al is considered to be an effective electron donor in doping into other metal oxide matrix[7,8].

In many of the synthesizing methods, solvothermal method is a widely applied technique. In this paper, Al-B-TiO$_2$ photocatalysts were prepared by solvothermal method using tetrabutyl titanate, tributyl borate and aluminum isopropoxide as the initial precursors. The N$_2$-adsorption and desorption of the sample were measured and the activity of Al-B-TiO$_2$ was evaluated by degradation of methyl orange solution under UV light irradiation.

EXPERIMENTAL

Material preparation: Al-B-TiO$_2$ photocatalysts were prepared by solvothermal method. Tetrabutyl titanate of chemical pure grade was chosen as the Ti precursor and tributyl

borate (99.5 %) was used as the boron source. Aluminum isopropoxide was used as aluminum source. Hydrochloric acid and anhydrous ethanol were in the analytical reagent grade. 8 mL anhydrous ethanol and 0.1 mL hydrochloric acid were mixed in a beaker and then 2 mL tetrabutyl titanate and desired volume of tributyl borate and aluminum isopropoxide were added drop wise to the former solution under constant magnetic stirring to prepare solution 1. Meanwhile, 1 mL of distilled water was mixed with 4 mL anhydrous ethanol to prepare solution 2. After solution 1 was stirred for 0.5 h, solution 2 was added drop wise into solution 1. The solution was moved to a 100 mL PTFE high pressure stainless reactor and was maintained at 120 ℃ for 24 h. After cooling, the solid was filtered and dried at 80 ℃ for 8 h. After that, the solid was grinded and calcined at 400 ℃ or 500 ℃ for 3 h. The obtained materials were ascribed as Al-B-TiO$_2$ in the following experiments. Boron content in the materials was fixed at 3 wt % of the amount of TiO$_2$. Aluminium content was indicated in the following experiments.

Characterization: The N$_2$-adsorption and desorption of the sample were 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 activity of Al-B-TiO$_2$ was evaluated by degradation of methyl orange (MO) solution

under UV light irradiation. Before photocatalytic experiment, adsorption of methyl orange solution in the dark on the photocatalyst was measured in the suspension. 50 mL of 10 mg/L methyl orange aqueous solution was mixed with 30 mg photocatalyst in a 250 mL beaker. The suspension was stirred magnetically for 20 min to reach adsorption equilibrium. After that, 5 mL suspension was taken out of the reactor and filtrated through a millipore filter (pore size 0.45 μm) to remove the photocatalyst. Finally, absorbency of the solution was measured using a 721E spectrophotometer at the methyl orange maximum absorption wavelength of 468 nm. Photocatalytic activities of the prepared catalysts were evaluated afterwards. A 20 W ultraviolet lamp was located over the 250 mL beaker with a distance of 11 cm from the lamp to the surface of the solution. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 1100 μW/cm^2. Irradiation time in the subsequent experiments was set for 0.5 h except for the prolonged time reaction. After photocatalytic reaction, 5 mL of the suspension was filtrated through millipore filter to measure the change of methyl orange concentration.

RESULTS AND DISCUSSION

In this paper, tetrabutyl titanate, tributyl borate and aluminum isopropoxide were used as the initial precursors in solvothermal method. Boron doping content was fixed at 3 % in all the samples and aluminum content varied in different samples. Therefore, the purpose of this paper was to study the influences of aluminum content on properties of the composite material. The samples were prepared at calcination temperatures of 400 and 500 ºC.

Photocatalytic activities of Al-3 % B-TiO$_2$ samples with different Al contents were studied (Fig. 1). The Al-3 % B-TiO$_2$ containing different amount of Al were all calcinated at 400 ºC. Methyl orange decoloration was composed of two parts, photocatalytic degradation and adsorption of the dye on the materials. It is very interesting that, adsorption rate of methyl orange on the materials increased greatly with the increase of doped Al amount. Although the material without doping of Al had very low adsorption capacity, the adsorption rate on the material containing 10 % Al was as high as 85 %. That means nearly most of the dye was adsorbed on the surface of the material. The addition of Al had a complex influence on photocatalytic activity of the materials. The maximum degradation rate, 34.1 % degradation of the initial methyl orange, appeared on the material containing 1 % Al. Photocatalytic activity of the materials containing higher amount of Al had much lower values.

Although adsorption and photocatalytic degradation can both result in decoloration of the dye, the mechanisms are different. In our purpose, a photocatalytic material is the one that has good photocatalytic activity and certain adsorption ability because adsorption is also important for the photocatalytic degradation mechanism. However, adsorption of the dye does not mean that the dye is degraded. The photocatalytic oxidation of organic substances can lead to entire degradation of the pollutants. In this paper, the materials containing high amount of Al had too high adsorption capacity and not too high photocatalytic activity, so that the optimal material can be chosen as containing 1 % Al.
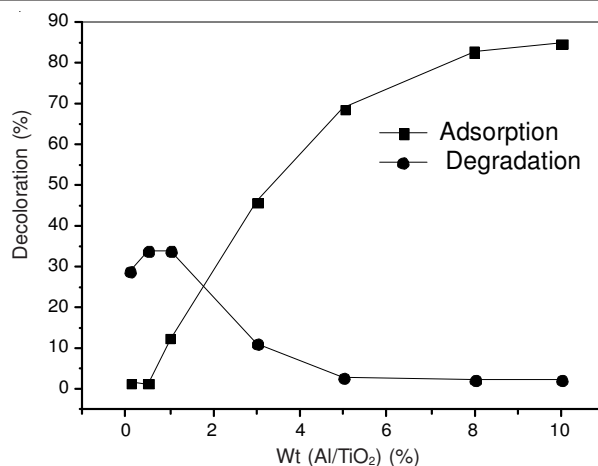

Fig. 1. Photocatalytic activities of Al-3 % B-TiO$_2$ samples with different Al contents at calcination temperature of 400 ºC

Fig. 2 shows N$_2$ desorption isotherms of 1 % Al-3 % B-TiO$_2$ sample. The adsorption volume of N$_2$ on the material increased at higher N$_2$ relative pressure P/P$_o$. When N$_2$ relative pressure was low, the N$_2$ molecules covered on the surface of the material in monolayer and multilayer. When the relative pressure P/P$_o$ was between 0.75 and 0.9, desorption amount changed largely since the porous structure of the material detained the desorption of N$_2$ molecules from surface of the material. The N$_2$ molecules condensed in the micropores inside the material due to capillary effect.
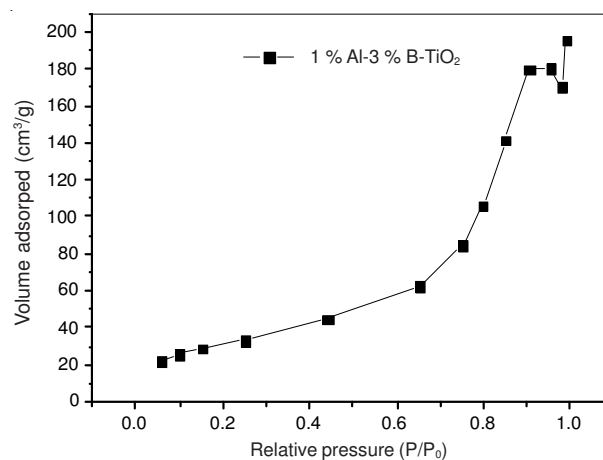

Fig. 2. N$_2$ desorption isotherm of 1 % Al-3 % B-TiO$_2$ sample calcinated at 400 ºC

BJH pore size distribution of 1 % Al-3 % B-TiO$_2$ sample is presented in Fig. 3. The pore sizes of the material distributed mainly in the range from 2 to 20 nm. The large pores appeared in the figure came from interface of large particles in the material. Although pore size distribution was not in a narrow range, the most appeared pore size was around micropore size and the average pore size was 12.45 nm. The total pore volume was 0.352 mL/g and BET specific surface area was 113.24 m^2/g for the material. As compared with the 3 % B-TiO$_2$, which had a surface area of 109.6 m^2/g, the sample containing Al had a higher surface area. The increase of surface area can inevitably add influence on adsorption capacity of the material.
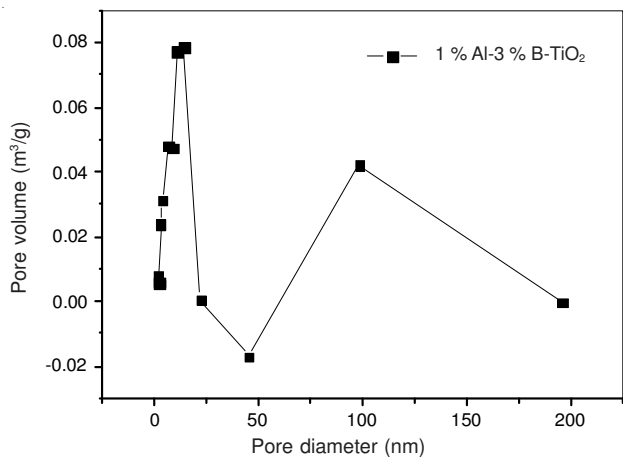
Fig. 3. BJH pore size distribution of 1 % Al-3 % B-TiO$_2$ sample calcinated at 400 ºC

Photocatalytic activities of Al-3 % B-TiO$_2$ samples with different Al contents calcinated at 500 ºC are shown in Fig. 4. The maximum photocatalytic activity occurred in the sample with composition of 0.5 % Al. The activity of the sample without Al doping was weaker than the 0.5 % Al-3 % B-TiO$_2$ sample. On the other hand, the samples containing more Al showed much lower photocatalytic activities than the sample 0.5 % Al-3 % B-TiO$_2$. The optimum photocatalytic activity was 31.7 % in the sample 0.5 % Al-3 % B-TiO$_2$.
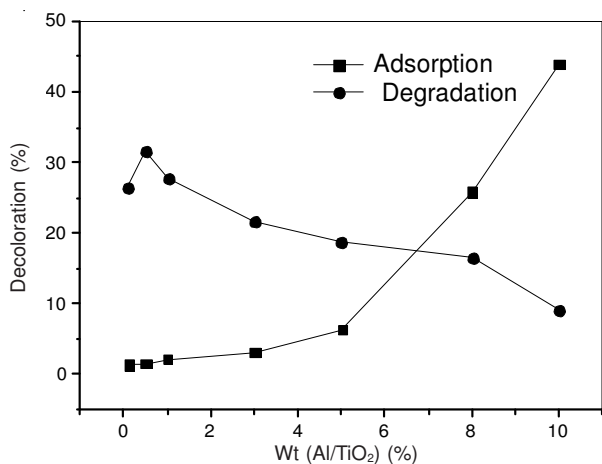

Fig. 4. Photocatalytic activities of Al-3 % B-TiO$_2$ samples with different Al contents calcinated at 500 ºC

The adsorption of methyl orange on the materials increased with the increase of Al content in the samples. The adsorption capacity raised drastically after the Al content was more than 5 %. The adsorption rate was even more than photocatalytic degradation rate when Al content was more than 7 %. It indicates that the addition of Al can obviously influence photocatalytic activity and adsorption capacity of the materials.

Fig. 5 shows N$_2$ desorption isotherms of 0.5 % Al-3 % B-TiO$_2$ samples. N$_2$ adsorption volume increased constantly with increasing relative pressure of N$_2$ up to P/P$_o$ = 0.7. Porous structure is very important for the adsorption capacity of the composite material. Microporous material becomes more and more popular recently in the field of photocatalysis. Fig. 6 shows BJH pore size distribution of 0.5 % Al-3 % B-TiO$_2$
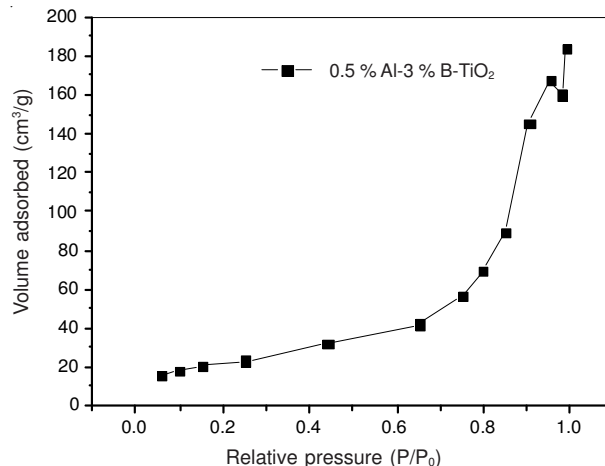

Fig. 5. N$_2$ desorption isotherms of 0.5 % Al-3 % B-TiO$_2$ samples calcinated at 500 ºC
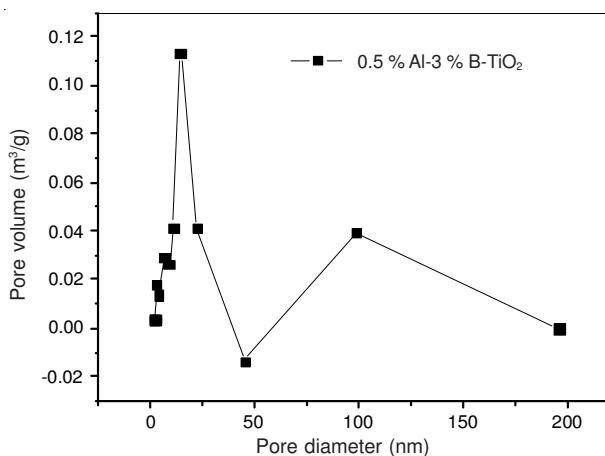

Fig. 6. BJH pore size distribution of 0.5 % Al-3 % B-TiO$_2$ sample calcinated at 500 ºC

samples. It indicates that pore size of the material mainly distributed in the range between 2 and 20 nm. Pore size distribution is not even in the whole range. The average pore diameter of 0.5 % Al-3 % B-TiO$_2$ was 16.34 nm, as calculated using BJH method. The total pore volume of the material was 0.321 mL/g and the BET specific surface area was 78.65 m^2/g. High temperature calcination may cause particles growing in the material. Pore size in the material may also become larger with the growing up of particles size. These might in turn cause shrink of surface area.

Conclusion

Al-B-TiO$_2$ photocatalysts were prepared by solvothermal method at calcination temperature of 400 and 500 ºC. The N$_2$-adsorption and desorption of the sample were measured and the activity of Al-B-TiO$_2$ was evaluated by degradation of methyl orange solution under UV light irradiation. Pore size distribution was not in a narrow range and the most appeared pore size was around micropore size. Although the material without doping of Al had very low adsorption capacity, methyl orange adsorption on the materials increased with the increase of Al content in the samples. The addition of Al can obviously influence photocatalytic activity and adsorption capacity of the materials.

ACKNOWLEDGEMENTS

REFERENCES

1. M. Cho, H. Chung, W. Choi and J. Yoon, *Water Res*., **38**, 1069 (2004).
2. A. Kalaivani, P. Satheeshkumar, G. Senguttuvan, V. Sivakumar and C.S. Dilip, *Asian J. Chem.*, **25**, S324 (2013).
3. L.H. Mahajan and S.T. Mhaske, *Mater. Lett*., **68**, 183 (2012).
4. R. Khan, S.W. Kim, T.J. Kim and C.M. Nam, *Mater. Chem. Phys*., **112**, 167 (2008).
5. N. Lu, H.M. Zhao, J.Y. Li, X. Quan and S. Chen, *Sep. Purif. Technol*., **62**, 668 (2008).
6. Zaleska, E. Grabowska, J.W. Sobczak, M. Gazda and J. Hupka, *Appl. Catal. B*, **89**, 469 (2009).
7. H. Song, M. Dai, Y. Guo and Y. Zhang, *Fuel Process Technol*., **96**, 228 (2012).
8. I. Alekseeva, O. Dymshits, M. Tsenter and A. Zhilin, *J. Non-Crystall. Solids*, **357**, 2209 (2011).