Sol-Gel Method on the Preparation of Boron-doped Activated Alumina

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Abstract. In this paper, the crystal phase, pore structure, and surface properties of boron doping γ-alumina were investigated systematically, by the sol-gel method. The influence of the chemical environment and the modification mechanism of aluminium was explored in boron doping alumina. The samples were characterized by using XRD, N₂ adsorption at low temperature, NH₃-TPD, TEM, and NMR. The X-ray diffraction peaks of boria-alumina have no obvious change with the increasing content of boron, which still gives priority to the characteristic diffraction peaks of γ-Al₂O₃. Both the specific surface area of boria-alumina and pore volume diameter increase. The result of NMR indicates that boron alters the chemical environment of aluminium, then causes the difference in physical and chemical properties on the surface.

1. Introduction
γ-alumina is known as active alumina because it shows excellent properties in its specific surface, as well as its adjustable pore structure, so it is used as catalytic support widely [1]. As the crude oil becoming heavier and poorer in quality, the standard of sulfur content in fuel oil is greatly reduced, it puts forward higher requirements for the catalyst. The fundamental ways to solve these problems are to improve the carrier’s properties, so the research work of modified γ-alumina is of great importance [2].

There is a large number of researches on boron-modified alumina [3-10]. However, most of them focus on the properties and catalytic activity of the loaded active component, but no unified understanding of the interaction between boron and activated alumina. The following paper will systematically examine the effect of boron on the physical and chemical properties of activated alumina and provide a reference for further in-depth study on hydrogenation catalysts.

2. Experimental
2.1. Preparation of catalysts
Aluminum nitrate and ammonia water are selected as the aluminum source and the alkali source, respectively. The doping boron element is added in the form of boric acid at the stage of aluminum hydroxide. After neutralization to form the aluminum hydroxide gel, the boron-doped activated alumina oxide is made by aging and drying. It calcined for 3 h in flowing air at 550°C finally. The prepared samples were called boria-alumina with being the atomic B: Al ratio of 0.02.
2.2. Characterization of catalysts

Phase: Examination was using an X’Pert PRO MPD X-ray powder diffraction (XRPD) system from PANalytical (Almelo, The Netherlands) equipped with a graphite monochromator and employing Cu Ka radiation, with tube voltage 40kV, tube current 40mA, step size 0.02°.

Specific surface area and pore volume: The analysis was conducted by Micrometrics ASAP2420 physical absorption-desorption instrument. By analysing the N2 physical adsorption-desorption data and the adsorption-desorption isotherm curve, a series of information about the pore structure, such as specific surface area, pore volume, average pore size and pore size distribution, are obtained.

Acidity: AutoCehem2920 chemical adsorption instrument was used for testing and characterization. The analysis conditions were: He was used as the carrier gas, and the sample was pre-treated at 600°C for 1 hour. Then the temperature was lowered to 120°C to adsorb NH3, and finally the program temperature was raised at a heating rate of 8°C/min.

Appearance: The transmission electron microscope (TEM) was characterized by JEM-2100 high-resolution TEM produced by JEOL Ltd. The acceleration voltage is 200kV and the lamp current is 105μA.

Aluminum coordination: The Swiss Bruker AV-500 nuclear magnetic resonance instrument is used for detecting. The 27Al spectrum acquisition frequency is 130.3MHz; the sampling time is 30mS; the magnetic field strength is 11.7T.

3. Results and discussion

3.1. Structure property and morphology

Figure 1 shows typical γ-Al2O3 characteristic diffraction peaks at 37.5°, 46.2° and 66.4°. There were no characteristic diffraction peaks of boron-containing crystal phases in the spectrum. This is because the content of boron doped into Al2O3 is relatively small, and the dispersion is quite well, without clusters (such as B2O3) being formed. The diffraction front and peak intensity demonstrated that the diffraction peak of boron-doped activated alumina was significantly broadened and the crystallinity was relatively low, when adding boric acid in the aluminum hydroxide phases. According to Scherrer formula: D=Kλ/Bcosθ, it is known that the particle size of γ-Al2O3 is small. The result shows that doping this boron content will not change the crystal phase of γ-Al2O3. The weak and broad peaks indicate that the boria-alumina was consists of small crystals with a nano-scale crystal structure.

![Figure 1. X-ray diffraction patterns of pure alumina (a) and boria-alumina (b).](image-url)
Figure 2 presents TEM images of the boria-alumina. The microstructure of the primary particles of boria-alumina carrier was mainly fibrous structure and plenty of orderless accumulation. Fig. 2 shows that boria-alumina are the nanostructures with a length of 12nm and a width of 2nm can be clearly observed. Furthermore, no other morphologies emerge.

![Figure 2. The microcosmic appearance of boria-alumina.](image)

### 3.2. Surface area and porosity

Figure 3 shows the N$_2$ adsorption-desorption diagram of the boria-alumina sample and pure alumina. It suggests that there is an obvious hysteresis loop in the range of $p/p_0=0.45$–$0.85$, indicating that irreversible adsorption-desorption occurs on N$_2$ in the $\gamma$-Al$_2$O$_3$ channel. This conforms to the Langmuir IV curve, which is the most common adsorption-desorption behavior of mesoporous solids. The appearance of such hysteresis loop is usually caused by the different size of the orifice and the hole body (ink bottle-shaped hole) or a different adsorption and desorption of the nearly cylindrical hole. This type of pore saturation adsorption platform is remarkable, indicating that the pore size distribution in the samples is relatively uniform.

![Figure 3. Nitrogen adsorption-desorption isotherms of pure alumina (a) and boria-alumina (b).](image)
It can be seen from the data in Table 1 that the specific surface area of pure alumina is 256 m²/g. Compared with pure alumina, the specific surface area of boron-doped alumina prepared by adding boric acid in the aluminium hydroxide phases increased by 25.77%. The pore volume increased from 0.42 to 0.51 cm³/g, and the average pore width decreased from 6.7 to 6.4 nm.

| Table 1. The surface area and porosity of pure alumina and boria-alumina. |
|-------------------|------------------|------------------|
|                   | pure alumina     | boria-alumina    |
| surface area (m²/g) | 256              | 322              |
| pore volume (cm³/g)  | 0.43             | 0.51             |
| average pore (nm)    | 6.7              | 6.4              |

3.3. Surface acidity

The corresponding numbers of acid sites on the boria-alumina is presented in Table 2. The activated alumina modified by boron contains more weak acid sites and medium strong acid sites, little strong acid sites.

| Table 2. The distributing of acid site of boria-alumina. |
|-------------------|-------------------|-------------------|-------------------|
|                   | Total acidity mmol/g | weak acid sites /% | medium strong acid sites /% | strong acid sites /% |
| boria-alumina     | 0.726              | 41.56             | 35.89             | 22.55             |

3.4. ²⁷Al-MAS–NMR analysis

There are three states [11-13] of aluminium in the aluminium spectrum, with characteristic peaks near chemical shifts near 0, 30, and 60, representing hexacoordinated aluminum (AlVI), pentacoordinated aluminium (AlV), and tetrahedral aluminium (AlIV), respectively. Figure 4 illustrates that the samples have characteristic peaks of hexacoordinated aluminum and tetrahedral aluminum near the chemical shifts of 8 ppm and 65 ppm. After classical peak decomposition, there is a fitting peak at δ=30 ppm. The characteristic peak near 30 ppm belongs to pentacoordinated aluminium (AlV), indicating that there are pentacoordinated aluminium ions (AlV) in the samples. When the hexacoordinated aluminium in alumina is attached to the surface hydroxyl group, the charge density around aluminum is greater than tetrahedral aluminum (AlIV) and less than hexacoordinated aluminum(AlVI), resulting in the production of five coordination aluminum. This is because the boron in the sample is doped into the bulk or core structure of the activated alumina particles, which is not only present on the surface of the sample or embedded in the surface layer of the sample, but also may cause the coordination unsaturation of the hexacoordinated aluminum ions, thereby increasing the amount of pentahedral aluminum (AlV). Realizing that if doping boron in the process of sol-gel forming, boron is located in the center of the gel cluster, which plays the role of core, we could prepare activated alumina with doping boron equally.
4. Conclusion
Boron-doped activated alumina was prepared by a sol-gel method. XRD results showed doping this boron content will not change the crystal phase of γ-Al₂O₃. NH₃-TPD results demonstrated that boron-doped alumina contains more weak acid sites and higher specific surface area. The result of NMR indicates that boron alters the chemical environment of aluminum, then causes the difference of physical and chemical properties on the surface. It is believed that with its special properties, boron-doped activated alumina will play an important role in the field of catalyst supports.

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