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Study on the synthesis of organized mesoporous alumina in a rotating packed bed

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ABSTRACT

In this study, a novel precipitation technology was used to synthesize organized mesoporous alumina (OMA) in a rotating packed bed (RPB) by using aluminum nitrate and ammonium carbonate as the reactants and polyethylene glycol 1540 as the template. The properties of the as-prepared OMA were analyzed by BET, XRD and TEM. The effects of the synthesis conditions, surfactant and pore-expanding agent on OMA properties were explored, and the formation mechanism of OMA was discussed. The experimental results indicated that the excellent micromixing capability of the RPB resulted in the formation of OMA with narrow pore size distribution and uniform structure. It was also found that the high-gravity level, liquid flow rate and mixing time had significant effect on the pore structure of OMA.

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1. Introduction

The first successful synthesis of M41S mesoporous molecular sieves by Mobil researchers [1,2] opened a new era in the research of inorganic molecular sieves. This discovery exhibited exciting possibilities for new types of molecular sieves with a significantly higher surface area and a narrow pore size distribution. These materials have huge potential in many industrial applications including microelectric circuits, electrochemical devices, gas sensors, fuel cells, absorption, and catalysis [3–5].

Organized mesoporous alumina (OMA) is a very interesting molecular sieve [6]. Because of the remarkable features of OMA and its potential applications in industry, many studies have been directed to the production of OMA with high surface area and narrow pore size distributions in the mesoporous range. Wu et al. [7] presented the synthesis of mesoporous alumina materials with an ordered 2D hexagonal structure, surface area of 309 m²/g, pore volume of 0.51 cm³/g, pore size of 7.5 nm, and thermal stability of 900 °C. Deng et al. [8] reported the synthesis of mesoporous aluminas by using the nonionic templating method, and investigated the characterization the mesoporous aluminas. Žilková et al. [9] presented the synthesis of organized mesoporous alumina by using 1-methyl-3-octylimidazolium chloride as a structure-directing agent. Similar mesoporous alumina has also been synthesized [10-12]. However, the above methods need expensive sources of aluminum and template and exhibit difficulty to scale up.

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Rotating packed bed (RPB) is an effective intensification technology, which has been applied to many processes including distillation [13], absorption [14], evaporative cooling [15], ozonation [16] and precipitation [17]. It has been reported that RPBs can greatly enhance mass transfer and micromixing, and is an enabling precipitation technology for nanoparticles preparation with a good control of particle size distribution [17,18]. We have reported the mass production of mesoporous alumina by the precipitation method in an RPB [19]. Inexpensive inorganic aluminum salts and polyethylene glycol 1540 (PEG 1540) were used as the sources of aluminum and template, respectively. The comparison of experimental results between the RPB and a stirred tank, and the effects of operating conditions including reactant concentration, addition rate of precipitator on mesoporous structure were investigated in the previous study. The results indicated that OMA with ordered wormlike pores, narrow pore size distributions, and a surface area of $250 \text{ m}^2/\text{g}$ was synthesized in an RPB. The study provided a feasible technology for mass production of mesoporous alumina. However, the effects of the synthesis conditions, surfactant and pore-expanding agent on OMA properties and the formation mechanism of OMA are unclear and deserve a further study.

Herein, we report the synthesis of OMA in an RPB, and the effects of the operation conditions, surfactant and pore-expanding agent on OMA properties were studied. Besides, the OMA formation mechanism was analyzed according to micromixing theory.

2. Experimental

2.1. Synthesis procedure

The reagents used were aluminum nitrate, ammonium carbonate and PEG 1540. All of the chemicals used in this work

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were AR grade. The experimental setup is illustrated in Fig. 1. It consisted of an ammonium carbonate feeding system, an aluminum nitrate and PEG 1540 mixture circulating system and an RPB. The specifications of the RPB employed in this work are given in Table 1. The packing consisted of stainless wire mesh purchased from Beijing Hongyahong Mesh Sale Center, Beijing, China. Liquid was jetted onto the inner edge of the rotor via a liquid distributor, which has a circular titanium alloy nozzle with a diameter of 0.003 m to ensure a certain initial speed of the liquid flow.

The experimental procedure was as follows: after 11 g of PEG 1540 was dissolved into 2200 ml of 0.6 M aluminum nitrate solution, the as-prepared solution was poured into the circulating tank, and then forced to circulate between the RPB and the circulating tank by a centrifugal pump at 0.2 m³/h. 1800 ml of 0.6 M ammonium carbonate solution was slowly introduced into the RPB by a precision pump. The aluminum nitrate solution and the ammonium carbonate solution flowed co-currently through the packing of the RPB and reacted to produce a gel-like mixture. If necessary, aqueous ammonia was added into the mixture to reach or maintain a pH of 7.6. After ammonium carbonate was consumed, the mixture further circulated between the RPB and the circulating tank for a certain time (varying from 0 to 10 min, called subsequent mixing time) before discharged into a beaker and aged at 293 K for 6 h and then filtered to collect the precipitate. The precipitate was washed by distilled water and dried at 353 K for 12 h, followed by calcinating at 573 K in nitrogen for 3 h, 703 K in nitrogen for 2 h, and 823 K in oxygen for 3 h. The temperature ramp rate between all stages was 2 K/min.

2.2. Characterization

Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 analyzer. The total spore volumes (PV) and pore size distributions of the samples were calculated by the Barrett–Joyner–Helenda (BJH) equation, and surface area (SA) was calculated by the Brunauer–Emmett–Teller (BET) equation.

The structure of the samples was analyzed by powder X-ray diffraction (XRD) on a Siemens D500 diffractometer using Cu K_{α} radiation source (λ = 0.154 nm). Low angle diffraction with a 2 θ range of 0.5–10° was used to investigate the long range order, and



Fig. 1. Experimental setup (1) RPB; (2) motor; (3) liquid distributor; (4) liquid flow meter; (5) centrifugal pump; (6) electrode; (7) pH meter; (8) circulating tank; (9) frequency modulator; (10) precision pump; (11) storage tank.

Table 1

Specifications of the RPB used in this study.

Item	Unit	Value
Inner radius of RPB casing, Rc	m	0.10
Inner radius of the packing, r _i	m	0.025
Outer radius of the packing, r _o	m	0.075
Axial length of the packing, Z	m	0.05
Volume of the rotor, V	m ³	7.85×10^{-4}
Diameter of stainless wire mesh, D	m	0.00023
Volume of the packing, V	m ³	$\textbf{3.93}\times \textbf{10}^{-5}$
Surface area of the dry packing per unit volume of the rotor a	m^2/m^3	871
Voidage of the dry packing, ε	m³/m³	0.95

wide angle scans were performed at a 2θ range of $10-90^{\circ}$ to validate the amorphous state of the alumina.

The morphology of the samples was observed on a JEOL 4000 electron microscope operated at 200 kV. The samples were ultrasonically dispersed in ethanol and then dropped onto the carbon-coated copper grids prior to the observation.

3. Results and discussion

Table 2 shows the specific surface area (SA), total pore volume (PV) and pore diameter (PD) of OMA synthesized under different rotating speed, ammonium carbonate solution flow rate, aluminum nitrate solution flow rate and mixing time. It is found that SA value was in the range of $191-277 \text{ m}^2/\text{g}$, PV in the range of $0.21-0.31 \text{ cm}^3/\text{g}$, and particle size (PS) in the range of 3.1-4.0 nm.

The transmission electron microscope (TEM) image of OMA sample R0330 is shown in Fig. 2. The as-prepared OMA exhibited wormhole channel motifs while it was reasonably uniform in pore size distribution. The XRD pattern of the OMA is shown in Fig. 3, which confirms that the mesoporous alumina was amorphous.

Previous studies revealed that the high-gravity environment in an RPB provides a significant amount of mechanical energy for the suspension and greatly intensifies the efficiency of micromixing and dispersion, which are the crucial conditions for the synthesis of mesoporous alumina. Further studies suggested that the size and dispersion of nano-sized inorganic precursor is the key factor to form the organized mesoporous structure [17,18]. Thus, the synthesis was performed at different high-gravity levels in order to understand the formation mechanism of OMA.

By adjusting the level of high-gravity, a series of mesoporous alumina samples were obtained. The nitrogen adsorption–desorption isotherms of the samples are shown in Fig. 4, and the corresponding pore size distributions are shown in Fig. 5. It can be seen that the as-synthesized OMA exhibited a narrower PD distribution and a smaller PV at a higher gravity level of 1850 m/s^2

Table 2

Properties of OMA synthesized at different conditions.

Sample	Different condition		$\mathrm{SA}/\mathrm{m}^2\mathrm{g}^{-1}$	$PV/cm^3 g^{-1}$	D/nm
	Factor	Value			
R0327	Rotating speed (rpm)	1500	226	0.21	3.1
R0328		900	216	0.22	3.1
R0514		300	201	0.30	4.0
R0327	Ammonium carbonate	10	226	0.21	3.1
R0330	flow rate (ml/min)	30; 10 ^a	243	0.24	3.1
R0907		30	191	0.29	3.9
R0330	Aluminum nitrate	0.26	243	0.24	3.1
R0912	flow rate (m ³ /h)	0.42	198	0.26	3.6
R6171	Subsequent mixing	0	270	0.29	3.2
R6172	time (min)	5	277	0.31	3.3
R6173		10	277	0.31	3.3

^a The flow rates of ammonium carbonate solution were 30 ml/min for 40 min and then 10 ml/min until ammonium carbonate was totally consumed.



Fig. 2. TEM image of OMA sample R0330.



Fig. 3. XRD pattern of OMA sample R0330.



Fig. 4. The nitrogen adsorption-desorption isotherms of OMA synthesized in the RPB.

and 665 m/s². The results can be explained in terms of the pore structure pileup mechanism and the RPB features. Liquid was dispersed into tiny drops, filaments and films in the packing of the RPB, resulting in an excellent micromixing effect. Therefore, the inorganic precursor particles, a main constituent of OMA pore wall,



Fig. 5. The pore size distribution of OMA synthesized in the RPB.



Fig. 6. The nitrogen adsorption-desorption isotherms of OMA synthesized at different flow rate of ammonium carbonate solution.

tended to become smaller and more uniform with the increase of the high-gravity level. Thus the narrow pore channel was formed, leading to the formation of the mesopores after further treatment. It can be concluded that the high-gravity level has great effects on the pore size distribution, surface area, and mesoporous structure.



Fig. 7. The pore size distribution of OMA synthesized at different flow rate of ammonium carbonate solution.



Fig. 8. The nitrogen adsorption-desorption isotherms of OMA synthesized at different flow rate of aluminum nitrate solution.



Fig. 9. The pore size distribution of OMA synthesized at different flow rate of aluminum nitrate solution.



Fig. 10. The nitrogen adsorption-desorption isotherms of OMA synthesized with different mixing time.



Fig. 11. The pore size distribution of OMA synthesized with different mixing time.

It can be found from Figs. 6 and 7 that the flow rate of ammonium carbonate solution had a significant influences on OMA properties. The OMA synthesis process can be divided into two stages: the nucleation stage and the figuration stage. Figs. 6 and 7 show that the mesoporous structure of OMA was improved when the flow rates of ammonium carbonate solution were 30 ml/min (40 min) and 10 ml/min (60 min) in comparison with 10 ml/min. But when the flow rate of ammonium carbonate solution maintained 30 ml/min in the entire synthesis process, the OMA structure changed significantly. It reveals that the figuration stage in OMA synthesis is the key stage for the formation of mesopores, and the nucleation stage is helpful to improving the pore structure.

The flow rate of aluminum nitrate solution also had a pronounced effect on OMA properties. A higher liquid flow rate induces a higher injecting velocity, which could enhance the micromixing efficiency of the liquid in the RPB. Figs. 8 and 9 show that increasing the flow rate of aluminum nitrate solution could enlarge the pore diameter and narrow the pore size distribution, and the surface area of OMA decreased with the increase of the pore volume and diameter, It is deduced that the similar residence time of the inorganic precursor in the RPB is the key factor in the formation of ordered mesopores.

Besides the factors discussed above, the subsequent mixing time after the pH value was adjusted to 7.6 was also very important to the OMA structure. The effects of mixing time on OMA properties were investigated in the presence of the poreexpanding agent, and the results are shown in Figs. 10 and 11. Fig. 10 shows that the nitrogen amount adsorbed increased slightly when subsequent mixing time increased from 0 to 5 or 10 min, while Fig. 11 demonstrates that the effect of subsequent mixing time on the pore size distribution can be ignored. Therefore, it can be deduced that the mechanical stirring has little effect on the OMA microstructure, indicating a high stability of such microstructure.

4. Conclusions

OMA was synthesized in an RPB with a reaction between aluminum nitrate and ammonium carbonate in this work. It was found that the level of high-gravity, liquid flow rate and the mixing time had great effect on the mesoporous structure, and the structure changed with the variation of the operation conditions. It was deduced that the excellent micromixing capability of the RPB is helpful to the formation of OMA with narrow pore size distribution and uniform structure, and the formation process of OMA involves the nucleation stage and the figuration stage. This work may provide a novel pathway for the synthesis of quality OMA.

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