Asian Journal of Chemistry; Vol. 26, No. 6 (2014), 1670-1672

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17319

Preparation of Nano-Al_2O_3 Powder Using Huainan Coal Gangue by Ultrasonic†

LINYI ZHENG*, YIN LIU, BIAO HU and CHUYANG XU

School of Materials Science and Engineering, Anhui University of Science and Technology, Huinan, Anhui-232001, P.R. China

*Corresponding author: E-mail: lyzheng@aust.edu.cn

Published online: 10 March 2014; AJC-14860

Preparation of nano-Al_2O_3 powder was investigated by ultrasonic using Huainan coal gangue in this work. The calcine activation temperature was determined by differential thermal analysis combined with thermal gravity analysis (DTA/TG). The products were characterized by X-ray diffractometry, scanning electron microscopy and laser particle size analyzer. The results showed that kaolinite in Huainan coal gangue turned from crystal to amorphous at 515 ºC, the conversion rate of aluminum was 89.14 % by ultrasonic assisted acid leaching after calcination at 600 ºC and ultrasonic and dispersant had pronounced effects on preventing agglomeration in the process of generating ammonium aluminum carbonate hydroxide gel in high purity $AlCl_3$ solution. Granulometric distributions of Al_2O_3 powder, calcinate of ammonium aluminum carbonate hydroxide were 11-42 nm. Those Al_2O_3 particles were near-spherical and the median particle diameter (D_{50}) was 20 nm.

Keywords: Coal gangue, Calcine activation, Acid leaching, Ultrasonic, Nano-Al_2O_3.

INTRODUCTION

The discharge of coal gangue, waste of coal industry, takes up 15 to 20 % of raw coal output. According to statistics, the accumulated stacking of coal gangue in China exceeds 4.5 billion tons and it has brought a great many negative effects on the ecological environment of mining areas[1-5]. Many scholars have laid strong foundations for the preparation of Al_2O_3 by using coal gangue, which not only utilizes the high valued-added coal gangue but provides effective ways to improve the ecological environment[6-9].

EXPERIMENTAL

Chemical composition and phases of coal gangue: Due to the different mineralization and origins, the chemical composition and phases of coal gangue vary greatly. The main chemical composition (Table-1) of Huainan coal gangue, which is adopted in this experiment, are SiO_2 and Al_2O_3 and its main phases are kaolinite and quartz.

Chemical reactions during preparation: Related chemical reactions during preparation of nano-Al_2O_3 by using coal gangue are as following.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{550\sim650\ ^{\circ}C} Al_2O_3 \cdot 2SiO_2 + H_2O \uparrow$$

$$Al_2O_3 \cdot 2SiO_2 + 6HCl + H_2O \rightarrow 2AlCl_3 + 2H_4SiO_4 \downarrow$$

$$Al^{3+} \xrightarrow{OH^-;pH=9-10} Al(OH)_3 \xrightarrow{OH^-;pH=10-12} AlO_2^-$$

$$Fe^{3+} \xrightarrow{OH^-,pH=7\sim8} FeOOH \xrightarrow{OH^-,pH=9\sim12} Fe(OH)_3 \downarrow$$

$$Ti^{4+} \xrightarrow{OH^-;pH=9-12} Ti(OH)_4 \downarrow$$

$$NaAlO_2 + HCl \rightarrow NaCl + AlCl_3 + H_2O$$

$$AlCl_3 + 4NH_4HCO_3 \rightarrow NH_4AlO(OH)HCO_3 \downarrow + 3NH_4Cl + 3CO_2 \uparrow + H_2O$$

$$NH_4AlO(OH)HCO_3 \rightarrow NH_3 \uparrow + H_2O \uparrow + CO_2 \uparrow + AlO(OH)$$

$$AlO(OH) \rightarrow Al_2O_3$$

Elimination method of powder agglomeration: In the process of precipitation, ultrasonic and dispersant were used to prevent agglomeration. Ultrasonic cavitation exists in ultrasonic field and that in liquid could produce high temperature and high pressure microenvironment (cavitation nucleus), shock wave and micro-jet. Consequently, it significantly improves the nucleation rate of the precipitation and simultaneously inhibits secondary nucleation and aggregation of crystal nucleus[10]. Dispersant absorbs on the surface of particles, thereby forming a layer of hydrophilic film. The film increases

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

TABLE-1
CHEMICAL COMPOSITION OF HUAINAN COAL GANGUE (wt. %)

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	TiO_2	Na_2O
wt. (%)	61.14	29.47	4.70	1.33	1-3	0.45	0.74	1.28

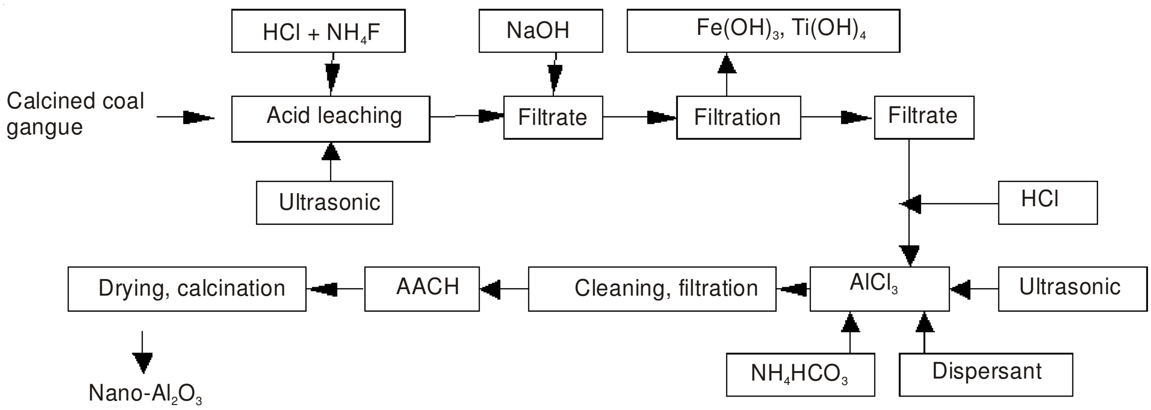

Fig. 1. Flow chart of preparation of nano-Al_2O_3 from coal gangue

the steric hindrance and widens the distance among colloidal particles so as to prevent agglomeration[11]. Before drying, ammonium aluminum carbonate hydroxide should be washed by absolute ethyl alcohol to eliminate agglomeration[12]. The mechanisms of action are as following: First, the functional groups of ethyl alcohol are able to replace the unbridging hydroxide radicals, which are on the surface of colloidal particles, thus increasing the steric hindrance among particles and inhibiting secondary grain growth. Second, ethyl alcohol is capable of washing off the water molecules those are on the surface of colloidal particles to avoid the formation of hydrogen bonds and to decrease the water absorbed on the particles, consequently to prevent hard agglomeration.

Experimental procedures: After being calcinated and activated, coal gangue was ultrasonic-assisted leached by adding in 20 % HCl solution. Then high purity $AlCl_3$ solution was obtained by adding in NaOH solution to remove the impurities. Ammonium aluminum carbonate hydroxide gel came into being after adding excessive amounts of NH_4HCO_3 and dispersant into high purity $AlCl_3$ solution under the effect of ultrasonic. Finally, nano-Al_2O_3 was obtained through filtration, cleaning by ethyl alcohol, drying and calcination. Fig. 1 shows the flow chart of preparation of nano-Al_2O_3 from coal gangue.

Characterization methods: The structure change of coal gangue after calcination was examined by X-ray powder diffraction (XRD-6000, Shimadzu Co., Japan). The calcining process of coal gangue was analyzed by DTA/TG technology (SDT2960, TA, USA). The size, feature and agglomeration of the Al_2O_3 particles were observed by the scanning electron microscope (S-3000N, Hitachi Ltd., Japan). The distribution of the Al_2O_3 particles was analyzed by using laser particle size analyzer (S-3000N, Shimadzu Co., Japan).

RESULTS AND DISCUSSION

Calcination activation of coal gangue: A series of physical, chemical and structural changes took place during the heat treatment of coal gangue. Fig. 2 showed the DTA-TG curve of coal gangue (test conditions: air atmosphere, heating rate

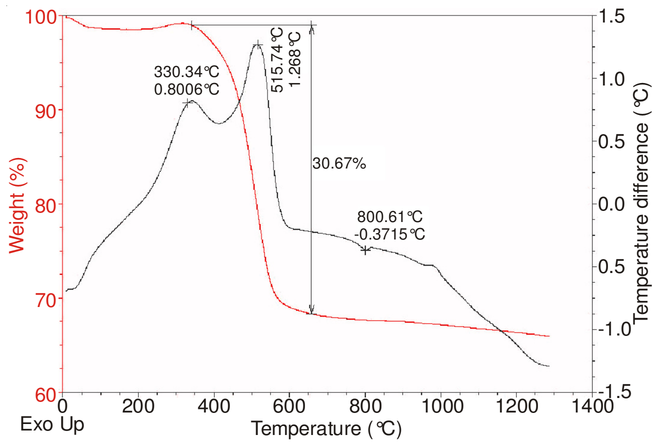

Fig. 2. DTA-TG curve of coal gangue

of 10 °C/min, from room temperature to1300 °C). Fig. 3 presented the XRD patterns of calcined coal gangue at 600 °C (test conditions: CuK$_\alpha$ radiation, step length of 0.02°, at 40 kV and 300 mA). As can be seen from Figs. 2 and 3, below 330 °C, water absorbed on the surface of kaoline and water of crystallization evaporated. The weight loss was unapparent and the crystal structure did not change obviously. The stage from 330-600 °C was an endothermic process and the weight loss was obvious. More specifically, the endothermic peaks between 330 and 515 °C were caused by the heat absorption and volatilization of the volatile components in coal gangue and the heat absorption and weight loss were caused by the structure transformation of kaoline between 515 and 600 °C. It can be seen from Fig. 3, the XRD patterns of calcined coal gangue at 600 °C turned out to be the amorphous diffraction peaks, which indicated that kaoline turned from crystal to amorphous and its reactivity increased after calcination. The conversion rate of aluminum in coal gangue was 89.14 % by ultrasonic assisted acid leaching.

Particle shape and granulometric distributions of product: Fig. 4 showed the SEM appearance of calcined product Al_2O_3 powder, which was aggregate of near-spherical fine particles with a particle size around 40 nm at 1150 °C. Fig. 5,

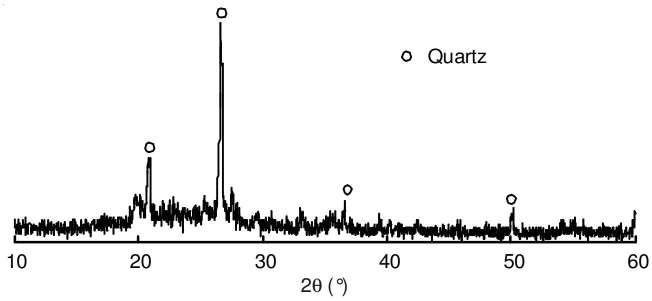

Fig. 3. XRD patterns of calcined coal gangue at 600 ºC

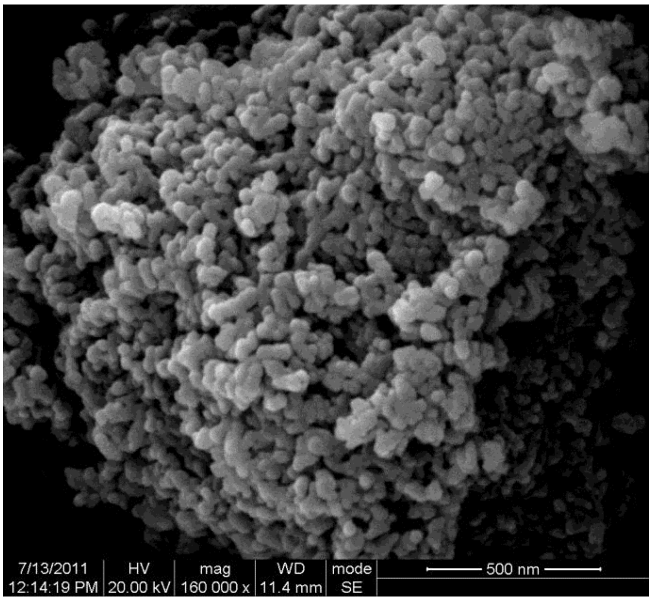

Fig. 4. SEM appearance of Al_2O_3 powder

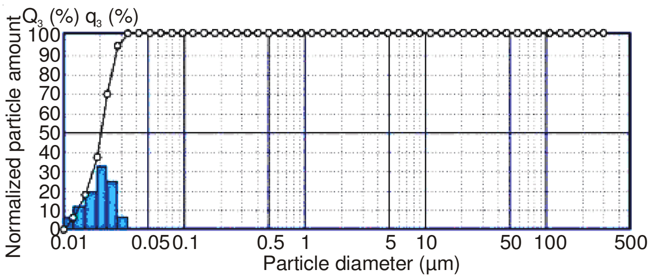

Fig. 5. Laser particle size analysis of Al_2O_3

the laser particle size analysis of Al_2O_3, indicated that granulometric distributions of Al_2O_3 powder were 11-42 nm and the median particle diameter (D_{50}) was 20 nm, which proved that ultrasonic and dispersant had pronounced effects on preventing agglomeration.

Conclusion

Kaolinite in Huainan coal gangue turned from crystal to amorphous at 515 ºC. The reactivity of Huainan coal gangue increased after calcination at 600 ºC and the conversion rate of aluminum was 89.14 % by ultrasonic assisted acid leaching. Ultrasonic and dispersant had pronounced effects on preventing agglomeration in the process of generating ammonium aluminum carbonate hydroxide gel in high purity $AlCl_3$ solution. Granulometric distributions of Al_2O_3 powder, calcinate of ammonium aluminum carbonate hydroxide, were 11-42 nm. Those Al_2O_3 particles were near-spherical and the median particle diameter (D_{50}) was 20 nm.

ACKNOWLEDGEMENTS

This work was supported by research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (Grant No. AE201307) and the Opening Project of Henan Key Discipline Open Laboratory of Mining Engineering Materials (Grant No. MEM20126).

REFERENCES

1. H.J. Wu, F.Y. Zeng and H.F. Yao, *Coal Sci. Technol.*, **4**, 42 (2013).
2. B.Z. Tian and L. Li, *Coal Technol.*, **7**, 195 (2012).
3. R.F. Chalken, L.E. Dalverny and A.G. Kim Controlled burnout at the Albright coal waste banlfire, US Bumines RI19345_(1991).
4. F.G. Bell, S.E.T. Bullock, T.F.J. Halbich and P. Lindsay, *Int. J. Coal Geol.*, **45**, 195 (2001).
5. W.J. Robertson, P.H.M. Kinnunen, J.J. Plumb, P.D. Franzmann, J.A. Puhakka, J.A.E. Gibson and P.D. Nichols, *Miner. Eng.*, **15**, 815 (2002).
6. N.T. Bailey and R.J. Chapman, *Hydrometallurgy*, **18**, 337 (1987).
7. L.X. Gu, J.P. Xia and Z.S. Zhang, *J. Safety Environ.*, **12**, 88 (2012).
8. C.Z. Liu, *Coal Proc. Compreh. Utiliz.*, **1**, 49 (2009).
9. F.Q. Cheng, L. Cui, H. Zhang, J.C. Zhang and S.M. Fan, *Chinese J. Environ. Eng.*, **11**, 99 (2007).
10. C.F. Chen and Z.G. Chen, *Mater. Mech. Eng.*, **27**, 30 (2003).
11. S.Y. Lu and Y.Q. He, *Mater. Rev.*, **20**, 149 (2006).
12. A. Singhal, G. Skandan, A. Wang, N. Glumac, B.H. Kear and R.D. Hunt, *Nanostructured Mater.*, **11**, 545 (1999).