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Research on Synthesis of Mesoporous Alumina Based on Utilization of Red Mud

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Abstract. A novel green controlled synthesis method is proposed in this paper. Mesoporous alumina was prepared by using sodium aluminate extracted from red mud as an aluminum source. The influence mechanism of temperature, template agent and sodium aluminate concentration on MA properties was studied systematically. The results show that the prepared mesoporous γ -alumina has a good catalytic activity of short-range arrangement, medium acidity, narrow pore size distribution, thermal stability and hydrothermal stability. This economical and green synthesis method can also be used to prepare other mesoporous or porous materials.

Keywords. Mesoporous alumina, red mud, in situ method, synthesis, characterization

1. Introduction

Nowadays, the research on mesoporous materials [1], such as mesoporous silicon, mesoporous alumina, mesoporous titanium, etc., becomes a hot topic [1]. Compared with ordinary alumina, mesoporous alumina shows many excellent and special properties, such as strong wear resistance, excellent electrical insulation, excellent structural properties and surface acid-base properties, which are high thermal stability and chemical stability. Therefore, it is widely used in ceramics [2], electronics [3], adsorbent [4,5], catalyst [6-9], catalyst carrier [10-13] and so on.

The preparation methods of mesoporous materials are sol-gel method [14,15], hydrothermal reaction method, precipitation method, emulsification and microemulsion method, etc. [16].

Red mud is the industrial solid waste produced after the process of extracting alumina from bauxite. At present, the total amount of red mud in storage has exceeded 2.7 billion tons, and more than 120 million tons of red mud is generated annually throughout the world [17,18]. Traditionally, red mud would be directly discharged and stored in the open-air storage yard without any further treatment [19-21]. On the one

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hand, red mud has strong alkalinity, complex composition and properties. These properties affect the treatment of red mud and the safety of the surrounding environment. On the other hand, red mud, which has rich content of metal oxides, especially high content of aluminum, could makes great achievements in building materials, environmental protection and other fields [22].

The alumina extracted from the red mud can be used as an aluminum source, looking for a suitable template, using template method [23,24], after hydrolysis and polymerization reaction. Finally, mesoporous alumina can be obtained by drying and roasting the samples [25,26]. However, few researchers use waste to prepare mesoporous alumina materials. That is true that red mud and other solid waste issues have a great impact on people's daily life. Studying and dealing with them is the main task of current scientific research. Therefore, in this research, mesoporous alumina was prepared by this method and its properties were characterized.

2. Experimental

2.1. Raw Materials

The main raw materials of the experiment are sodium aluminate which is extracted from red mud [27,28], sodium bicarbonate, methylcellulose (MC) template, aluminum standard liquid, sodium standard liquid, deionized water, etc.

The experimental device mainly consists of a trough reactor, pH value and conductivity on-line monitoring and recording, agitation control, System, feeding control (multi-channel longer peristaltic pump) and temperature control system.

The tank reactor has a capacity of 750ml, and the reactor cover is equipped with a feed port, a discharge port, pH and temperature probes Screw thread and digital display mixer mounting port. The tank reactor is placed in a heat collection constant temperature heating oil bath with a temperature control accuracy of ±0.1°C.

Digital display agitation is kept at about 500rpm to ensure uniform suspension and mixing of materials.

2.2. Experimental Methods and Sample Analysis Test

First of all, add a tank reactor into the solution of sodium aluminate, continuously stirring at a speed of 500rpm. Heat the solution to a predetermined temperature and slowly add the template MC. After finishing the mixture, the newly configured quantitative sodium bicarbonate solution was drip-fed into the trough reactor at a certain speed controlled by a multichannel longer pump. Continue to stir for 5h after dropwise adding. The liquid and solid separation of the reaction material is carried out through the vacuum extraction and filtration device. Choose the washing method according to the state of the filter cake to remove the attached liquid and impurities in the filter cake: When the filter cake is precipitated, the filter cake is washed with deionized water at about 70°C for about 3 times. When the filter cake is sol-gel, the filter cake is washed 3-5 times by centrifugal separation with deionized water at about 70°C. Then, the filter cake was placed in an air-blast drying oven at 80°C for 24 h.

The dried filter cake is heated in a muffle oven according to the preset heating procedure. (for example, from room temperature to 80°C at 10°C/min and from 80°C to 600°C at 1.5°C/min for 2-3h). Alumina with mesoporous structure was obtained by roasting to remove the template.

The measure and methods of sample analysis and characterization include structural characterization (Wide-angle XRD crystal morphology and small-angle XRD mesoporous characteristics analysis), Morphology analysis (SEM, TEM).

3. Results and Discussion

In the process of synthesis of mesoporous alumina by inorganic acid-base pairing method with sodium chlorate extracted from red mud as the aluminum source. The reaction temperature (T), the concentration of reactant sodium aluminate (c1) and the concentration of template have a great influence on the final product.

3.1. Effect of Reaction Temperature MA on the Pore Structure of Product Reaction Temperature

As shown in table 1, different reaction temperatures and corresponding results of MA materials reflect the effect of reaction temperature on the pore junctions of MA products

Other reaction conditions were the molecular ratio of $NaAlO_2$ to $AlCl_3$ was 2.5:1, the concentration of $NaAlO_2$ and $AlCl_3$ solution was 2.0mol/L, the concentration of template agent MC was 40g/L, the feeding speed of $AlCl_3$ solution was 0.6ml/min, and the stirring speed was 500 RPM.

Table 1. Properties of the prepared MA at a different synthesis temperature.

Experiment number	T(°C)	BET (m^2/g)	Vp (m^3/g)	dp(nm)
D1	50	245.5	0.2765	4.67
D2	60	287.1	0.3043	4.24
D3	70	235.9	0.3225	5.98
D4	80	236.8	0.3907	6.89
D5	90	238.1	0.4199	7.05

In the experimental range, with the increasing reaction temperature (50~90°C), the pore size and volume of MA products are increasing, which is mainly related to the physical properties of template MC. The phase transformation temperature of MC in an aqueous solution is about 45°C. When the reaction temperature is higher than 45°C, MC is gradually dispersed in the reaction system as an insoluble solid with a porous structure, providing guidance for the formation of MA precursor pore structure.

The higher the temperature, the more obvious MC diastolic. When the reaction temperature was 60°C, we can obtain the maximum specific surface area of MA.

3.2. Effect of Concentration of Template on the Pore Structure of MA Products

The effect of template MC concentration on the pore structure of MA products was examined in table 2. Other reaction parameters were a reaction temperature of 60°C, a solution concentration of 2.0mol/L, a molar ratio of NaAlO2 to AlCl3 of 2.5:1, a feeding speed of 0.6 mL/min, and a stirring speed of 500rpm.

Table 2. Effect of MC concentration on the properties of prepared MA.

Experiment	C2	BET(m^2/g)	Vp(m^3/g)	dp(nm)
D1	20.0	273.3	0.2663	3.89
D2	40.0	287.1	0.3043	4.24
D3	60.0	275.3	0.2874	4.18
D4	80.0	238.1	0.2686	3.97

The results in table 2 showed that when the concentration of template MC was low (experiment D1, 20g/L), the MC plays a less role in template guiding. The characteristic values of MA products are so little. With the increase of MC concentration (experiment D2, 40g/L), the specific surface area, pore size and pore volume of MA products are increased, and the guiding effect of MC template has a better performance. When the concentration of MC is overtopped (D4, 80g/L), the too dense template had a certain inhibition effect on the formation of mesoporous structure. Within the scope of the experiment, In the process of synthesis of mesoporous alumina by inorganic acid-base pairing method, the concentration of MC is about 40g/L, which is a favorable Formation of mesoporous structures

3.3. Effect of Sodium Aluminate Concentration on the Pore Structure of MA Products

The effect of NaAlO2 solution concentration on MA product pore structure is shown in table 3. Other reaction conditions were reaction temperature ws 80°C, the molar ratio of NaAlO2 to AlCl3 was 2.5:1, the concentration of template agent MC was 40g/L, the feeding speed of AlCl3 solution was 0.6 mL /min, and the stirring speed was 500rpm.

The effect of sodium aluminate solution concentration on the mesoporous properties of MA products is not a single function, as shown in table 3. (With the increasing concentration of sodium aluminate solution, MA index values fluctuate up and down), which shows that the concentration of sodium aluminate solution is not the only influential factor. It is the synergistic effect of other factors on the mesoporous characteristics of MA products. The data in the table shows that the concentration of sodium aluminate is 1.0mol/L (experiment E2), the pore size of MA was 4.22nm, and the specific surface area and pore volume were significantly larger than those of other concentrations were.

Table 3. Effect of NaAlO2 concentration on the properties of the prepared MA.

Experiment number	C_1	BET(m^2/g)	Vp(m^3/g)	dp(nm)
E_1	0.5	233.2	0.3097	5.31
E_2	1.0	260.5	0.3935	4.22
E_3	2.0	222.4	0.3661	6.59

E_4	4.0	193.3	0.2275	4.71
E_5	5.0	104.4	0.2515	5.10

3.4. Mesoporous Structure Characterization

According to the wide Angle XRD, we could find that the crystal shape of representative mesoporous alumina is γ -Al2O3.

Small-angle XRD shows in figure 1 that the strong peak at 2θ value 1.154°is the mesoporous characteristic peak of d100, which confirms the experimental results.

The mesoporous characteristics of typical alumina products are obvious.

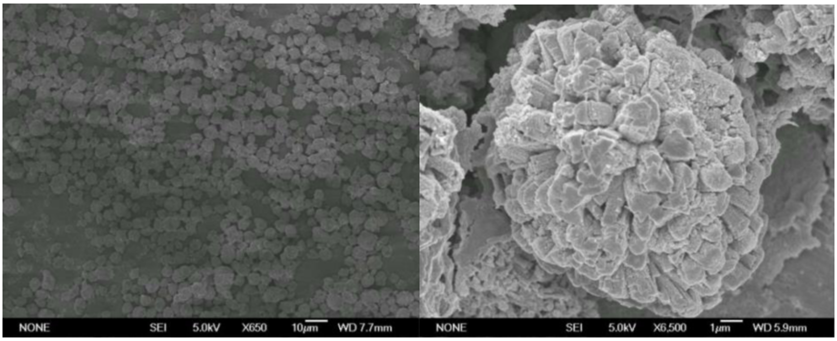

Figure 1. SEM images of representative MA sample.

SEM in figure 1 shows that MA production prepared under optimized conditions was synthesized by inorganic acid-base pairing method of mesoporous alumina.

The product particle morphology is a nearly spherical aggregate formed by irregular columnar outward growth along the radius direction, and the product particles are relatively uniform. The particle size is about 16μm.

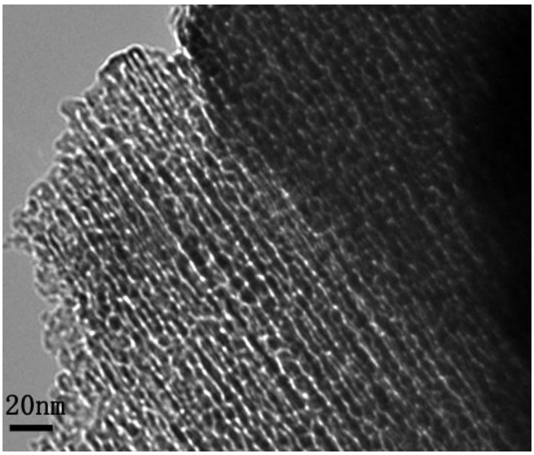

Figure 2. TEM image of the representative MA sample.

TEM in figure 2 shows that the MA product prepared by inorganic acid-base pairing synthesis of mesoporous alumina in this study has a wormlike structure with a pore diameter of about 3.7nm, and the mesoporous growth and arrangement are near parallel lines with good order degree.

4. Conclusions

Sodium chlorate extracted from red mud was used as the aluminum source for the first time in this research. By the acid-base pairing method (Using the Al3+ and AlO2- self-regulating pairs of two aluminum salts). MA was successfully prepared by self-assembly of polymer MC dispersed in an aqueous solution and aluminum hydroxide precursor. The main conclusions are as follows:

(1) The prepared MA product is γ -Al2O3, mesoporous alumina with large specific surface area (313.8m^2/g), narrow pore size distribution (average pore size 3.7nm), and ordered pores. The particle morphology of the product is nearly spherical.

(2) We could be clarified with the effects of various synthetic conditions on the apparent morphology and microporous structure of mesoporous alumina products.

(3) Mesoporous alumina was successfully prepared by using sodium aluminate extracted from red mud as the aluminum source. It provides a new way for green, low-cost and controllable synthesis of mesoporous materials.

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