

The Preparation of Boron-doped Activated Alumina by impregnating boron in the period of boehmite

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Abstract. This paper systematically studied the pore structure, crystal phase, surface acidity and the chemical environment of aluminum of boron-doped γ -alumina, by impregnating boron in the period of boehmite. The nitrogen adsorption, XRD, FTIR etc. technique was used to determine the pore texture, crystallography, acid/base properties and aluminum coordination. the XRD spectrum of boria-alumina have no significant change due to the addition of boron. The specific surface area and pore volume diameter of B-Al₂O₃ increase significantly. The NMR spectra of B-Al₂O₃ shows that boron changed the chemical environment of aluminum, which caused differences in the physical and chemical properties of the surface.

1 Introduction

Alumina is called activated alumina due to its special surface properties, as well as its thermal stability, also it has surface acidity and adjustable pore structure, so its applications in the fields of catalytic materials, drying materials, adsorption materials are very significant. Especially in the high temperature reaction fields, such as the oil hydrogenation cracking, hydrogenation and dehydrogenation, catalytic purification of automobile exhaust, γ -alumina is widely used as a catalyst support. However, γ -alumina which has the cationic defects in its spinel structure, belongs to the transitional type of metastable phase. At present, researches of the preparation of modified γ -alumina are most focused on sol-gel method[1,2], precipitation method, microemulsion method, combustion synthesis[3] etc, but all these methods have its only disadvantages.

As the quality of crude oil declines, while the existing hydrofining catalyst by changing, the process conditions can be produced the products to meet the standard of euro VI gasoline and diesel oil. But a series of problems emerges, such as reaction severity, high energy consumption and low selectivity. The fundamental ways to solve these problems was to develop new type of efficient hydrogenation catalysts with high intrinsic activity and selectivity. To solve this problem, we must understand deeply of some key scientific problems, 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

Aluminum nitrate and ammonia water are selected as the aluminum source and the alkali source, respectively. After neutralization to form the aluminum hydroxide gel, Continue to add ammonia, adjust the pH of the sol-gel to 8. after stirring for 2 h, let stand at room temperature for 24 h, then dry it in the oven for 24 hours at 80 °C. The sample is synthesized by impregnating H₃BO₃ with equal volume in the pseudo-boehmite stage. 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.

3 Results and discussion

3.1 Crystal phase and morphology

Figure 1 shows the XRD of pure alumina and boron-doped alumina. It can be seen from the figure that there were obvious characteristic diffraction peaks of γ -Al₂O₃ at 37.5°, 46.2° and 66.4°.

At this time, there was still no characteristic peak of boron-containing species in the XRD spectrum, indicating that phosphorus it still exists in an amorphous state or the boron compound is highly dispersed in alumina. Doped boron does not affect the structure of activated alumina. The characteristic peak intensity of γ -Al₂O₃ phase is reduced, indicating that its crystal phase structure is incomplete and its crystallinity is poor. The result is that the alumina surface is covered with a layer of amorphous borate, which causes the intensity of the alumina diffraction peak to decrease.

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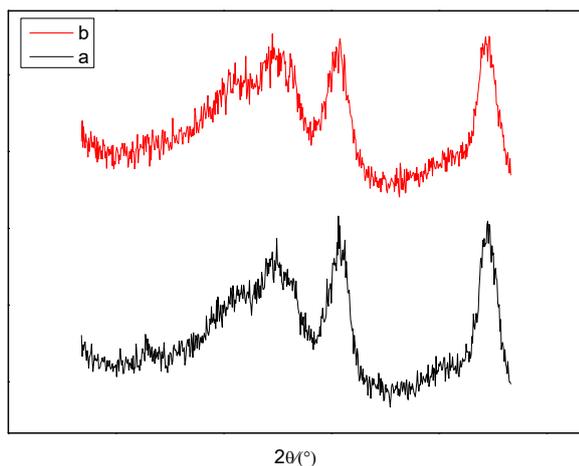


Figure 1. The XRD of pure alumina (a) and boron-alumina (b)

The modified γ -Al₂O₃ powder is in irregular particle shape, with a relatively uniform particle size distribution, with a particle size of about 20 nm, which is larger than the average particle size calculated by Scherrer's formula. This is because the particles have high surface energy and attract each other, resulting in a certain agglomeration of the powder. Therefore, the result of electron microscopy characterization is slightly larger.

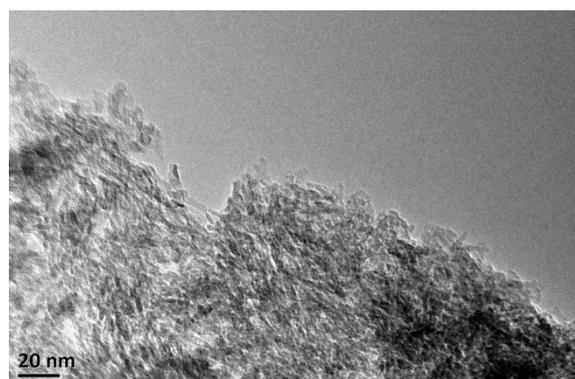


Figure 2. The TEM of boron-alumina.

3.2 Surface area and porosity

Figure 3 shows the adsorption isotherms of the boron-alumina sample and pure alumina. After calcination, the adsorption isotherms are similar in shape, which are all ink bottle-shaped pores, indicating that the pore type of the sample is not affected by the boron content. The characteristic of this type of hole is that the size of the orifice is similar to that of the cavity, which is generally a hole formed by the accumulation of particles. The reason is that the hole of the ink bottle-shaped hole is small, which is easy to be closed due to high temperature sintering. At the same time, the particles grow and accumulate with each other, so the hole type turns into a slit hole.

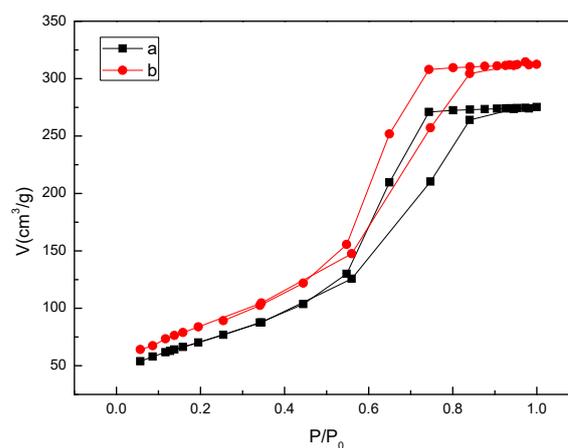


Figure 3. Nitrogen adsorption-desorption isotherms of pure alumina (a) and boron-alumina (b)

Table 1 shows the specific surface area, pore volume and average pore of the pure alumina and the boron-alumina sample. The addition of boric acid did not significantly change the pore size of activated alumina, but compared with pure alumina. Specific surface area increased by 19%, the pore volume increased by 14%, and the average pore width decreased by 4%.

Table.1 The surface area and porosity of pure alumina and boron-alumina

	pure alumina	boron-alumina
surface areas (m ² /g)	256	305
pore volume (cm ³ /g)	0.43	0.49
average pore (nm)	6.7	6.4

3.3 Surface acidity

The Table 2 shows the surface acidity of B-Al₂O₃. In boron-doped activated alumina, strong acid and medium strong acid account is more, while weak acid account is less.

Table.2 The surface acidity of B-Al₂O₃

	weak acid sites /%	medium strong acid sites /%	strong acid sites /%	Total acidity mmol/g
B-Al ₂ O ₃	38.59	39.75	21.66	0.724

3.4 The chemical environment of aluminum

There are three states of aluminum in the aluminum spectrum[4-6], which are distributed as characteristic peaks near chemical shifts 0, 30, and 60 ppm, which represent six-coordinate aluminum (AlVI), five-coordinate aluminum (AlV), and four-coordinate aluminum (AlIV). It can be seen from Figure 4 that the boron-doped activated alumina has characteristic peaks of six-coordinate aluminum and four-coordinate aluminum around chemical shifts of 8 ppm and 65 ppm.

After fitting the peak to the sample, there is a fitting peak at $\delta=30$ ppm. The characteristic peak near 30 ppm belongs to five-coordinate aluminum, indicating the presence of five-coordinate aluminum ion (AlV) in this sample. This may be due to the dehydration reaction between boric acid and pseudo-boehmite, which distorted the crystal structure of pseudo-boehmite on its surface, and the crystal became incomplete, resulting in more AlVI ions exposed to OH.

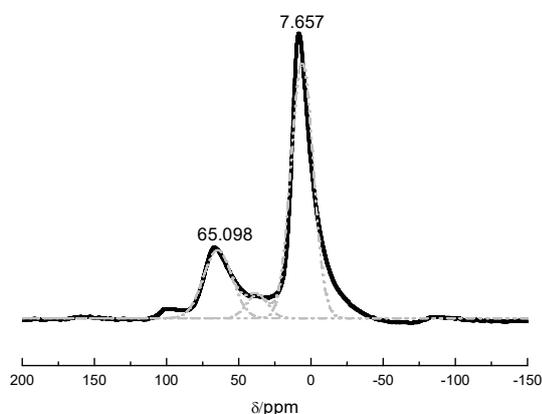


Figure.4 The 27Al CP/MAS NMR spectra of B-Al₂O₃

In the boron-doped activated alumina sample, the ratio of Al^{VI}/Al^{IV} is 3.57/1, which exceeds the theoretical value. It is speculated that boron occupies tetrahedral sites in the form of boron-oxygen tetrahedrons, so that during the transformation of the precursor to γ -Al₂O₃, the migration of Al^{VI} to Al^{IV} is inhibited, and the number of Al^{IV} is reduced.

Table.3 The Effect of Boron Doping on fitting profiles of 27Al NMR

sample	center	width	height($\times 10^8$)	area ($\times 10^9$)	Al ^{VI} /Al ^{IV}
pure alumina	6.857	15.230	3.815	7.283	2.50
	64.921	19.937	1.163	2.905	
boria-alumina	4.643	17.395	4.016	8.755	3.57
	64.959	15.359	1.273	2.451	
	44.876	18.137	0.451	1.026	

4 Conclusion

Boron-doped Activated Alumina was impregnated in the period of boehmite. XRD results showed that the boron-doped activated alumina will not form a new phase, but reduce the intensity of the diffraction peak. NH₃-TPD results showed that the acidity is mainly the medium strong acid and the weak acid and the specific surface area increase. The result of NMR indicates that boron changes the chemical environment of aluminum, then causes the differences in physical and chemical properties of the surface.

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