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Synthesis and characterization of mesoporous γ-alumina templated by saccharide molecules

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ABSTRACT

A series of mesoporous alumina was prepared using a selected group of saccharide molecules including glucose, sucrose, starch and β -cyclodextrin as structure-directing templates in aqueous system. The influence of pH value was also investigated. The products were characterized using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Magic-Angle Spinning Nuclear Magnetic Resonance (^{27}Al MAS NMR) and N_2 sorption methods. The results show that the properties of products are influenced by the initial pH value of the system, and the molecular size of the templates has a great effect on the physical properties of products. According to the results and disccusion, the templating formation mechanism was tentatively postulated.

1. Introduction

Since the discovery of the M41S family [1], a number of attempts have been made to synthesize mesoporous alumina having a high surface area with a uniform pore size distribution, because of their potential importance as commercial adsorbents, catalysts and catalysts supports. Many synthetic strategies have been developed based on surfactant assisted (template) sol–gel methods and organic additives [2,3]. Calcination of the produced materials at ≥500 °C normally leads to the formation of thermally stable mesoporous alumina. Preparation of mesoporous aluminas using nanocasting [4,5], template-free solvothermal [6] and microemulsions [7] approach has also been reported. However, up to now, the preparation of relatively stable mesoporous alumina requires strict control of the synthesis condition.

Saccharide molecules have been utilized to prepare mesoporous silica [8]. In this paper, we demonstrate the synthesis of mesoporous alumina using different saccharide molecules in aqueous system. The resultant mesoporous γ-alumina has high surface area and tunable pore size. The effect of the molecular size of template and the pH value was examined and a possible formation mechanism was proposed.

2. Experimental

2.1. Chemicals

Nitric acid was purchased from Beijing Chemical Reagents. Glucose, sucrose, starch, β-cyclodextrin and aluminum isopropoxide were all purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis

In a typical synthesis, 4.2 g of aluminium *i*-propoxide and 3.6 g of glucose were dissolved in 54 mL of distilled water, the resultant solution was stirred at room temperature for 30 min. The molar ratio of Al:glucose:H_2O in the solution was 1:1:75. Then a diluted aqueous nitric acid (10 wt.%) solution was added dropwise to adjust the pH value to 6.0. After standing for 5 h, the mixture was heated at 373 K in open air to remove water and all other volatiles. The resulted solid was then calcined at 873 K for 6 h to remove the template. For sucrose, starch and β-cyclodextrin template, the synthesis procedure is similar to that for glucose, and the pH values are all kept at 6.0. According to the templates used during preparation, the samples were labeled as Al_2O_3-1, Al_2O_3-2, Al_2O_3-3 and Al_2O_3-4 to represent the mesoporous alumina products templated by glucose, sucrose, starch and β-cyclodextrin, respectively, and the molar ratios of template to aluminum are displayed in Table 1. It should be noted that the ratio of starch to aluminum cannot be provided because the molecular weight of starch is not constant. According to the amount of starch utilized during

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Table 1
Characteristics of the mesoporous aluminas templated by different saccharide molecules.

Sample	Template	Template/Al	BET surface area (m^2/g)	Total pore volume (cm^3/g)	BJH pore diameter (nm)
Al_2O_3-1	Glucose	1	404	0.53	4.1
Al_2O_3-2	Sucrose	1	464	0.61	4.4
Al_2O_3-3	Starch	–	299	0.58	5.7
Al_2O_3-4	β-Cyclodextrin	1/7	260	0.66	6.9

The pore diameters were calculated from the desorption branches of their nitrogen adsorption–desorption isotherms.

preparation, the ratio of starch to aluminum can be written to 1 if the molecular formula of starch is considered as $(C_6H_{10}O_5)_1$.

2.3. Characterization

XRD patterns were recorded with Cu Kα radiation on a Philips X'Pert Pro Alpha1 diffractometer.

Porosity and surface area studies were performed on a Micromeritics Tristar 3000 automated gas adsorption system. All the samples were outgassed at 350 °C under vacuum prior to N_2 adsorption at −196 °C. Surface areas were calculated according to the BET equation, while pore size distributions were derived from the desorption isotherm using the BJH model.

TEM studies were performed using a JEOL 4000EX microscope operated at 300 kV. Mesoporous alumina samples were dispersed in acetone using sonication and placed onto formvar carbon covered copper grids and dried under air.

^{27}Al MAS NMR spectra were recorded in the solid state with a Varian Chemagnetics CMX infinity 400 spectrometer.

3. Results and discussion

3.1. XRD

As shown in Fig. 1, the XRD patterns of all the materials exhibit only one diffraction peak, at low angles (1–10° 2θ), which signifies the presence of mesoporous materials with no long range order pore structure.

Fig. 2 shows the XRD patterns of the high angle (10–75° 2θ) area for calcined materials. The diffractogram exhibits some broad crystalline peaks around 35–40° and especially at 45°and 67° 2θ due to the reflection (of X-rays) from the (4 0 0) and (4 4 0) crystal planes, respectively, of the cubic γ-alumina [9].

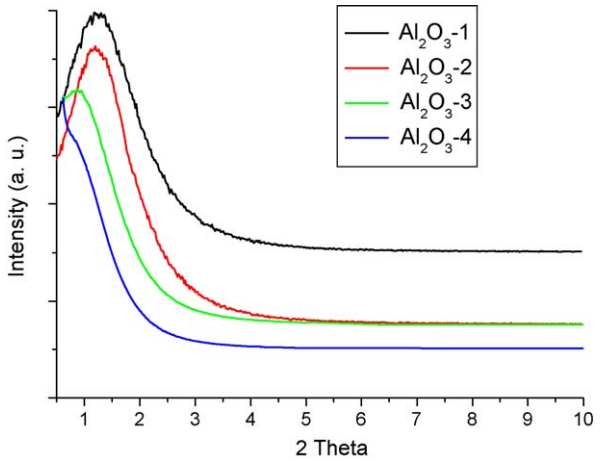


Fig. 1. Powder XRD patterns at low angle of calcined materials prepared with different templates.

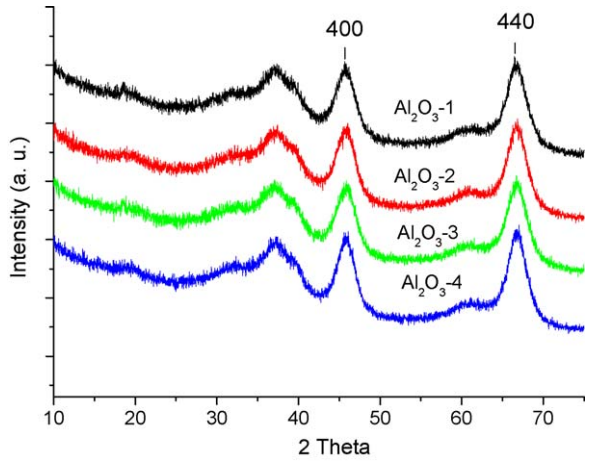


Fig. 2. Powder XRD patterns at high angle of calcined materials prepared with different templates.

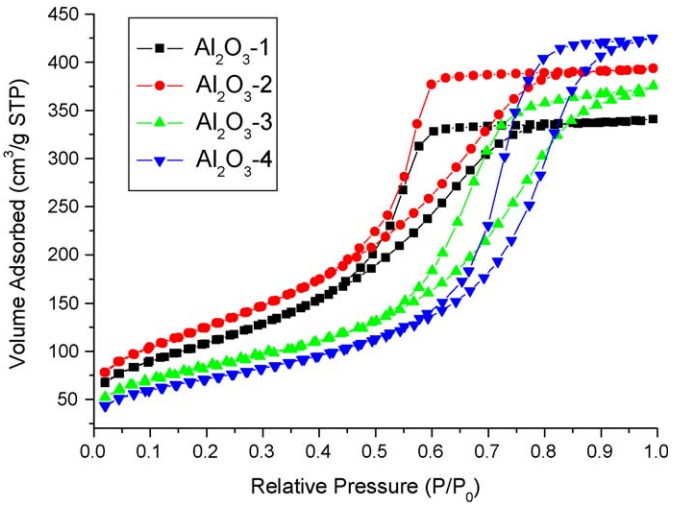


Fig. 3. Nitrogen adsorption–desorption isotherms for mesoporous aluminas templated by different saccharide molecules.

3.2. N_2 adsorption/desorption analysis

The mesoporous structure of γ-alumina has been confirmed by N_2 adsorption/desorption isotherms (Fig. 3). All the samples

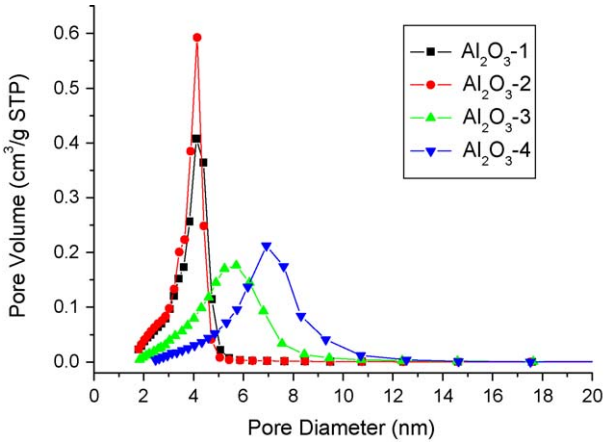


Fig. 4. Pore size distributions for mesoporous aluminas templated by different saccharide molecules.

Table 2
Characteristics of the mesoporous aluminas templated by β-cyclodextrin.

Sample	pH	BET surface area (m^2/g)	Total pore volume (cm^3/g)	BJH pore diameter (nm)
Al_2O_3-5	5.5	282	0.66	7.0
Al_2O_3-4	6.0	260	0.66	6.9
Al_2O_3-6	6.5	253	0.62	6.9
Al_2O_3-7	7.0	242	0.57	6.9

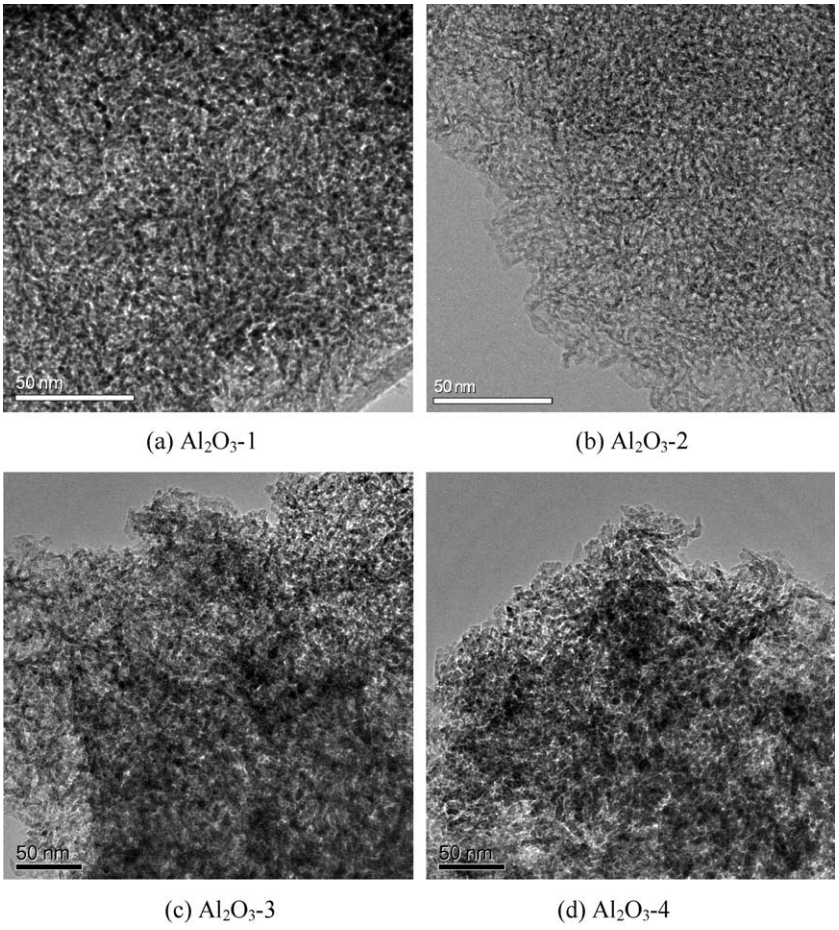
The pore diameters were calculated from the desorption branches of their nitrogen adsorption–desorption isotherms.

present type IV isotherm (definition by IUPAC) [10] which is a characteristic of mesoporous material. The appearance of type H-2 hysteresis loop in the isotherms indicates the presence of "ink-bottle" type pores in the mesoporous Al_2O_3 [11]. They present a well-defined step in the desorption branch of the isotherm curves at P/P_0 value of ca. 0.6–0.8. This is characteristic of capillary condensation within uniform pores, which can be confirmed by the pore size distributions calculated from the corresponding desorption isotherms shown in Fig. 4. And Fig. 4 indicates that the pore distributions of mesoporous aluminas templated by starch and β-cyclodextrin are much broader than those of mesoporous aluminas templated by glucose and sucrose. The reason will be described below.

Textural properties of the mesoporous aluminas prepared by different saccharide molecules templating are presented in Table 1. According to these results, some trends can be identified. For glucose, sucrose and β-cyclodextrin, the most probable pore size and pore volume increased with the increase of molecular size.

It should be noted that the textural properties of the mesoporous aluminas prepared by different saccharide molecules templating can be adjusted by the change of the initial pH value of the system. The influence of pH value on the products templated by glucose has been discussed before [12]. Here, the influence of pH value on the products synthesized from β-cyclodextrin is shown in Table 2. The surface area and pore volume of the prepared mesoporous alumina can be tuned by the pH value. However, the most probable pore size seems to keep stable with the change of pH value. The aggregating of aluminate species can be able to be affected by the pH value of the aqueous system, which will result in the change of the surface area and the pore volume of products. However, the influence of pH value to the β-cyclodextrin's aggregating is very limited because β-cyclodextrin is a kind of oligosaccharide itself, which contains seven glucose monomers in a ring. Therefore, the pore size of the mesoporous alumina products almost has no change with the change of pH value.

Actually, the amount of template used also has great influence on the textural properties of the mesoporous alumina products. It is suggested that one mole of sucrose should be hydrolyzed to one mole of glucose and one mole of fructose in the acidic condition. It is suggested that fructose and glucose should have act as template in the same way because they both have five hydroxyl groups. Therefore, for sample Al_2O_3-2, the amount of template used is equivalent to the double amount of template used for sample Al_2O_3-1. And the surface area, pore volume and pore size of sample Al_2O_3-2 all increase compared to sample Al_2O_3-1 (Table 1), which confirms that the amount of template utilized during preparation also has significant effect on the properties of mesoporous alumina products.



(a) Al_2O_3-1 (b) Al_2O_3-2

(c) Al_2O_3-3 (d) Al_2O_3-4

Fig. 5. TEM image of mesoporous aluminas templated by different saccharide molecules (a) Al_2O_3-1; (b) Al_2O_3-2; (c) Al_2O_3-3; (d) Al_2O_3-4.

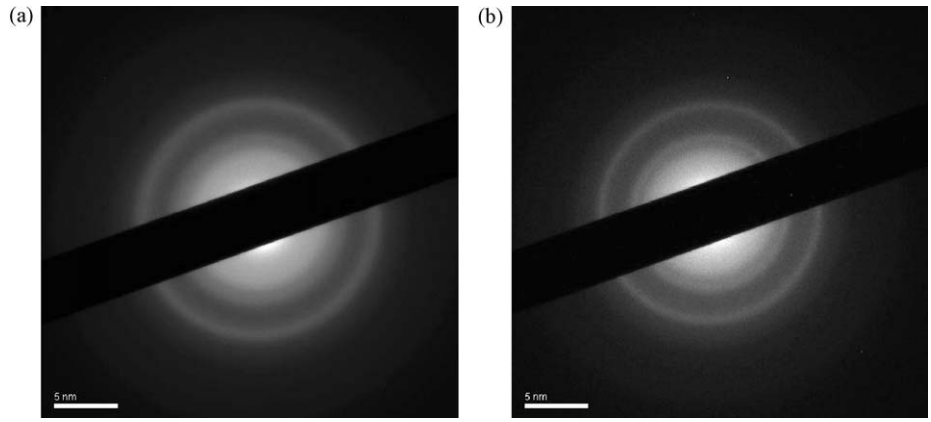


Fig. 6. Electron diffraction patterns of a region of Fig. 5(a) and Fig. 5(b) respectively.

3.3. TEM

TEM images (Fig. 5) of all the mesoporous aluminas prepared by different saccharide molecules templating show wormhole-like appearance and no significant order of pore arrangement, which is in good agreement with the absence of high order peaks in the small-angle X-ray diffraction patterns (Fig. 1).

The electron diffraction patterns (Fig. 6) of mesoporous aluminas synthesized from glucose and sucrose both reveal crystalline phase, which is also in good agreement with the large-angle XRD patterns (Fig. 2). It should be noted that the same results could be obtained for the starch and β-cyclodextrin templated mesoprous aluminas.

3.4. ^{27}Al MAS NMR spectra

The ^{27}Al MAS NMR spectra of the glucose and sucrose templated mesoporous alumina are shown in Figs. 7 and 8. The most intense signal in the spectra at 5.0–6.5 ppm is attributed to the aluminium atoms in an octahedral coordination, and a small signal at 61.0–62.0 ppm is assigned to the tetrahedrally coordinated aluminium [4]. The similar results could also be obtained for the starch and β-cyclodextrin templated mesoprous aluminas.

3.5. Mechanism of mesophase formation

As it is mentioned above, the sucrose template should be hydrolyzed to glucose and fructose in the acidic condition, and the glucose and fructose could be present in forms of aggregates or assembly of the aggregates, whose interactions with the aluminate species through hydrogen bonding might play a significant role in directing the mesophase formation prior to and/or during the gelation [8,12]. The aggregating of aluminate species and saccharide molecules is influenced by pH value, therefore, the surface area, pore size and pore volume can be tuned by the change of pH value. For β-cyclodextrin and starch template, the similar mechanism is also proposed. But the difference is that β-cyclodextrin is a kind of oligosaccharide, and starch is a kind of polysaccharide. It is suggested that β-cyclodextrin and starch should be hydrolyzed to glucose as well in acidic condition, but not completely, and the products hydrolyzed by starch also contain dextrins with different molecular weights, which will lead to the formation of template including various saccharide molecules with different molecular sizes. This will result in the formation of aggregates with different sizes, which will finally lead to the broader pore distribution of mesoporous alumina products templated by β-cyclodextrin and starch (Fig. 4). The larger pore size of mesoporous alumina templated by β-cyclodextrin (Table 1) can be attributed to the much harder hydrolysis of β-cyclodextrin compared with starch, which leads to higher content of β-cyclodextrin in the solution. Therefore, the congeries with larger size can be formed easily, and the aggregating of β-cyclodextrin is hardly influenced by the pH value, which leads to the constant and larger pore size of mesoporous alumina products.

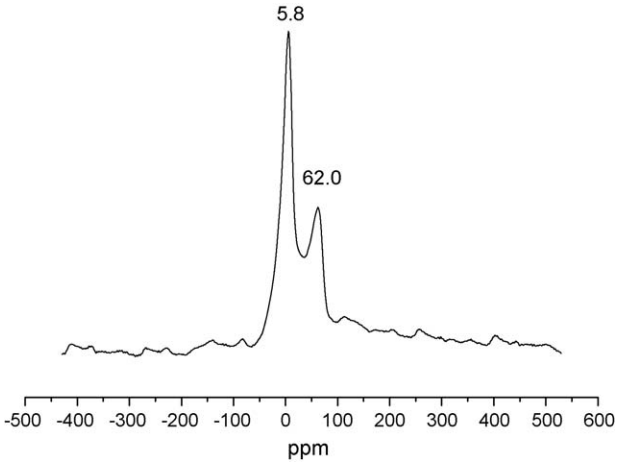


Fig. 7. Solid state ^{27}Al MAS NMR spectrum of sample Al_2O_3-1.

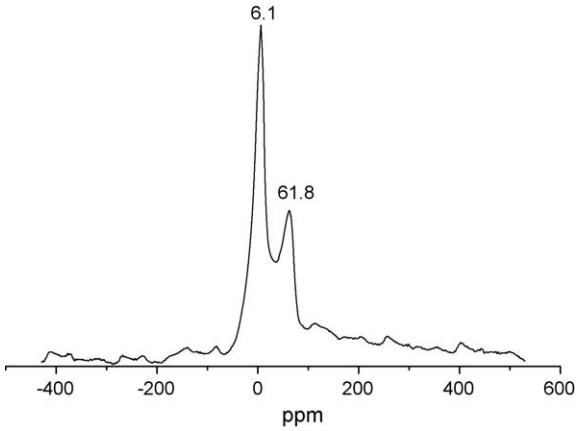


Fig. 8. Solid state ^{27}Al MAS NMR spectrum of sample Al_2O_3-2.

4. Conclusions

Mesoporous aluminas can be produced using a selected group of saccharide molecules including glucose, sucrose, starch and β-cyclodextrin as structure-directing templates in aqueous system. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) results show that the mesoporous alumina products have meosoporous structure with no long range order. The N_2 sorption results show that the physical properties of products are influenced by the molecular size of templates and the initial pH value of the system. It is suggested that the saccharide molecules could be present in forms of aggregates or assembly of the aggregates, whose interactions with the aluminate species through hydrogen bonding might play a significant role in directing the mesophase formation prior to and/or during the gelation. The pore distribution of mesoporous alumina products templated by β-cyclodextrin and starch are much broader. The pore size of mesoporous alumina templated by β-cyclodextrin is hard to be tuned by the change of pH value.

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