One-Step Synthesis of Nanoporous Alumina by an Intelligent Gel Template

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Abstract. In this research, an novel green method for one-step synthesis of nanoporous alumina based on an intelligent recyclable template, which has sensitive response to temperature and can be easily removed from product and recycled to reuse by its phase changes with temperature, was applied. Using $NaAlO_2$ as the aluminum source and temperature-sensitive intelligent gel methylcellulose (MC) as the template, the nanoporous alumina products with large specific surface area, narrow pore size distribution and worm-like pore channels were successfully prepared. And the influence of reaction time, template concentration and $NaAlO_2$ solution concentration on the preparation of nanoporous alumina was studied.

Keywords: Nanoporous Alumina, Intelligent Gel, In Situ Method, One-step Synthesis, Green Process.

1. Introduction

Nanoporous materials have been widely used in chemical environmental[1], biomedical[2] and functional materials fields, because of their large specific surface and good adsorption capacity. Among them, the nanoporous alumina material shows a huge potential to be used as catalyst[3][4] catalyst support[5][6] and absorbent. It has excellent structural properties which is conducive to the diffusion and reaction of macromolecules, and it's surface acid-base properties allows it support metal active components, that lead to high catalytic activity. In terms of purification and adsorption, compared with ordinary alumina materials, it has higher adsorption capacity and can absorb large amount of many kinds of volatile pollutants at the room temperature. Therefore, nanoporous alumina materials have great application prospects in petrochemical catalysis and environmental protection, and are becoming a hot topic in materials research.

In the process of preparing nanoporous alumina, it is necessary to add template agent to achieve effective control of the structure of the product[7][8]. The reaction of preparing nanoporous alumina can be divided into hard and soft template method according to different types of template agent. Hard template method, also known as absorption template method, mostly uses existing porous materials as template agents. Hard template make the formation structure of porous materials easy to control because of its inherent stable form structure. But such template needs to be decomposed at high temperature to achieve the removal of template agent in the finished material, which cannot be effectively recycled, and there is a certain pollution. At the same time, the high price of template makes the use of disposable hard template costly, so the recyclability and reusability of the template is emphasized. Soft template method including two types of surfactant method and non-surfactant method. Under certain conditions, the template agent of surfactants can generate the required structure for the reactants to attach. In the synthesis of nanoporous alumina, the common surfactants include anionic template, cationic template and neutral surfactants. After the reaction is completed, the template can be removed by high temperature calcination, microwave, solvent extraction, oxidation[9] and other methods. Although the soft template method can realize the effective recovery of template agent to a certain extent, the reaction is difficult, and the recovery process of template agent may damage the shape and structure of the target product nanoporous alumina. Moreover, the lack of the recovery of the soft template keeps the cost of the experiment at a high level, and fails to effectively meet the demand for the recyclable template agent that can reduce the cost.

Therefore, to address the high cost issue of traditional soft and hard template agents, intelligent template method was researched[10][11]. The intelligent template, like the common soft template, can form the required microstructure under certain conditions to synthesize the nanoporous alumina material. After the reaction is completed, the template agent is removed from the finished product by changing the pH value, temperature and other corresponding conditions to achieve efficient recycling of the template agent. Compared with the traditional formwork method, the material loss is effectively reduced and the cost is saved. Therefore, intelligent template method has become a hot topic in recent years.

In order to solve the problems of high cost, difficult to control the structure of the product, and possible carbon emission in the reaction process, this study will use a novel green controllable synthesis method to prepare nanoporous alumina by the intelligent template. The influence of reaction time, template concentration and the $NaAlO_2$ solution concentration will be studied.

2. Experiment

2.1. Raw materials and Experimental devices

Raw materials: Sodium aluminate (Analytical), Aluminium chloride (Analytical), methylcellulose (MC) template, Deionized water.

Experimental device: Tank reactor, Collector constant temperature heating water bath instrument, Digital display stirrer, Peristaltic pump, Vacuum filtration device, Blast drying oven, Muffle furnace, N_2 adsorption/desorption isotherm instrument.

2.2. Experimental methods and analysis tests

The synthesis of Nano Alumina was performed using a method of Acid-base paring. Firstly, a certain amount of $NaAlO_2$ solution was added to the tank reactor, and the solution was continuously stirred and heated to a predetermined temperature at a speed of 500rpm, the template MC was slowly added and mixed evenly, and the newly configured quantitative $AlCl_3$ solution was added to the tank reactor dropwise at a certain speed through a peristaltic pump and continue stirring and react for 5h. After the reaction is completed, the reaction material is separated from liquid and solid by vacuum filtration device and followed the washing process to remove the impurities and to recycle the template. Then the filter cake is washed by centrifugal separation with deionized water at about 30°C for about 3-5 times. The washed cake was placed in a blast drying oven at 80°C for 24 h. After drying, the filter cake is heated from room temperature to 600°C in a muffle furnace and then roasted continuously for 2-3h to remove the residual template agent and obtain a porous alumina material.

The reaction formula are as follows in Figure 1:

$$AlCl_3+3NaAlO_2+6H_2O \xrightarrow{\text{Heat}} 4Al(OH)_3+3NaCl$$

$$MC_{(\text{Liquid})} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} MC_{(\text{Nanoporous pore template})}$$

$$MC_{(\text{Left})}+O_2 \xrightarrow{500^\circ C\text{-}700^\circ C} CO_2+H_2O$$

$$2Al(OH)_3 \xrightarrow{500^\circ C\text{-}700^\circ C} Al_2O_3+3H_2O$$

Figure 1. Reaction formula

The analytical characterization methods include structural characterization (wide-angle XRD crystal form and small-angle XRD nanoporous characterization), topography analysis (TEM) and N_2 adsorption/desorption isotherm.

For the qualitative and quantitative analysis of the template agent used in the study, the temperature-sensitive intelligent hydrogel MC was used as an analytical method by the UV2000 ultraviolet spectrophotometer produced by LabTech in the United States as an analytical means to quantitatively analyze the content of the template agent MC in the solution by diphenylamine colorimetric method. The BET, pore size, and pore distribution of the product will be detected by the N_2 adsorption/desorption isotherm.

3. Results and discussion

In the synthesis of nanoporous alumina using MC as template, the reaction temperature T, the $NaAlO_2$ solution concentration C_1 and the template concentration C_2 had great effects on MA products. In this research, the effects of the above reaction conditions on the pore structure of MA was investigated by a series of experiments.

3.1. Effect of synthesis temperature on the preparation of nanoporous alumina

In Table 1, different reaction temperatures and the related data of MA materials show the effect of reaction temperature on the pore structure of MA.

Other experimental conditions in this experiment were as follows: the molecular ratio of $AlCl_3$ to $NaAlO_2$ was 1:2.5, the concentration of $AlCl_3$ and $NaAlO_2$ solution was 2.0 mol/L, the MC concentration was 40 g/L, the $AlCl_3$ solution was added at 0.6 ml/min, and the mixing speed was 500 rpm.

Table 1. Properties of the prepared MA at different synthesis temperatures.

Experiment number	T (℃)	BET (m^2/g)	dp (nm)
C1	50	245.5	4.67
C2	60	287.1	4.24
C3	70	235.9	5.98
C4	80	236.8	6.89

Table 1 indicates that within the experimental limits, the continuous increase of the reaction temperature (50~80°C), lead to the increase of the pore size and pore volume of MA products, which was primarily associated with the physical properties of the template MC at different temperatures: the phase transition temperature of MC in water solution is approximately 45°C, as the reaction temperature exceeds 45°C, the template is gradually dispersed in the reaction system to form a porous structure with an insoluble solid structure, which provided guidance for the formation of the pore structure of the MA precursor. And the higher temperature make the diastolic pressure of MC more pronounced, so that the pore size of the synthesized MA increases. When the reaction temperature reached 60°C, the prepared MA can obtain the largest specific surface area.

3.2. Effect of $NaAlO_2$ concentration on the preparation of nanoporous alumina

Table 2 shows the effect of $NaAlO_2$ solution concentration on the pore structure of MA products.

Other experimental conditions in this experiment were as follows: the molecular ratio of $AlCl_3$ to $NaAlO_2$ was 1:2.5, the concentration of $AlCl_3$ and $NaAlO_2$ solution was 2.0 mol/L, the MC concentration was 40 g/L, the $AlCl_3$ solution was added at 0.6 ml/min, and the mixing speed was 500 rpm.

Table 2. Effect of $NaAlO_2$ concentration on the properties of the prepared MA.

Experiment number	C_1	BET (m^2/g)	dp (nm)
E1	0.5	233.2	5.31
E2	1.0	260.5	4.22
E3	2.0	222.4	6.59
E4	4.0	193.3	4.71

Table 2 shows that the influence of the $NaAlO_2$ solution concentration on the nanoporous characteristics of MA products was not a single (with the gradual increase of $NaAlO_2$ solution concentration, the index values of MA show jagged changes), indicates that the concentration of $NaAlO_2$ solution and other influencing factors synergistically affect the nanopore characterization of MA products. The data from the table show that when the $NaAlO_2$ solution concentration was 1.0 mol/L (experiment E2), the MA pore size was 4.22 nm, its specific surface area was significantly greater than those under other concentrations.

3.3. Effect of template concentration on the preparation of nanoporous alumina

Table 3 investigated the influence data of concentration of template MC on the pore structure of MA products.

Other experimental conditions in this experiment were as follows: the molecular ratio of $AlCl_3$ to $NaAlO_2$ was 1:2.5, the concentration of $AlCl_3$ and $NaAlO_2$ solution was 2.0 mol/L, the MC concentration was 40 g/L, the $AlCl_3$ solution was added at 0.6 ml/min, and the mixing speed was 500 rpm.

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

Experiment number	C_2	BET (m^2/g)	dp (nm)
D1	20.0	273.3	3.89
D2	40.0	287.1	4.24
D3	60.0	275.3	4.18
D4	80.0	270.6	3.97

Table 3 shows that when the MC concentration is relatively low (experiment D1), the template guiding effect is low, and the characterization value of MA products are also low. As the concentration of template MC increased (experiment D2), the specific surface area and pore size of MA products enhanced, and the guiding effect of template MC was well reflected. When the MC concentration is too high (experiment D4), the generation of nanoporous materials is inhibited by dense template. In the experimental range, in inorganic acid-base pairing for the synthesis of nanoporous alumina, the concentration of MC was about 40 g/L, that was conducive to the formation of a better nanoporous structure.

3.4. Nanoporous structure characterization

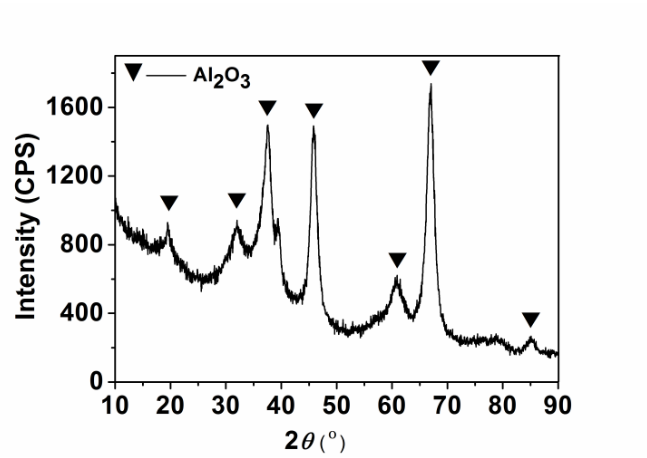

Figure 2. Wide-angle XRD pattern of the representative MA sample.

The wide-angle XRD Figure 2 identified the crystal phase of the prepared MA sample as γ-Al_2O_3.

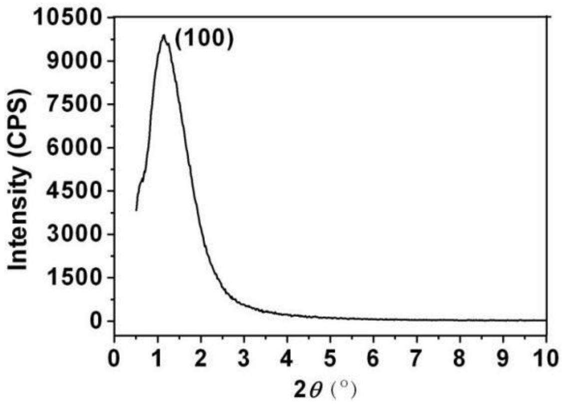

Figure 3. Small-angle XRD pattern of the representative MA sample.

Small-angle XRD Figure 3 indicates that the mesoporous characteristic peak of d_{100} is the strong peak at 1.154° at 2θ value, which conformed the mesoporous structure of the prepared alumina.

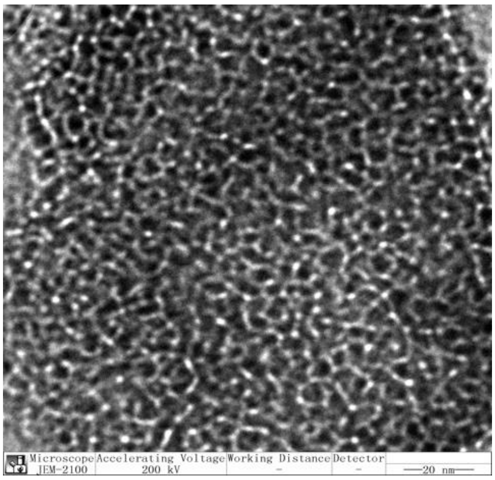

Figure 4. TEM image of the representative MA sample.

Figure 4 indicates that the pore of the MA product prepared in this study is a worm-like structure with a pore size of about 6.0 nm.

4. Conclusion

In this paper, the recyclable temperature-sensitive intelligent gel methylcellulose MC was used as a template, and the MA was successfully prepared by the in-situ synthesis through acid-base pairing reaction of inorganic aluminum raw-materials $AlCl_3$ and $NaAlO_2$. In this acid-base pairing reaction, the preparation process does not require additional acid or alkali, which led to the environmental pollution and high cost. And the temperature-sensitive template can be recycled and reused, which reduced the costs and carbon emissions. And the following main conclusions were obtained:

- A green, controllable and low-cost synthesis method was studied to successfully prepare nanoporous alumina.
- The prepared MA product was identified as nanoporous γ-Al_2O_3, with large specific surface area of 287.1 m^2/g, the average pore size of 6.0 nm and orderly worm-like pore channels.
- The effects of synthesis conditions, such as reaction temperature, the $NaAlO_2$ solution concentration and the template concentration, on the micropore structure of nanoporous alumina products were discussed.

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