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Synthesis and characterization of porous aluminum hydroxide materials with oleic acids

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Porous aluminum hydroxide materials were synthesized by means of a hydrothermal method with oleic acid and sodium oleate as templates. The resulting aluminum hydroxide ($Al(OH)_3$) powders with layer structures had the highest porosity and specific surface area when the reaction occurred at 393 K for 12 h. Transmission electron microscopy (TEM) revealed that these powders had multi-level pore and layer structures, which can be used for the adsorption of lithium ions and in other industrial applications.

Keywords: aluminum hydroxide, surfactant, hydrothermal synthesis, porous

Синтез і характеристика пористих алюміній-гідроксидних матеріалів з олеїновими кислотами. *Юнлінь Сюй*

Пористі матеріали гідроксиду алюмінію були синтезовані за допомогою гідротермального методу з олеїновою кислотою та олеатом натрію як шаблони. Отримані порошки гідроксиду алюмінію ($Al(OH)_3$) з шаруватою структурою мали найвищу пористість і питому площу поверхні, коли реакція відбувалася при 393 До протягом 12 год. Просвічуюча електронна мікроскопія (TEM) показала, що ці порошки мають багаторівневі пори та шарові структури, які можна використовувати для адсорбції іонів літію та в інших промислових цілях.

1. Introduction

Lithium and its compounds have been widely used in the energy, glass, ceramics, aerospace, metallurgy, chemical, and medical industries [1]. In recent years, lithium batteries have been increasingly used in electronic products and alternative-energy vehicles and for large-scale energy storage, which has promoted the large-scale development of lithium resources. Globally, due to the high cost of extracting lithium from ore, lithium extracted from salt lake brine has become a major component of the global supply of lithium [2]. Modern technologies include extraction, membrane separation, calcination, and ion exchange absorption. Among these, the adsorption method is highly selective and enables the extraction of lithium from low-grade raw brine or mother liquor at a rate of up to 90%. This method requires little energy and raw materials, saves energy and protects the environment, which opens up great potential for application [2, 3].

There are two primary types of lithium sorbents: manganese-based and aluminum-based sorbents. Aluminum-based sorbents (aluminum hydroxide and aluminate) are the most promising for industrial applications due to their high adsorption selectivity for lithium ions, low cost, ease of synthesis and high stability in brines with high calcium and magnesium concentrations [4]. Most aluminum-based sorbents have layered structures. Aluminum hydroxide is an example: gibbsite is composed of two layers of hydroxides, aluminum ions occupy 2/3 of the octahedral vacancies between the layers, which are connected by hydrogen bonds, creating an AB-BA-AB… structure [5]. The preparation of high-performance aluminum-based lithi-

Fig. 1. The products without (left) and with (right) the addition of surfactants

um sorbents requires the synthesis of porous aluminum hydroxide materials with high porosity and specific surface areas. In the present paper, aluminum hydroxide was synthesized by means of a hydrothermal method using aluminum chloride and sodium hydroxide as starting materials and oleic acid and sodium oleate as template reagents [6]. The method discussed in this paper provides a good platform for the development of aluminum salt-based sorbents with multi-level pores [7].

2. Experimental

2.1 Reagents and equipment

The reagents include aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$) (AR), sodium hydroxide ($NaOH$) (AR), ammonium hydroxide (NH_4OH) (AR), urea (AR), oleic acid (AR), ethanol, and cyclohexane. The equipment includes a 100 mL Teflon hydrothermal autoclave, an electric hot air-blowing oven, a low-speed centrifuge, a magnetic stirrer, and an analytical balance.

The characterization instruments include an automated analyzer for the surface area and pore size (Autosorb-iQ2-MP, Quantachrome Instruments) for analyzing the specific surface area and adsorption capacity of the products; an X'Pert Pro X-ray diffractometer (PANalytical, Netherlands) for characterizing the structures of the products; and a transmission electron microscope (H-7700, Hitachi) used to reveal the morphology at an accelerating voltage of 100 kV.

2.2 Synthesis of aluminum hydroxide

A certain amount of sodium hydroxide was dissolved in 20 mL DI water, or 20 mL ammonium hydroxide of a certain concentration. The solution was then slowly dropped into 50 mL oleic acid-ethanol (1:1 (v/v)). The solution was stirred for 10 min at a gradually increasing speed. Subsequently, 2.415 g aluminum chloride hexahydrate was dissolved in 30 mL DI water, and then, the solution was dropped into the previously prepared mixture, quickly at first and then slowly. The resulting solution was stirred for 30 min before being placed in the autoclave reactor. To maintain the basic conditions of the solution during hydrothermal synthesis, a small amount of urea could be added to the autoclave. To test the role of surfactants, an autoclave containing no oleic acid was used as a control. After sealing, the autoclave was placed in the oven and heated at a given temperature for a predetermined period of time.

After heating, the PTFE vessel was removed from the autoclave. The supernatant oleic acid was discarded. The aluminum hydroxide powder at the bottom was collected, washed with ethanol-cyclohexane (1:1 (v/v)) in a centrifuge tube, centrifuged, and dried to obtain the final product.

2.3 Characterization of the product

X-ray diffraction (XRD) and compositional analysis were performed to confirm that the product was aluminum hydroxide. Then, the product was dispersed in ethanol; the resulting dispersed product was subsequently precipitated on a copper grid for morphological observations using TEM. Representative images were used. Finally, the surface analyzer was used to measure the specific surface area.

3. Results and discussion

3.1 Results of the synthesis of aluminum hydroxide

When no surfactants were added, the product was a white gel. In contrast, when surfactants were added, all of the products were white powders after washing and drying (Figure 1). The XRD spectra of the products are shown in Figure 2. The analysis shows that, except for the impurity peak corresponding to approximately 1% sodium chloride ($NaCl$), the peaks are essentially characteristic peaks of aluminum hydroxide [8].

3.2 The effect of the ratio of the starting materials on the product

Before the onset of hydrothermal synthesis, the following primary reaction occurs in the solution:

$$AlCl_3 + 3NaOH =$$
$$= Al(OH)_3 + 3NaCl \text{ (adding } NaOH\text{)}$$

Since in the oleic acid system, a portion of the oleic acid must react with sodium hydroxide to produce sodium oleate acting as a template reagent in the hydrothermal synthesis, an appropriate amount of excess sodium hydroxide should be available [9,10]. In the reacting solution, the amount of aluminum chloride hexahydrate in each reactor was 2.415 g (0.01 mol); the theoretical yield was 0.78 g. The amount of sodium hydroxide added was 1.2 g (0.03 mol), 2.4 g (0.06 mol), 4.0 g (0.1 mol), or 4.8 g (0.12 mol). The corresponding yields were 0 (no product), 27.18% (0.2122 g product), 77.12% (0.6015 g product), and 64.74% (0.5050 g product). These results show that with the addition of 4.0 g (0.1 mol) sodium hydroxide, i.e., when the molar ratio of aluminum chloride hexahydrate to sodium hydroxide was 1:10, the yield was the highest.

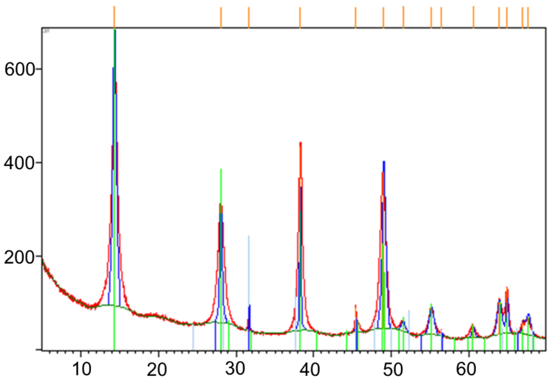

Fig. 2. XRD spectra of the aluminum hydroxide products

3.3 The effect of surfactants on the product

When no surfactants were added, the product was gel-like. After drying, the product appeared to be white rubber that was soft and elastic. In contrast, when surfactants were added, the product was a white powder that agglomerated easily after drying; after grinding the agglomerate, a white powder was obtained again. TEM images show that the gel-like aluminum hydroxide has a network microstructure (Figure 3), while the powder-like aluminum hydroxide exhibits a layered microstructure (Figure 4).

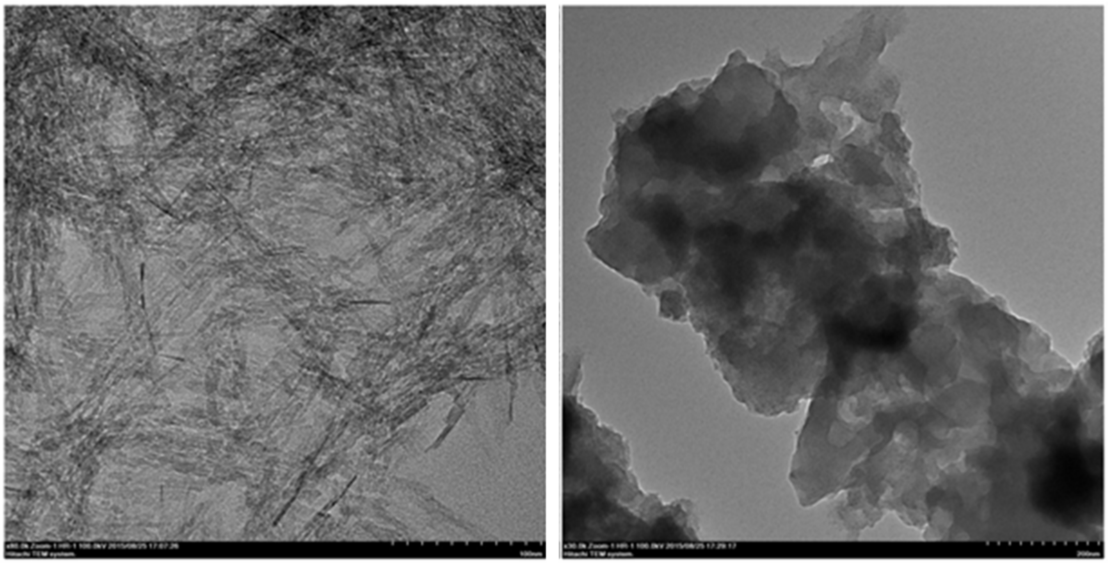

Figure 3. TEM images of the gel-like (left) and powder-like (right) aluminum hydroxide

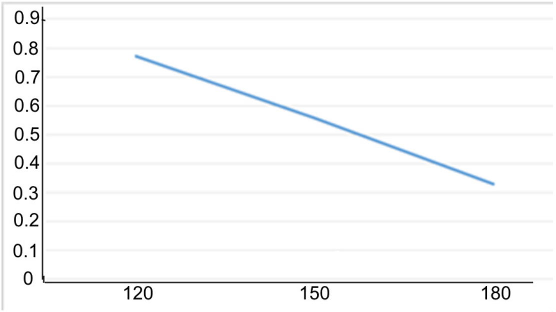

Fig. 4. Relationship between hydrothermal yield and reaction temperature

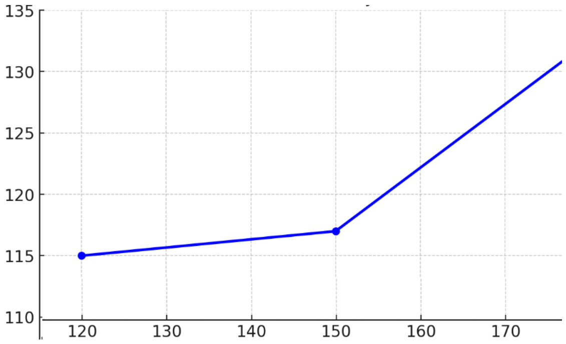

Fig. 5. The relationship between the specific surface area and the reaction temperature

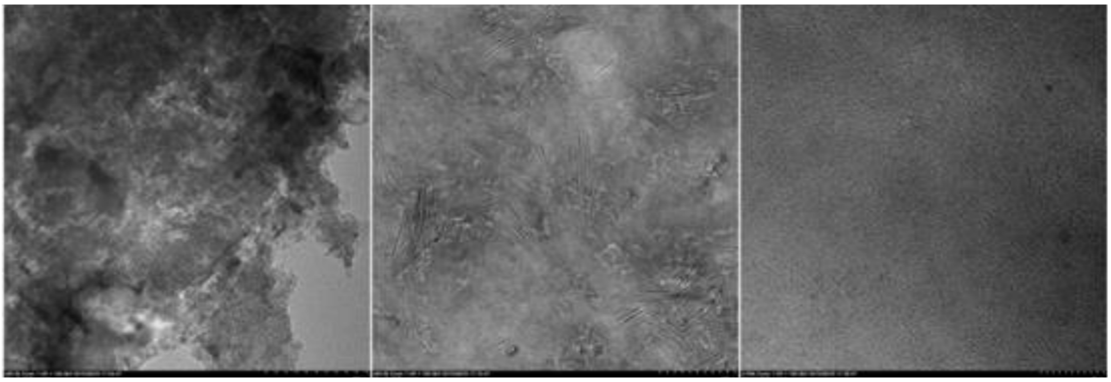

Fig. 6. TEM images of the aluminum hydroxide products obtained at different temperatures (from left to right: 120°C, 150°C, and 180°C)

3.4 The effect of the hydrothermal reaction temperature on the product

The literature has shown that the hydrothermal synthesis of porous aluminum hydroxide materials temperature occurs in the range from 120°C to 210°C. Four temperatures (120°C, 150°C, 180°C and 200°C) were selected for this experiment, and the porosity and specific surface areas of the final products were measured to determine the optimal reaction temperature. The results indicate that when the temperature was increased to 200°C, the oleic acid tended to polymerize, and the product was a yellow aggregate rather than a white powder (Figure 4). Elemental analysis revealed that the carbon content of the yellow aggregate was 44.9%, which confirmed that the final products were the organic products of the polymerization of oleic acid. At the reaction temperature of 120°C, 150°C or 180°C, we obtained 0.6015 g, 0.4354 g, or 0.2566 g of the product, respectively, and the yield was 77.12%, 55.82% or 32.90%, respectively (Figure 4). It can be seen that the yield decreased linearly with the temperature.

The Brunauer-Emmett-Teller (BET) analysis of the specific surface area showed that the reaction temperature affects the specific surface area and porosity to a certain extent. When the reaction temperature was 120°C, the specific surface area of the product was 114.910 m^2/g, the mean pore size was 16.992 Å, and the mean pore volume was 0.419 cc/g; when the reaction temperature was 150°C, the specific surface area of the product was 116.231 m2/g, the mean pore size was 17.103 Å, and the mean pore volume was 0.452 cc/g; and when the reaction temperature was 180°C, the specific surface area of the product was 132.656 m2/g, the mean pore size was 17.020 Å, and the mean pore volume was 0.479 cc/g (Figure 5). It can be seen that with increasing the reaction temperature, the specific surface area of the products increased; however, the increase was not pronounced.

The TEM images shown in Figure 6 reveal the layered structures of the products. As the reaction temperature increased, the texture of the layers became more even and dense, and the layers were easier to separate.

3.5 The effect of the hydrothermal reaction time on the product

The reaction time ranged from 5 h to 23 h; reaction times of 5 h, 12 h and 23 h were selected for this study. The results showed that oleic acid tended to polymerize after the hydrothermal reaction occurred for 12 h or 23 h. The products were yellow aggregates rather than white powders (such as the one synthesized at 200°C). Elemental analysis showed that the carbon content of the yellow aggregates was 45.6%, confirming that the final products were organic polymerization products of oleic acid. Therefore, the reaction time cannot be too long for the synthesis of aluminum hydroxide using oleic acid; the optimum time is 5 h.

4 Conclusions

The feasibility of a system for synthesizing aluminum hydroxide nanomaterials using oleic acid has been demonstrated. The optimal initial molar ratio of aluminum chloride hexahydrate to sodium hydroxide is 1:10. The role and necessity of oleic acid as a surfactant and template regent in the process of oleic acid-aided synthesis has been demonstrated; the product obtained was an aluminum hydroxide gel when no oleic acid was added; this product was dramatically different from the product obtained when oleic acid was added. By varying the reaction conditions, it was found that a reaction temperature above 200°C and a reaction time of greater than 5 h polymerization of oleic acid occurs, resulting in the formation of yellow aggregates of organic products instead of powdered aluminum hydroxide nanomaterials. It was found that the yield decreased linearly with the change in reaction temperature, and the specific surface area and adsorption capacity increased as the temperature increased, although the increase was small. The optimal conditions for industrial synthesis are 120°C for 5 h.

Acknowledgments

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