Front. Chem. China 2008, 3(2): 198–202
DOI 10.1007/s11458-008-0038-8

RESEARCH ARTICLE

Fang LI, Kejing XU, Cheng DONG, Juan CHEN

Study on catalyst carrier nano-α-alumina with high specific surface area

Abstract A nano-alumina with high specific area was prepared using a homogeneous precipitation method with titanium dioxide and barium oxide as modifying additives. Results showed that 5 wt% TiO_2 or BaO added in the alumina gels can decrease the particle size and increase the specific area, but excessive TiO_2 or BaO could deteriorate the properties of α-Al_2O_3.

Keywords nano-alumina, homogeneous precipitation method, TiO_2/BaO-doping, specific surface area

1 Introduction

The surface effect is one important feature of nanomaterials. With the decrease of particle size, the surface area increases greatly. The activity of particles is closely related to its surface area. The catalytic activity is proportional to the surface area of catalysts if the catalytic reaction rate is not restricted by the mass transfer process. High specific surface area helps the active component of catalysts to disperse well and is extremely beneficial in improving catalytic activity. Nano-alumina particles with the features of resistant high-temperature, corrosion resistance, large specific surface area and high reactive activity are used as carriers of petroleum cracking catalysts [1]. Nano-alumina particle catalysts with small particle size have many fine pores and high reactive selectivity, and their pore size, pore volume and the voidage distribution could be controlled. The crystal phase, specific surface area, pore distribution and other physical-chemical properties of nano-alumina particles specific to the needs of catalytic reactions of petroleum cracking can be obtained by changing the preparation conditions of nano-alumina particles. The performance of nano-alumina particle carriers are much more superior to similar products used currently [2]. TiO_2-doping has potential application in catalytic reactions owing to its excellent electrical, optical, catalytic nature and unique surface properties, as well as steady physical and chemical properties. In addition, TiO_2-doping can promote the diffusion of aluminum vacancies in alumina, prevent high-temperature sintering, and increase the reactive activity and thermal stability of alumina [3]. Similarly, BaO-doping can also modify the properties of alumina [4]. In this work, nano-alumina particle carriers with high specific surface area were prepared via a homogeneous precipitation method with TiO_2 or BaO as modifying additives.

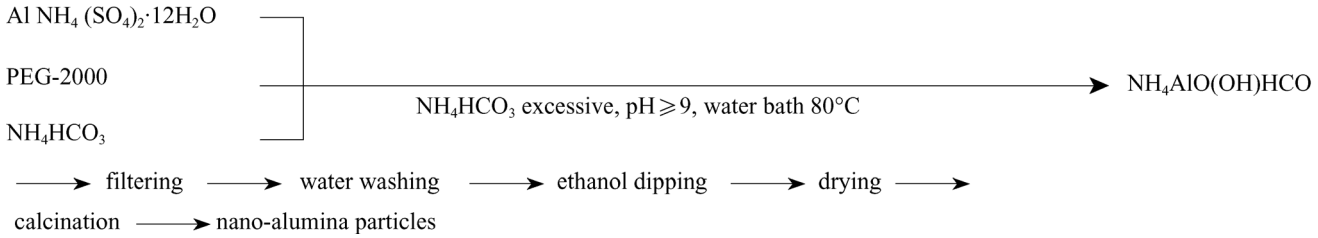
Translated from *Journal of Shandong University of Technology* (*Natural Science Edition*), 2007, 27(3): 23–26 [译自: 山东理工大学学报(自然科学版)]

Fang LI, Kejing XU (✉), Cheng DONG, Juan CHEN
School of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, China
E-mail: xukj@sdut.edu.cn

2 Experimental

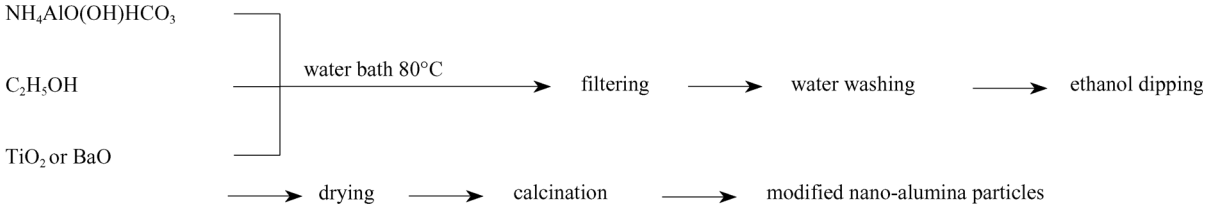
2.1 Preparation of nano-α-Al_2O_3 particles

A 0.5 mol/L ammonium aluminum sulfate (Al $NH_4(SO_4)_2 \cdot 12H_2O$) solution was used as the starting solution, a 1.7 mol/L ammonium bicarbonate (NH_4HCO_3) solution was used as a precipitant, and polyethylene glycol 2000 (PEG-2000) of appropriate quantities were used as dispersers. Nano-α-Al_2O_3 particles were prepared via a homogeneous precipitation method, and the sample was numbered as sample Al. The preparation process of sample Al is shown as follows.



2.2 Preparation of modified nano-α-Al_2O_3 particles

The nano-alumina samples were modified using TiO_2 or BaO as modifying additives with suitable proportions. The TiO_2/Al_2O_3 samples prepared by adding TiO_2 of 5 wt% and 10 wt% were named as sample T1Al and sample T2Al, respectively. The BaO/Al_2O_3 samples prepared by adding BaO of 5 wt% and 10 wt% were named as sample B1Al and sample B2Al, respectively. The modification process is shown as follows.



2.3 Characterization of performances

The microstructure and particle distribution of the samples were observed by Sirion 200 scanning electron microscopy (SEM). The specific surface areas of the samples were determined by a NOVA300 BET meter. The elemental contents of the samples were determined by a ZXS100e 5700 X-ray fluorescent analyzer. Results are shown in Table 1.

Table 1 Elemental content of the samples

elemental content/%	Ti	Ba	Al	O
Sample Al	0	0	22.57	77.55
Sample T1Al	3.42	0	21.32	75.26
Sample T2Al	6.63	0	18.34	75.03
Sample B1Al	0	4.49	19.69	75.82
Sample B2Al	0	8.78	16.09	75.13

3 Results and discussion

3.1 Controlling for synthetic conditions

The concentration of reactants and pH value are the key points in the preparation of nano-alumina particles by the homogeneous precipitation method. Al $NH_4(SO_4)\cdot 12H_2O$ and NH_4HCO_3 reacted under different concentration of reactants and pH conditions to obtain different products.

$$AlNH_4(SO_4)_2\cdot 12H_2O + 4NH_4HCO_3 \rightarrow NH_4AlO(OH)HCO_3\downarrow + 2(NH_4)_2SO_4 + 3CO_2\uparrow + 13H_2O \quad (1)$$

$$AlNH_4(SO_4)_2\cdot 12H_2O + 3NH_4HCO_3 \rightarrow AlO(OH)\downarrow + 2(NH_4)_2SO_4 + 3CO_2\uparrow + 13H_2O \quad (2)$$

The following reactions could have occurred before $NH_4AlO(OH)HCO_3$ was obtained [5].

$$NH_4^+ + AlO(OH)_2^- + HCO_3^- \rightarrow NH_4AlO(OH)HCO_3 + OH^- \quad (3)$$

$$AlO(OH)_2^- \rightarrow AlO(OH) + OH^- \quad (4)$$

When the concentrations of $[NH_4^+]$, $[AlO(OH)_2^-]$ and $[HCO_3^-]$ are high enough, precipitation of the $NH_4AlO(OH)HCO_3$ occurs. Experiments have shown that when the initial concentrations of NH_4HCO_3 and $NH_4Al(SO_4)_2$ are more than 1.5 mol/L and 0.5 mol/L, respectively, and the pH value is 8.0~10.0, the concentrations of $[NH_4^+]$, $[AlO(OH)_2^-]$ and $[HCO_3^-]$ in this reactive system become high enough to enable reaction (3) to proceed in a positive direction and form $NH_4AlO(OH)HCO_3$ precipitate. Thus, the concentration of the reactants were set at $[Al\ NH_4(SO4)_2.12H_2O] = 0.5$ mol/L and $[NH_4HCO_3] = 1.7$ mol/L, respectively, and the pH value was controlled between 9.0 and 10.0. The excess coefficient of the reactants was more than 1.2 under these experimental conditions. Suitable quantities of polyethylene glycol 2000 (PEG-2000) were then added into this reactive system. The alumina particle sample that was prepared was loose,

and was calcined at 1050°C for 1 h. Finally, the α-Al_2O_3 particle sample was obtained.

The SEM photographs of sample Al are shown in Fig. 1. As seen from Fig. 1, the particle size was 65.5 nm~82.7 nm and the distribution of particles was uniform without obvious hard aggregates. The specific surface area of the sample Al was 85.25 m^2/g. There were no impurities according to the elemental analysis results.

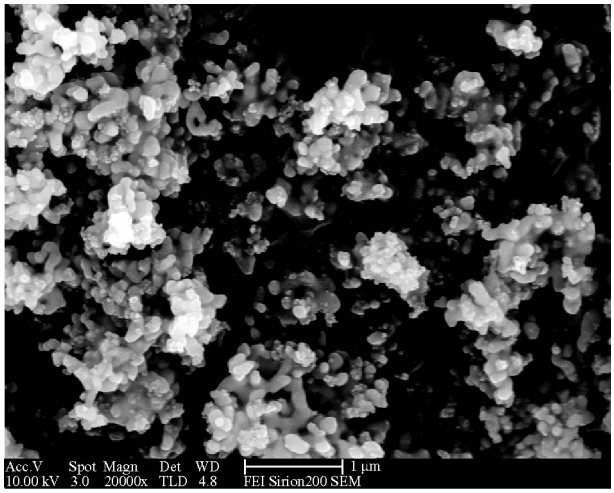


Fig. 1 SEM photograph of sample Al

3.2 Modification of alumina by TiO_2

The microscope photographs of α-Al_2O_3 with 5 wt% TiO_2 (sample T1Al) and 10 wt% TiO_2 (sample T2Al) are shown in Figs. 2 and 3, respectively. The particle size of sample T1Al was 30.33 nm~48.29 nm, and the specific surface area was 91.67 m^2/g. The particle size of sample T1Al was 38.42 nm~53.77 nm, and the specific surface area was 80.43 m^2/g. As seen from Figs. 2 and 3, the crystal phase of the alumina in the two samples were both of the α-Al_2O_3 phase. The alumina particles modified by TiO_2 (5 wt%) were arranged automatically in an ear-corn structure with 500 nm long and 200 nm width. Such a structural arrangement increases the specific surface area by about 6.42 m^2/g. It shows that the particles were arranged together without obvious hard aggregates and were placed with each other in a seemingly automatic manner. There are reasons for this phenomenon, such as the static electricity effect of the powder surface.

TiO_2 has three crystal phases, *i.e.* brookite, anatase and rutile. The brookite and anatase phases can be irreversibly transferred into rutile at 642°C and 915°C, respectively. Therefore, the crystal phase of TiO_2 is rutile at 1050°C. Wang et al. [6] reported that the diffusion rate of aluminum vacancy is the key step when TiO_2 is added into Al_2O_3, and the self-diffusion coefficient of aluminum vacancy is

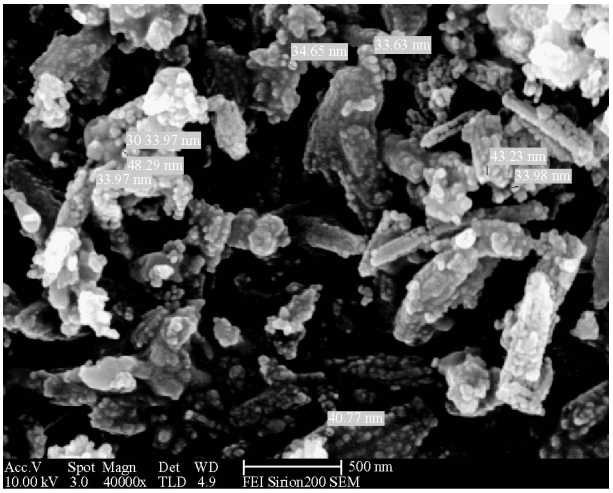


Fig. 2 SEM photograph of sample T1Al

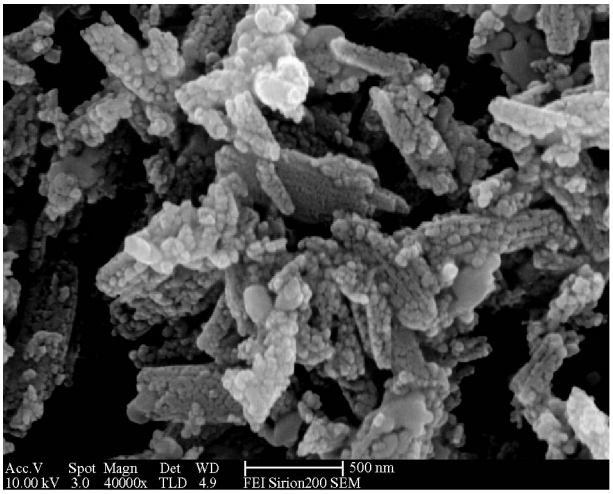


Fig. 3 SEM photograph of sample T2Al

$$D^* = (C_\gamma / S)_\chi D_v \tag{5}$$

Where, D^* is the self-diffusion coefficient, C_γ is the concentration of the aluminum vacancy, S is the case concentration of the aluminum, and D_γ is the body diffusion coefficient of the aluminum ions. The formulation (5) shows that D^* is directly proportional with C_γ. Ti exists in Al_2O_3 with three and four valences at the same time. The reaction mode is

$$3Ti_{Al}^{\times} + \frac{3}{4}O_2 \rightarrow 3Ti_{Al}^{\bullet} + V_{Al}''' + \frac{3}{2}O_O^{\times} \tag{6}$$

$$K_1 = \frac{\left[Ti_{Al}^{\bullet}\right]^3 \left[V_{Al}'''\right]}{\left[Ti_{Al}^{\times}\right]^3 (p_{O_2})^{\frac{3}{4}}} \tag{7}$$

When K_1 is larger, or most of the Ti atoms are of four valences, the reaction is

$$3TiO_2 \rightarrow 3Ti_{Al}^{\bullet} + 6O_O^{\times} + V_{Al}^{'''} \quad (8)$$

and the main aluminum vacancies result in Ti, so

$$\left[V_{Al}^{'''}\right] \approx \frac{1}{3}\left[Ti_{Al}^{\bullet}\right] \approx \frac{1}{3}[Ti]_{total} \quad (9)$$

Thus, Ti added into the Al_2O_3 can increase the diffusion coefficient of aluminum vacancies, and the α-phase transition can be carried out at a lower temperature. The reason may be related to the surface of the α-$A1_2O_3$ covered by TiO_2. In the calcination process, TiO_2 particles can accumulate on the surface of α-Al_2O_3 particles and increase the grain growth rate and form the ear-corn structure. The addition of TiO_2 in alumina particles not only modifies the microstructure of the particles, but also modifies the surface structures of alumina and makes the surfaces load a large number of negative charges. This may be because $Ti^{4+}$and $A1^{3+}$ ions have almost the same ionic radius ($r_{Ti^{4+}} = 0.065$ nm, $r_{Al^{3+}} = 0.061$ nm) [6]. Through atomic diffusion, small amounts of Ti^{4+} ions diffuse into the crystal of α-$A1_2O_3$ and result in the particles loading positive charges on their inner surface. In order to keep neutral, the external surfaces of the particles will load negative charges. At a higher temperature, more Ti^{4+} ions diffuse into the alumina crystal, and result in a greater surface potential. The particles could be dispersed because the electrostatic force and the particle size is smaller. On the other hand, the TiO_2 particles coating the surfaces of α-$A1_2O_3$ particles make the nanoparticles form "spike-like" or "rod" structures. Such structures have a greater specific surface area, which benefit the catalysis process.

A suitable amount of TiO_2-doping in the $A1_2O_3$ can decrease the particle size of α-$A1_2O_3$, and increase the specific surface area. But an excessive amount of TiO_2-doping could make TiO_2 react with α-$A1_2O_3$ to create an intermediate phase or to form liquid interface with α-phase. The atoms in the intermediate phase or liquid phase have a greater diffusion rate than those in the γ-phase. Therefore, the kinetic process of α-phase transformation is faster, and results in α-phase growth and agglomeration.

3.3 Modification of alumina by BaO

$BaCl_2$ was used as a source substance for the BaO modifier, which was mixed with the $A1_2O_3$ precursor, and the final process was the same as above. The specific surface area of sample B1Al with 5 wt% of BaO was 93.61 m^2/g, and that of sample B2Al with 10 wt% of BaO was 82.34 m^2/g. Compared with the pure α-Al_2O_3 without modification, the surface area of sample B1Al increased by 8.36 m^2/g, but the surface area of sample B2Al decreased. The SEM photographs of α-Al_2O_3 added with 5 wt% BaO (sample B1Al) and 10 wt% BaO (sample B2Al) are shown in Figs. 4 and 5, respectively. As seen from the SEM photographs, the samples modified by BaO had a similar shape with the ones modified by TiO_2, and that was a rod structure with a length of 500 nm. Their surface area obviously increased and the particle size decreased. Alkaline-earth metal oxides can also stabilize $A1_2O_3$ structure. Results show that BaO reacts with $A1_2O_3$ to form aluminate, which stops the diffusion of $A1^{3+}$ ions, and BaO added into alumina can also change the structure of the $A1_2O_3$ particles and form aluminate phases ($BaA1_2O_4$ and $BaA1_{12}O_{19}$). Therefore, BaO-doping helps the stability of α-Al_2O_3 catalytic properties at high-temperature. However, excessive BaO could cause the performance deterioration of α-$A1_2O_3$.

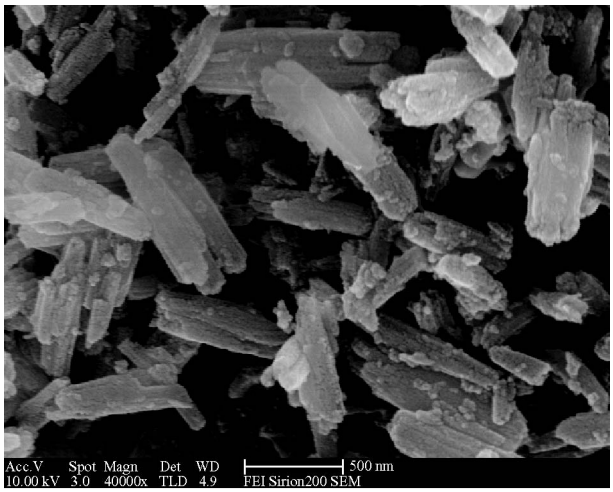


Fig. 4 SEM photograph of sample B1Al

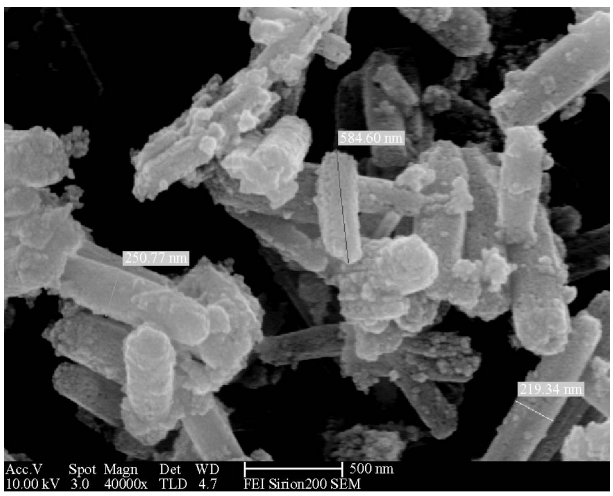


Fig. 5 SEM photograph of sample B2Al

4 Conclusions

(1) The perfect $NH_4AlO(OH)HCO_3$ precursor can be obtained by controlling the appropriate excessive NH_4HCO_3, more than 1.2 of the excess coefficient, and keeping pH at a value of 9~10, when α-Al_2O_3 particles are prepared via the homogeneous precipitation method.

When calcination is carried out at 1050°C for 1 h, nano-α-Al_2O_3 particles with a diameter of 65.5 nm~82.7 nm and a specific surface area of 85.25 m^2/g can be obtained.

(2) 5 wt% TiO_2 or BaO-doping can decrease the particle size of α-Al_2O_3 particles and increase the specific surface area to improve catalysis performance. However, excessive TiO_2 or BaO-doping could make α-Al_2O_3 particles grow, the specific surface area decrease, and the catalysis performance of α-Al_2O_3 worsen.

References

1. Wen H L, Chen Y Y, Yen F S, Huang C Y. Size characterization of θ- and α-Al_2O_3 crystallites during phase transformation. Nanostructured Materials, 1999, 11(1): 89–101
2. Wu Z H. Preparation of nanoparticle alumina and its application in catalysis. Industrial Catalysis, 2004, 12(2): 35–39 (in Chinese)
3. Zhu J F, Zhu Y Q. The influence of preparation conditions of Al_2O_3-TiO_2. Chinese Journal of inorganic chemistry, 1999, 15(4): 429–434 (in Chinese)
4. Shi W, He A D, Chen X Y, Chen J M. Comparison of effect of Ba-modification on the thermostabilities of alumina and alumina-supported Pd catalysts prepared from different alumina sources. Journal of Fudan University (Natural Science), 2003, 42(3): 423–427 (in Chinese)
5. Lin H Y, Zhang Z T, Huang Ch Y, Tang Z L, Chen Q M. Preparation of high purity and ultra-fine α-Al_2O_3 powders by pyrolysis of $NH_4AlO(OH)HCO_3$, Journal of the Chinese Ceramic Society, 1998, 13(6), 803–807 (in Chinese)
6. Wang X, Wang P L, Cheng Y B. Effect of TiO_2 and MgO additions on microstructures of Al_2O_3. Journal of inorganic Materials, 2001, 16(5): 979–984 (in Chinese)
7. Bogush G H, Zukoski C F. Study on the formation of mono disperse silica powders. In:Mackenzie J D, Ulrich Dr, eds. Ultrastructure Processing of Advanced Ceramics.New York: John Wiley, 1988, 477
8. Liu Yong, Niu Guoxing, et al. Effect of gelation on thermostability of alumina modified with barium. Chinese Journal of Catalysis, 1999, 20(6): 664–666