

研究论文

以三嵌段共聚物为模板介孔氧化铝的形貌控制合成

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摘要: 以三嵌段共聚物作为结构导向剂, 采用水热法合成了片状和棒状介孔氧化铝, 采用 X 射线衍射仪、场发射透射电子显微镜、低温氮气吸附实验对合成的介孔氧化铝的晶相、形貌和介孔结构进行表征。研究表明, 三嵌段共聚物的引入能够有效调控氧化铝的形貌、介孔结构以及孔参数。三嵌段共聚物在氧化铝前驱体表面的吸附诱导了晶体的取向生长, 并最终形成了棒状氧化铝。

关键词: 三氧化二铝; 介孔; 水热; 结构导向剂; 纳米棒

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Morphology-controlled synthesis of mesoporous alumina dependent on triblock copolymer

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Abstract: In this study, sheet-like and rod-shaped mesoporous aluminas were synthesized with a triblock copolymer as the structure-directing agent *via* hydrothermal method. X-ray diffraction, transmission electronic microscopy and nitrogen adsorption and desorption were performed to determine the crystalline phase, morphology and pore structure of the aluminas. It was found that the morphologies, mesostructures and pore parameters of aluminas can be altered by the introduction of the triblock copolymer. The adsorption of the triblock copolymer on the surface of the alumina gels induced the oriented growth of the crystallines, resulting in the formation of final aluminas nanorods.

Keywords: alumina; mesoporous; hydrothermal; structure-directing; nanorod

Introduction

Due to small size effect, quantum effect, surface

and interface effects, nanomaterials have the excellent performances different from the common materials^[1-2]. Alumina has a variety of different crystal structures^[3-4],

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among which γ - Al_2O_3 is widely used as adsorbent^[5], ceramics^[6], catalyst and catalyst support^[7] due to its large surface area, good mechanical properties, abrasion resistance, corrosion resistance, chemical stability, adsorption capacity, catalytic activity, and other prominent advantages.

It is known that the solution chemistry method is the most common method for alumina synthesis. The preparation methods include precipitation method^[8], microemulsion method^[9], hydrothermal/solvothermal synthesis^[10], solvent evaporation-induced self-assembly strategy^[11], nanocasting route^[10], sol-gel synthesis^[12] and cation-anion double hydrolysis method^[13]. Among these methods, the nanoparticles synthesized by hydrothermal method show good crystallinity and good dispersion. The morphology of alumina can be finely controlled over a wide range of conditions with the help of some structure-directing agents such as block copolymer^[14], cetyltrimethylammonium^[15], sodium tartrate^[16] and polyethylene glycol^[17].

In our previous work, mesoporous aluminas were successfully synthesized with agarose hydrogel or GP-1 (*N*-lauroyl-L-glutamic acid di-*n*-butylamide) organogel as the template by sol-gel method^[18]. The hierarchical meso/macroporous alumina was also obtained by using F127/agarose hydrogel as cotemplates^[19]. In this work, the triblock copolymer F127 was used as the structure-directing agent, aluminum isopropoxide as the aluminum source and water as the solvent to synthesize mesoporous alumina with different morphologies *via* hydrothermal method. The influence of the dosage of F127 on the synthesis of alumina was mainly investigated. The crystalline phase, morphology, mesostructure and surface properties of the synthesized materials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and N_2 adsorption-desorption techniques.

1 Experimental

1.1 Materials

F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) was from Sigma-Aldrich. Aluminum isopropoxide was from Tianjin Guangfu Chemical Reagents, China. Ammonia was obtained from Tianjin Jiangtian Chemical Reagent Company,

China. All the chemicals were used as received without further purification.

1.2 Synthesis of alumina

In a typical synthesis, 54 g distilled water were added to a three-necked flask and heated to 60°C . Then 6.13 g aluminum isopropoxide and 0.525 g F127 were slowly added with stirring. One hour later, ammonia was added to adjust pH of the solution to 8 and stirring was kept for 7.0 h to obtain milky suspension. Then, the white suspension was poured into a 50 ml PTFE-lined hydrothermal reactor and aged for 17 h at room temperature under sealed condition. After aging, the hydrothermal reactor was heated to 150°C for 10 h and then naturally cooled to room temperature. Then, the hydrothermal products were dried at 80°C . The calcination was carried out by heating to 600°C for 3 h with a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$. The molar ratio of water:aluminum isopropoxide:F127 was 1.5×10^5 :1500:1. The product was denoted as Al_2O_3 -*X*. Here *X* is the molar ratio of aluminum isopropoxide to F127, which is 1500:1, 1000:1, 500:1, 60:1 or 30:1. Al_2O_3 - ∞ means no F127 in the synthesis.

1.3 Characterization

X-ray diffraction analysis was carried out by using an X'Pert PRD X-ray diffraction system (Philips X'pert, CuK_α radiation $\lambda = 0.154056 \text{ nm}$, USA). The nitrogen adsorption and desorption isotherms at -196°C were measured using an ASAP analyzer (Tristar3000, Micromeritics, USA). Transmission electronic microscopy (TEM) was taken on JEM-2100F transmission electron microscope (Japan) under a working voltage of 200 kV. Thermogravimetric analyses (TGA) were performed at air atmosphere with a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$ using RIGAKU standard-type spectrometer (Rigaku Corporation).

2 Results and discussion

2.1 TG analysis

In order to determine the optimal calcination temperature, TGA of the hydrothermal product was performed over the temperature range from 100 to 800°C . From the TG curve in Fig. 1, it shows that the template F127 can be removed over 500°C . Therefore, alumina samples were calcined at 600°C to ensure the

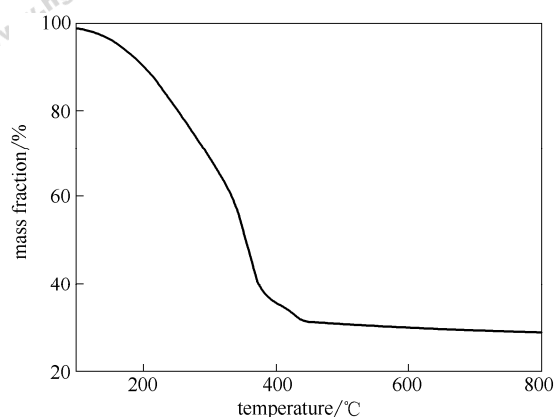


Fig. 1 TG analysis of hydrothermal product over temperature range from 100 to 800°C

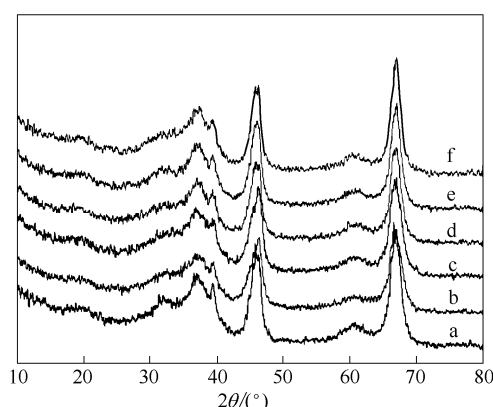


Fig. 2 Wide-angle XRD patterns of aluminas synthesized with different F127 molar ratios

a— Al_2O_3 -∞; b— Al_2O_3 -1500; c— Al_2O_3 -1000; d— Al_2O_3 -500;
e— Al_2O_3 -60; f— Al_2O_3 -30

entire removal of F127 in our experiments.

2.2 Crystalline phases of the aluminas

Fig. 2 illustrates the wide-angle XRD patterns of aluminas calcined at 600°C synthesized with different amounts of F127. All the six different aluminas show four well-resolved diffraction peaks that are indexed as (311), (222), (400) and (440) associated with γ - Al_2O_3 (PDF: 46-1131). Moreover, the diffraction peaks gradually become wider from curve a to f in Fig. 2, which suggests that the addition of F127 can weaken the crystallization process and the crystallite size becomes smaller with the increase of F127 amount. This result is consistent with the latter TEM images (Fig. 3), where the sheet-like structures transform into the rod-like structures, resulting in the smaller size of aluminas. Additionally, small-angle XRD analyses are also carried out. However, no obvious diffraction peak

is found in the SAXRD patterns of the six kinds of aluminas, indicating that their mesopores organizations are all disordered.

2.3 Morphologies of the aluminas

Fig. 3 shows the morphologies of the aluminas. It is obviously seen that alumina presents square-like alumina sheets with no addition of F127 [Fig. 3 (a)]. With the increase of the amount of F127, the dominant morphology keeps sheets with many pores and meanwhile small amounts of nanorods appear [Fig. 3 (b), (c)]. With further increase of the dosage of F127 as shown in Fig. 3 (d) and (e), the sheets incline to aggregate into large pieces with fewer pores. The alumina nanorods become more and more with the length of ca. 49 nm, diameter of ca. 1.7 nm and aspect ratio of ca. 29 when the molar ratio of aluminum isopropoxide to F127 reaches 30:1 [Fig. 3 (f)]. These results suggest that the amount of F127 has great impact on the morphologies of aluminas. Higher amount of F127 can induce the formation of rod-like aluminas.

2.4 Mesostuctures of the aluminas

The results of N_2 adsorption-desorption [Fig. 4 (a)] show that all the six kinds of aluminas exhibit classical type IV with a hysteresis loop at high relative pressure. In order to clearly show the curve of N_2 adsorption-desorption, vertical shifts to the curves are applied. All these hysteresis loops are in the high relative pressure range (0.75—1.0), indicating that these aluminas have large pores. Al_2O_3 -30 and Al_2O_3 -60 have similar hysteresis types and much higher adsorption amounts in the higher relative pressure ranged from 0.8—1.0, suggesting the presence of larger pores. From the TEM images [Figs. 3 (a)—(f)], it is found that all the six kinds of alumina mainly consist of nanosheets. It can be concluded that two types of pores including mesopores of alumina and slit-shaped pores attributed to the aggregation of the nanosheets are coexistent. Fig. 4 (b) shows the pore size distributions of the alumina. Clearly, the pore size increases with the increase of F127 amount. The pore size distributions of Al_2O_3 -500, Al_2O_3 -1000, Al_2O_3 -1500 and Al_2O_3 are centered at 10 nm. Al_2O_3 -60 has a bi-modal pore size distribution centering at 9 nm and 15 nm, while the pore size of Al_2O_3 -30 centers at 15 nm. It

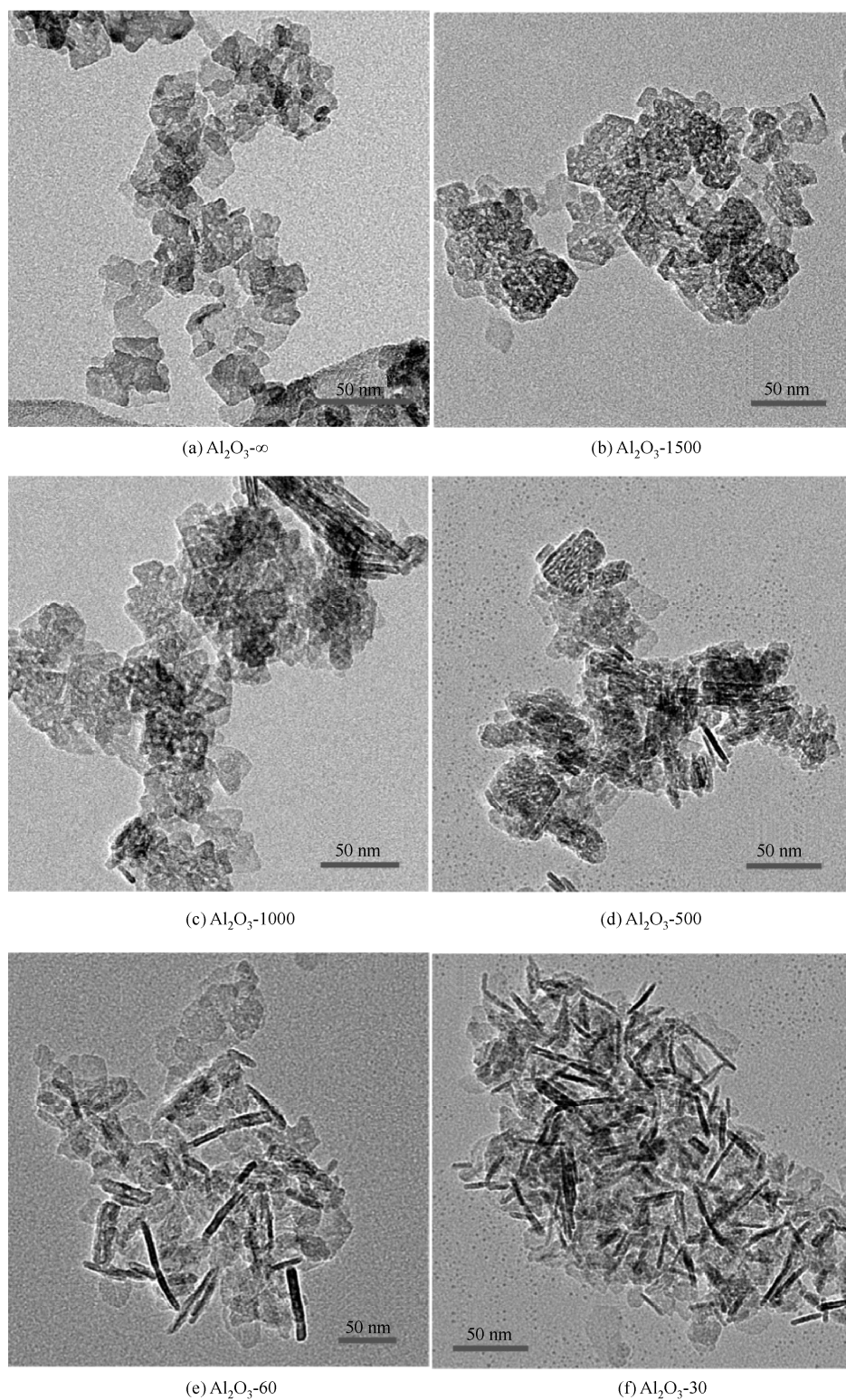


Fig.3 TEM images of aluminas synthesized with different F127 molar ratios

suggests that the increase of F127 amount in the reaction system can result in bigger congeries of F127, which leads to larger pores after the removal of F127. Furthermore, with the increase of the amount of F127, the BJH specific surface area of the samples gradually

increases until Al_2O_3-60 and Al_2O_3-30 have the similar high surface area of above $250 \text{ m}^2 \cdot \text{g}^{-1}$ (See Table 1).

All the above characterizations indicate that the morphology and mesopore structure of alumina can be changed with the introduction of F127. According to

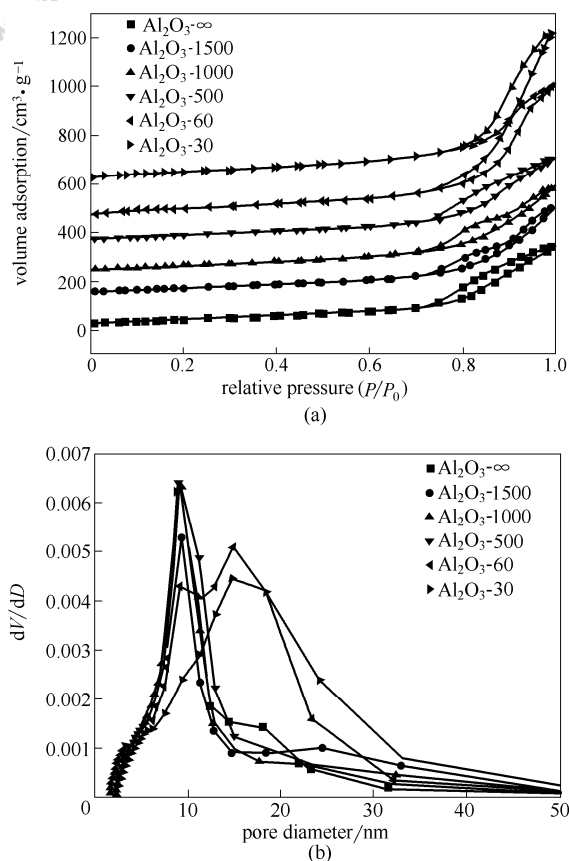


Fig.4 Nitrogen adsorption-desorption isotherms (a) and corresponding pore size distribution (b) for aluminas synthesized with different F127 molar ratios

Table 1 Pore structure parameters of alumina samples prepared with different F127 molar ratios

Sample	BJH surface area /m ² · g ⁻¹	Pore volume /cm ³ · g ⁻¹	Pore size/nm
Al ₂ O ₃ -∞	193	0.53	10.9
Al ₂ O ₃ -1500	188	0.57	12
Al ₂ O ₃ -1000	205	0.56	11
Al ₂ O ₃ -500	212	0.58	10.8
Al ₂ O ₃ -60	257	0.87	13.5
Al ₂ O ₃ -30	253	0.98	15.5

early studies^[20], the hydrophilic alkylene oxide segments forming the outer surface of the micelles are capable of forming crownether-type complexes with metal ions, resulting in coordination bonds between the copolymer and inorganic nanoparticles. During the preparation of the alumina gels, F127 micelles adsorb on the surfaces of the gels *via* hydrogen bonding. The primary boehmite crystallites self-aggregate and grow into nanorods along a certain direction with the lowest growth energy^[14]. As a result, the alumina nanorods

increase with the increase of the F127.

3 Conclusion

The mesoporous aluminas with sheet-like and rod-shaped morphologies are synthesized using triblock copolymer F127 as the structure-directing agent. The mesopore sizes of the synthesized aluminas range from 10.8 nm to 15.5 nm. At the low F127 amount, alumina nanosheets are obtained, and meanwhile, rod-like aluminas can be constructed at the high F127 amount. The adsorption of F127 micelles on the surface of the alumina gels induces the oriented growth of the crystallines and results in different morphologies.

References

- [1] Jun Y W, Choi J S, Cheon J. Shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes [J]. *Angewandte Chemie International Edition*, 2006, **45** (32): 3414-3439.
- [2] Zou G, Li H, Zhang Y, *et al.* Solvothermal/hydrothermal route to semiconductor nanowires [J]. *Nanotechnology*, 2006, **17** (11): S313-S320.
- [3] Al'myasheva O V, Korytkova E N, Maslov A V, *et al.* Preparation of nanocrystalline alumina under hydrothermal conditions[J]. *Inorganic Materials*, 2005, **41** (5): 460-467.
- [4] Zhu H Y, Gao X P, Song D Y, *et al.* Manipulating the size and morphology of aluminum hydrous oxide nanoparticles by soft-chemistry approaches [J]. *Microporous & Mesoporous Materials*, 2005, **85** (3): 226-233.
- [5] Zhang H Y, Shan G B, Liu H Z, *et al.* Preparation of (Ni/W)-gamma-Al₂O₃ microspheres and their application in adsorption desulfurization for model gasoline [J]. *Chemical Engineering Communications*, 2007, **194** (7): 938-945.
- [6] Bartsch M, Saruhan B, Schmücker M, *et al.* Novel low-temperature processing route of dense mullite ceramics by reaction sintering of amorphous SiO₂-coated gamma-Al₂O₃ particle nanocomposites [J]. *Journal of the American Ceramic Society*, 2004, **82** (6): 1388-1392.
- [7] Lietti L, Forzatti P, Nova I, *et al.* NO_x storage reduction over Pt-Ba/gamma-Al₂O₃ catalyst [J]. *Journal of Catalysis*, 2001, **204**: 175-191.
- [8] Wang S, Li X, Wang S, *et al.* Synthesis of γ-alumina *via* precipitation in ethanol [J]. *Materials Letters*, 2008, **62** (20): 3552-3554.
- [9] Lee Y, Hahn Y M, Lee D H. Preparation of spherical γ-Al₂O₃ powder by using aluminum salt under W/O emulsion method [J]. *Journal of Industrial & Engineering Chemistry*, 2005, **11** (1): 27-33.
- [10] Bai P, Su F, Wu P, *et al.* Copolymer-controlled homogeneous precipitation for the synthesis of porous microfibers of alumina [J]. *Langmuir*, 2007, **23** (8): 4599-4605.
- [11] Cai W, Yu J, Jaroniec M. Effect of nonionic structure-directing agents on adsorption and structural properties of mesoporous alumina [J]. *Journal of Materials Chemistry*, 2011, **21** (25): 9066-9072.
- [12] Vinogradov V V, Agafonov A V, Vinogradov A V, *et al.* Sol-gel synthesis, characterization and catalytic activity of mesoporous γ-alumina

- prepared from boehmite sol by different methods [J]. *Journal of Sol-Gel Science and Technology*, 2010, **56** (3): 333-339.
- [13] Bai P, Wu P, Zhao G, *et al.* Cation-anion double hydrolysis derived mesoporous gamma-Al₂O₃ as an environmentally friendly and efficient aldol reaction catalyst [J]. *Journal of Materials Chemistry*, 2008, **18** (1): 1554-1563.
- [14] Cai W, Hu Y, Chen J, *et al.* Synthesis of nanorod-like mesoporous gamma-Al₂O₃ with enhanced affinity towards Congo red removal: effects of anions and structure-directing agents [J]. *Crytengcomm*, 2012, **3**: 972-977.
- [15] Yu M J, Li X, Ahn W S. Adsorptive removal of arsenate and orthophosphate anions by mesoporous alumina [J]. *Microporous & Mesoporous Materials*, 2008, **113**: 197-203.
- [16] Cai W, Yu J, Cheng B, *et al.* Synthesis of boehmite hollow core/shell and hollow microspheres via sodium tartrate-mediated phase transformation and their enhanced adsorption performance in water treatment [J]. *J.Phys.Chem.C*, 2009, **113** (33): 14739-14746.
- [17] Zhu Z, Liu H, Sun H, *et al.* PEG-directed hydrothermal synthesis of multilayered alumina microfibers with mesoporous structures [J]. *Microporous & Mesoporous Materials*, 2009, **123** (1): 39-44.
- [18] Cui X, Tang S, Zhou H. Mesoporous alumina materials synthesized in different gel templates [J]. *Materials Letters*, 2013, **98** (5): 116-119.
- [19] Tang Shaokun, Cui Xili, Gu Ling, *et al.* A novel co-templating method for hierarchical mesoporous alumina monoliths replica [J]. *Functional Materials Letters*, 2013, **6** (1): 363.
- [20] Zhao D, Yang P. Generalized syntheses of large-pore mesoporous metal oxides with semicrystalline frameworks [J]. *Nature*, 1998, **396** (6707): 152-155.