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Effects of synthetic conditions on the textural structure of pseudo-boehmite

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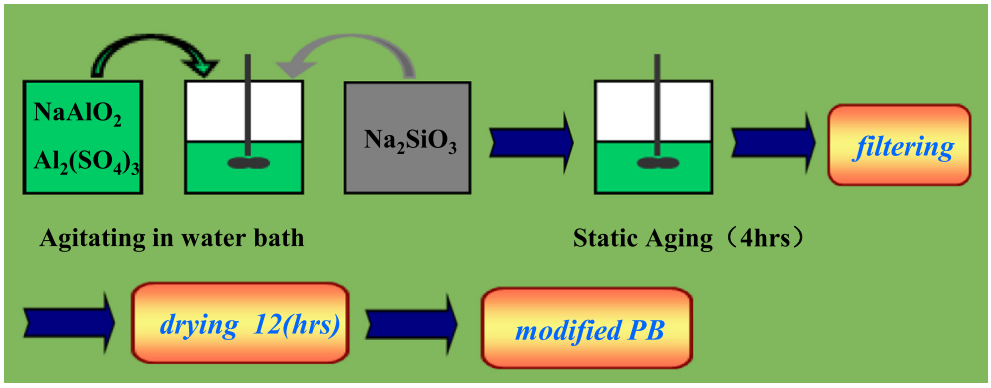
GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous alumina with pseudo-boehmite phase was prepared by using the cation–anion double hydrolysis method from mixed aqueous solution of aluminum sulfate and sodium aluminate. The effect of synthetic conditions on the crystal structure and textual properties of pseudo-boehmite was investigated, such as synthetic temperature, pH value and the addition of sodium silicate. With the assistance of characterization techniques, such as X-ray diffraction (XRD), N_2 adsorption–desorption isotherms (BET) and ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR), the relationship between textural properties of the mesoporous alumina samples and their synthetic conditions was discussed. The results displayed that an increase in synthesis temperature promoted the formation of higher crystalline pseudo-boehmite with the increase of its surface area and pore volume. Pure pseudo-boehmite phase could be obtained in the pH value range from 6.0 to 9.0, while bayerite phase occurred when the pH value was over 10.0. The introduction of sodium silicate could greatly improve the pore volume (1.20 cm^3/g) and surface area (480.2 m^2/g) of pseudo-boehmite. Interestingly, pure pseudo-boehmite phase was obtained at very high pH value without formation of bayerite phase when sodium silicate was initially added into the aluminum hydroxide colloid.

1. Introduction

Pseudo-boehmite (PB), poorly crystallized boehmite [1,2], consisting of $Al(O,OH)_6$ octahedral layers [3], is widely used as a catalyst or catalyst support in various processes, such as petroleum

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refining [4], alcohol dehydration [5], Claus reaction [6] and Fischer–Tropsch process [7], due to its inexpensiveness, high mechanical strength and tunable pore size. However, in China, with the increasing proportion of residue in FCC feedstock [8,9] and high demand for gasoline, conventional commercial PB featured by low surface area (<300 m^2/g) and narrow pore size distribution cannot meet the request of practical produce. So, low-cost approaches to synthesize PB with high surface and broad pore size distribution need to be developed.

According to previous studies, much attention has been focused on acid neutralization with the use of sodium aluminate as the only aluminum source [10] or the hydrolysis of expensive and toxic aluminum alkoxides [11]. However, it is difficult to obtain high surface area and large pore volume at the same time with simply using those methods. Pore-expanding agents, such as templates [12–16], alcohols [17] and other inorganics [18–22], are often added into aluminum hydroxide colloid to increase the two important parameters.

In this paper, mesoporous pseudo-boehmite was prepared by adopting a modified cation–anion double hydrolysis method [23] (CADH) with using water glass as the pore-expanding agent, by regulating synthesis conditions, namely temperature, pH value and the amount of water glass, and the effects of these synthesis conditions on the crystal structure and textual properties of pseudo-boehmite was comparatively studied.

2. Experimental section

2.1. Sample preparation

Raw materials: (1) aluminum sulfate solution, Al_2O_3:93.7 g/L, ρ = 1.294 g/cm^3; (2) sodium aluminate solution, Na_2O:241.4 g/L, Al_2O_3:167.9 g/L, ρ = 1.355 g/cm^3; (3) sodium silicate solution, module ($(SiO_2/Na_2O)_{mol}$ ratio) = 3.28, ρ_{SiO_2} = 3.92 g/cm^3.

A typical sample was prepared as follows: 40 mL $Al_2(SO)_4$ solution and 40 mL $NaAlO_2$ solution were dissolved in 40 mL and 30 mL deionized water, respectively, forming solution A and solution B. With two constant-flow pumps, solution A and solution B were put together into a three-neck flask while stirring vigorously. The whole suspension was stirred vigorously for 3 h at 75 °C. Thereafter, sodium silicate solution was added dropwise into the system under vigorous stirring for another 3 h. The resulting gel was subsequently washed with distillated water and dried at 110 °C for 12 h. The naming rule of our samples are as follows: (S)PB-X-Y-(Z), "PB" stands for pseudo-boehmite and "SPB" for pseudo-boehmite modified by sodium silicate, "X" for pH, "Y" for temperature and "Z" for the amount of sodium silicate. For example, SPB-9-75-12% means that pseudo-boehmite was prepared using 12 wt% sodium silicate at pH value of 9.0 under the temperature of 75 °C.

2.2. Characterization

X-ray diffraction (XRD) characterization was conducted on a X'Pert PRO MPD diffractometer (P A Nalytical B.V. Netherlands) with Cu K-Alpha radiation (k = 0.15418 nm), operated at 40 kV, 40 mA, and scanned from 5° to 75° at a speed of 0.01°/s.

Nitrogen adsorption–desorption measurements at −196 °C were carried out on a Micrometrics TRISTAR 3000 analyzer. Prior to the measurements, the samples were outgassed at 300 °C with a vacuum degree of 10^{-2} Torr for 5 h. The Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) method were used to determine the surface area and pore volume of the pseudo-boehmite samples.

Solid-state nuclear magnetic resonance (NMR) experiments were performed using a Bruker Advance III 400 spectrometer at resonance frequencies of 104.0 MHz for ^{27}Al. The Bruker 4.0 mm MAS probe was used for acquisition of 10 kHz MAS spectra. The single pulse sequence with rf-pulse duration of 0.3 μs (π/20°) and recycling time of 0.30 s was used.

3. Results and discussion

3.1. Effect of temperature on pseudo-boehmite

The samples were hydrolyzed at various temperatures under pH value of 8.5 to study the influence of temperature on the textural properties of pseudo-boehmite. Just as the XRD patterns shown in Fig. 1, all these samples exhibit the phase of pseudo-boehmite with different crystallinity [24]. It is evident that the relative intensity peaks of X-ray diffraction line sharpen increasingly upon increasing the temperature, indicating that higher crystallinity or larger crystal size of psedo-boehmite can be obtained under higher temperature. Especially, when temperature is below 55 °C, the sample shows very poor crystallinity. It is reported that high synthesis temperature plays important role in improving the nucleation rate of colloidal particles which favors in relatively well crystallinity or large crystal size [17]. Also, there is no evident shift of the diffraction lines, suggesting that the layers are not rotated or displayed due to the change of temperature.

The N_2 adsorption–desorption isotherms shown in Fig. 2 were used to determine the surface area and the type of porosity for pseudo-boehmite samples synthesized under different temperatures. The pore size distribution was measured using BJH method and is shown in Fig. 2B. Furthermore, the textural characteristics for all materials were tabulated in Table 1. In Fig. 2A, it is apparent that all isotherms are of classical type IV, which indicates that the materials are mesoporous in nature [25,26]. The hysteresis loops of these samples seem to be intermediate between type H2 and H3, indicating that they have good pore connectivity with channel-like or ink-bottle pores [27]. The higher closure points of the loops occurring above P/P_0 = 0.9 may imply the presence of large pore size and broad pore size distribution in line with the results shown in Fig. 2B. Generally, this phenomenon is observed for aggregates of plate-like particles giving rise to slit-shaped pores [17].

From the data shown in Table 1, it can be seen that before 85 °C, with the temperature climbing up, the surface area of these samples increases from 43.45 $m^2\ g^{-1}$ to 392.3 $m^2\ g^{-1}$, and correspondingly the average pore diameter decreases from 14.29 to 5.16 nm.

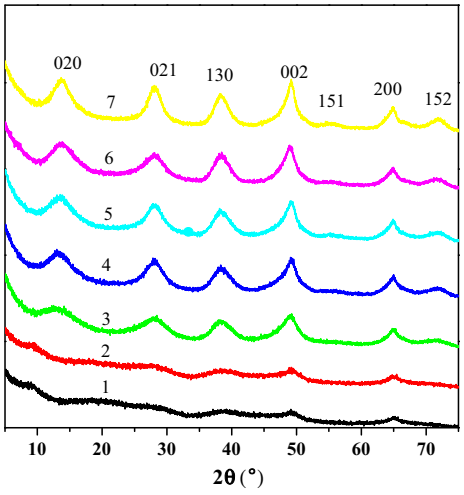

Fig. 1. Wide-angle XRD patterns for pseudo-boehmite samples prepared at different temperatures. (1 PB-8.5-35, 2 PB-8.5-45, 3 PB-8.5-55, 4 PB-8.5-65, 5 PB-8.5-75, 6 PB-8.5-85, 7 PB-8.5-95.)