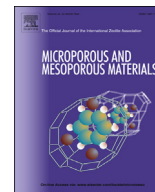




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Synthesis and characterization of mesoporous Si-modified alumina with high thermal stability

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ABSTRACT

Mesoporous alumina with pseudo-boehmite phase modified by water glass was prepared by using the cation–anion double hydrolysis method from mixed aqueous solution of aluminum sulfate and sodium aluminate. The texture structure and acidity of these samples was studied with the assistance of characterization techniques, such as X-ray diffraction (XRD), N₂ adsorption–desorption isotherms, ²⁷Al and ²⁹Si magic-angle spinning nuclear magnetic resonance (MAS NMR) and Fourier transform infrared (FTIR) spectroscopy. The XRD and N₂ adsorption–desorption results show that the addition of sodium silicate can decrease the crystallinity of alumina, but greatly improve pore volume and surface area. The highest pore volume (1.46 cm³/g) and surface area (427.69 m²/g) can be simultaneously obtained when the adding amount of silica is up to 12 wt%. The NMR and FTIR results display that the presence of a certain amount of silicon can generate Al^V in alumina, which is considered to be related with strong acid sites. In addition, the acidity of the Si-modified alumina samples can be adjusted by changing the amount of silica.

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1. Introduction

Since decades, solid acid catalysts have been adopted in hydrocarbon conversion technologies with the rapid development of fuel market [1–4]. For instance, Y zeolite or USY are often used in fluid catalytic cracking process [5], SAPO-11 and ZSM-5 perform well in isomerization with the aim to increase RON of gasoline [6,7] and SAPO-34 is specially designed for MTO (Methanol to Olefins) [8]. And the reason why these silica–alumina materials with crystal structure are widely used in those fields lies in their unique pore structure and suitable acid properties. Due to the fact that all the silicon atoms and aluminum atoms of the zeolite framework are located at the surface and stable unit cell have ordered arrangement [9], it is not difficult for researchers to investigate the nature of structure and acidity. However, for another important solid acid materials with stronger stability than Al₂O₃, amorphous silica–alumina or Si-modified alumina also possesses both Brønsted acid sites and Lewis acid sites and is widely used as the catalysts or matrix in the process of petroleum refining [10–12]. However, because of the complex surface composition of these mixed oxides,

there is still a conflicting view about the origin of acid sites in these materials, meaning an uncertain relationship between structure and its acidic properties. Many researchers have shared the same opinion that the formation of BAS in non-crystalline silica–alumina is due to the isomorphous substitution of Si⁴⁺ by Al³⁺ in the silica lattice [13–16], which is similar to the bridging hydroxyl groups in zeolites [17]. Theoretically, aluminum atoms diffuse into the silica surface after calcination, possibly with six-coordinated aluminum substituted by tetrahedral structure. Nevertheless, this hypothesis cannot be directly identified by IR spectra no matter what amount of SiO₂ is loaded, and partially, there is also a contradictory between the amount of BAS and ²⁹Si MAS NMR. Naturally, the desire for alternative explanation has been aroused to make further investigation. One of them that we think is deserved to consider and study is that the higher acidity of BAS is related with the structure “paired (SiOH and Al) sites”, reported by M. Trombetta [18]. This structure model has set the foundation of current proposals and enables us to account for the presence of strongly acidic OH groups in the IR spectra, but it is undeniable that there are still some problems confusing us a lot, such as what the relationship between aluminum coordination and acidity, what the environment of aluminum coordination is near the surface silanol groups and where the aluminum atoms in the vicinity of surface silanol groups locate, etc. So, to gain a better understanding and know about more

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detailed information of this structure is one of our aims in this work. It has been identified that aluminosilicates are composed of mixed silica–alumina phase and alumina-typed phase [19–21], so it is wise to determine the nature, strength, concentration and environment of acidic site by comparing with these in alumina prepared at the same conditions.

Secondly, to increase the yield of gasoline and kerosene, more medium acid sites which are supposed to be lower than zeolites are needed to meet the requirements [22–25]. If the acidity is too weak, the activity of the catalysts will be decreased dramatically. Therefore, another aim of this work is to obtain balanced acidity and control their acidic properties accurately. According to lots of previous works, different preparing methods can give rise to different distribution of acid sites with various strength [26–30]. Fortunately, a cation–anion double hydrolysis method (CADH) has been developed by Bai in our group [31]. This method is quite similar to what has been discussed by Hensen [32], a homogeneous deposition-precipitation method, which cannot only maximize the surface silicon atoms, but also enlarge the surface area and pore volume. And the main difference is that the behavior of sodium silicate (as the silicon source in this work) in solution is effected mostly by pH, so it is the key to adjust the BAS/LAS ratio in these materials instead of only changing the loading amount of SiO₂. In fact, it is an effective method to obtain various amount of Brønsted acid sites with different strengths.

Finally, IR spectroscopy is selected as the best tool to characterize the acidic properties with using pyridine which is most widely used as the basic probe molecule and also is effective for distinguishing BAS and LAS, qualitatively and quantitatively [33–37]. Furthermore, with the assistance of high-resolution solid-state NMR to determine the environment of aluminum atoms and silicon atoms coordination [38–42], respectively, we give a rational explanation about the relationship between structure and acidic properties.

2. Experimental section

2.1. Samples preparation

Raw materials: (1) aluminum sulfate solution, Al₂O₃:93.7 g/L, $\rho = 1.294 \text{ g/cm}^3$; (2) sodium aluminate solution, Na₂O:241.4 g/L, Al₂O₃: 167.9 g/L, $\rho = 1.355 \text{ g/cm}^3$; (3) sodium silicate, SiO₂: 250 g/L.

A typical sample was prepared as follows: 40 mL Al₂(SO)₄ solution and 40 mL NaAlO₂ solution were dissolved in 40 mL and 30 mL deionized water respectively, forming solution A and solution B. Solution A and solution B were put together into a three-neck flask while stirring vigorously, and the velocity of flow was determined by final pH value. 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 distilled water and dried at 110 °C for 12 h. Then, the solid material was obtained by calcination of the dried gel under air at 550 °C for 4 h at a heating rate of 2 °C/min. Finally, to lower the proportion of Na⁺ below 0.1 wt% in our samples, ion exchange was implemented with 1 mol/L NH₄NO₃ for 3 times. In this work, the variables are pH and the mass fraction of SiO₂, and it is the amount of sodium aluminate solution that determines the final pH value. But for the sake of easy-to-express, we use pH value to definite the parameter.

2.2. Characterization

X-ray diffraction (XRD) characterization was conducted on a X'Pert PRO MPD diffractometer (P A Nalytical B.V. Netherlands)

with CuK-Alpha radiation ($k = 0.15418 \text{ nm}$), operating at 40 kV, 40 mA, and scanning 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 ²⁷Al. 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 ($\pi/20^\circ$) and recycling time of 0.30 s was used.

Fourier transform infrared (FT-IR) transmission tests were performed on a Nicolet 6700 spectrometer controlled by OMNIC software with a MCT detector. Each spectrum was recorded by a total of 64 scans with a resolution of 4 cm⁻¹. To obtain surface information, pure powders were pressed into self-support wafer, and then they were activated in situ in the IR cell at 500 °C under primary vacuum at a speed of 5 °C/min. After maintaining at 500 °C for 2 h under secondary vacuum, the spectra were collected.

To measure the Brønsted acid site and Lewis acid site concentrations, pyridine vapor (P_{py} ~ 1 torr) was introduced into the IR cell with the outgassing manipulation for 30 min when the samples were cooled down to room temperature from 500 °C. Physically adsorbed pyridine on the acid sites were removed by a vacuum molecular pump at 150 °C and $<2 \times 10^{-3} \text{ Pa}$ for 1 h. 150, 200, 250, 300, 350, 400 and 500 °C were selected to test the acid strength, and the spectra were recorded in order at corresponding temperature by subtracting the related sample background spectra without pyridine recorded at the same temperature.

Ammonia temperature programmed desorption (NH₃-TPD) equipped with a TCD detector was carried out to determine the total acid site concentrations. Firstly, approximately 200 mg of sample was put into a “U”-typed quartz tube to be heated to remove water at 500 °C for 1 h under a helium flow of 30 sccm (standard cubic centimeters per minute). Secondly, NH₃ was introduced into this tube in a constant flow rate at 100 °C for 1 h after the pretreatment. Finally, He was used again to remove physisorbed ammonia at 100 °C for 30 min, and then the sample was heated to desorb ammonia at a ramp rate of 5 °C/min. At the same time, spectra were recorded in the form of mole fraction of desorbed species versus temperature. The amount of desorbed ammonia was assumed to be equivalent to the total concentration of acid sites.

3. Results and discussion

3.1. Crystal structure

Fig. 1 illustrates the XRD patterns of Si-modified alumina samples dried at 110 °C. It can be seen that all the samples are pseudo-boehmite, and the crystallinity of these samples decreases with the increasing amount of silica added. The XRD patterns of Si-modified alumina prepared at pH value of 6.0 and 9.0 after calcination at 550 °C are shown in Fig. 2. For the samples prepared at pH value of 9.0, the diffractograms exhibit some broad crystalline peaks around 35–40° and especially at 45° and 67° 2 θ due to the reflection (of X-rays) from the (4 0 0) and (4 4 0) crystal planes, respectively, of the cubic γ -alumina [43]. Furthermore, it can be observed that the crystallinity of the samples decreases with the increasing amount of silica added. To determine the effect of temperature on the crystal structure of Si-modified alumina, all the samples prepared

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