Alumina-aluminum borates as solid acid catalysts

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A series of alumina-aluminum borate (AAB) catalysts with various Al/B ratios were prepared with the coprecipitation method. The surface acidic properties of these catalysts were examined by temperature-programmed-desorption (TPD) of ammonia and the dehydration reaction of isopropanol. The dehydration reaction was carried out in a continuous-flow microreactor at 160°C under atmospheric pressure. The results of TPD of ammonia indicated that the surface acidity of AAB is medium-strong. The acidic strengths are approximately the same for all the samples. However, the acid concentration is increased with increasing the boron content of the catalyst. The dehydration activities of these catalysts are increased with increasing the boron contents of the samples. The results indicated that the addition of boron even in a small amount could significantly enhance the acidities of the catalysts.

Keywords: Solid acid; aluminum borate; isopropanol dehydration; temperature-programmed desorption of ammonina

1. Introduction

The applications of binary oxides such as silica-alumina, alumina-aluminum phosphate, and iron oxide-iron phosphate, to catalyze the dehydration, isomerization, and alkylation have been widely reported in the recent years [1–4]. Previous reports [1] have shown that alumina-boria can be used as a cracking catalyst. Pine [5] employed boria-alumina compositions on hydrocarbon conversion process. Sato et al. [6] reported that alumina-supported boria exhibited high catalytic efficiency for the vapor-phase Beckmann rearrangement of cyclohexanone oxime. Peil et al. [7] reported that aluminum borate is highly acidic. In this study, AAB is used to stand for alumina-aluminum borate material. It has been found that it is not just a mixture of alumina and aluminum borate [7]. Here we report a study of acidic properties of alumina-aluminum borates (AAB) as determined by temperature-programmed-desorption of ammonia. We also

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studied the dehydration reaction of isopropanol in order to understand the correlation with the acidic properties.

2. Experimental

CATALYST PREPARATION

An acidic solution was prepared by dissolving aluminum nitrate in distilled water and then adding solution of boric acid. A second solution was prepared using 1:1 volume mixture of ammonium hydroxide and distilled water. The two solutions were slowly added into a container of distilled water with the rate of addition controlled in order to maintain a constant pH of 8.00 + 0.02. After the addition of the acidic solution was completed, the reaction mixture was stirred for an additional 10 min. The precipitated AAB was then filtered, washed with distilled water and dried overnight at 120°C. The oven-dried material was calcined at 500°C in a muffle furnace for 12 hours.

A series of alumina-aluminum phosphates (AAPs) with various Al/P ratios were also included for comparison. The preparation of AAP is the same as that reported by Marcelin et al. [8]. The details have been reported in a previous paper [4].

We denote the AAB samples, its Al/B atomic ratio $=x$, as AABx. For example, AAB8 indicates that the Al/B atomic ratio is 8. Following the same expression, AAP8 indicates that the Al/P atomic ratio is 8.

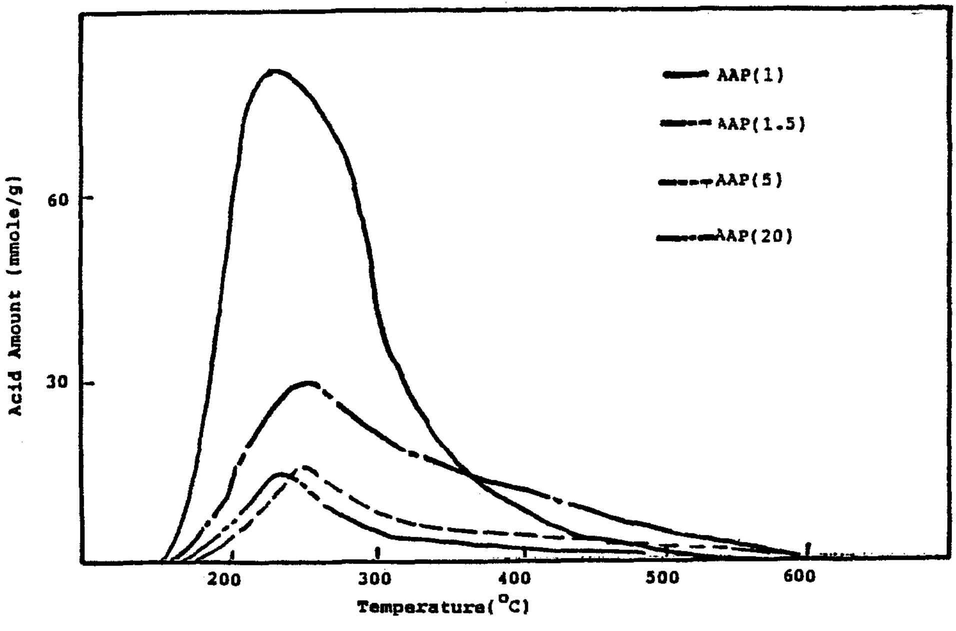

Fig. 1. NH_3 TPD of AAP.

NH_3 TPD

In a typical experiment, 100 mg of calcined sample in a U-shaped quartz tube was activated in dry air at 300°C for 3 hours. After cooling to room temperature, high purity ammonia (99.99%) was adsorbed. The temperature was raised and held at 150°C until no physically adsorbed NH_3 was desorbed. The temperature was then automatically raised at 5°C/min to 700°C under a stream of He at 30 mL/min. Ammonia desorbed from the sample was titrated with amidosulfonic acid using the Radiometer RTS822 automatic titrator. The total acid amount of the sample can be read in the automatic titrator.

ISOPROPANOL DEHYDRATION

In a typical experiment 100 mg of sample, fixed with 200 mg quartz wool in a U-tubed pyrex reactor, was activated in air at 300 ° C for 6 hours. A saturator containing the isopropanol was kept at a constant temperature of 25°C. Nitrogen was used as a carrier gas at a constant flow rate of 15 mL/min. The reaction temperature was at 160°C. The product was sampled by a six-port valve and analyzed by a Shimadzu gas chromatograph (GC-8A) with a thermal conductivity detector. The column was a 3 meters long and packed with 5% Carbowax in 60–100 mesh HMDS-treated acid-wash Chromsorb W.

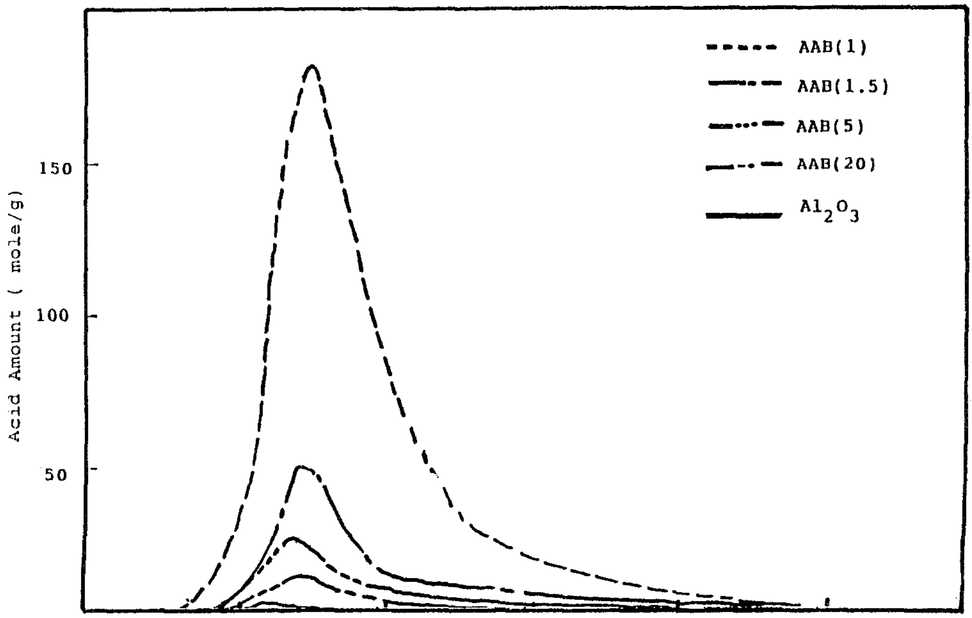

Fig. 2. NH_3 TPD of AAB.

3. Results and discussion

NH_3 TPD

Because ammonia gas is basic, it can be adsorbed on the surface acidic sites of AAB compounds. Thus, one can apply TPD to measure the acidic strength of these catalysts, and from the titration amount of desorbed ammonia gas, the concentration of surface acidic sites can be determined [9,10]. Fig. 1 shows that the maximum desorption temperatures (T_{max}) of AAPs with different Al/P ratios are in the range of 230–250°C, indicating that these catalysts belong to medium strength acids. As shown in fig. 2, the T_{max}. of AABs with different Al/B ratios are also in the vicinty of 230°C. Fig. 3 demonstrates that the total

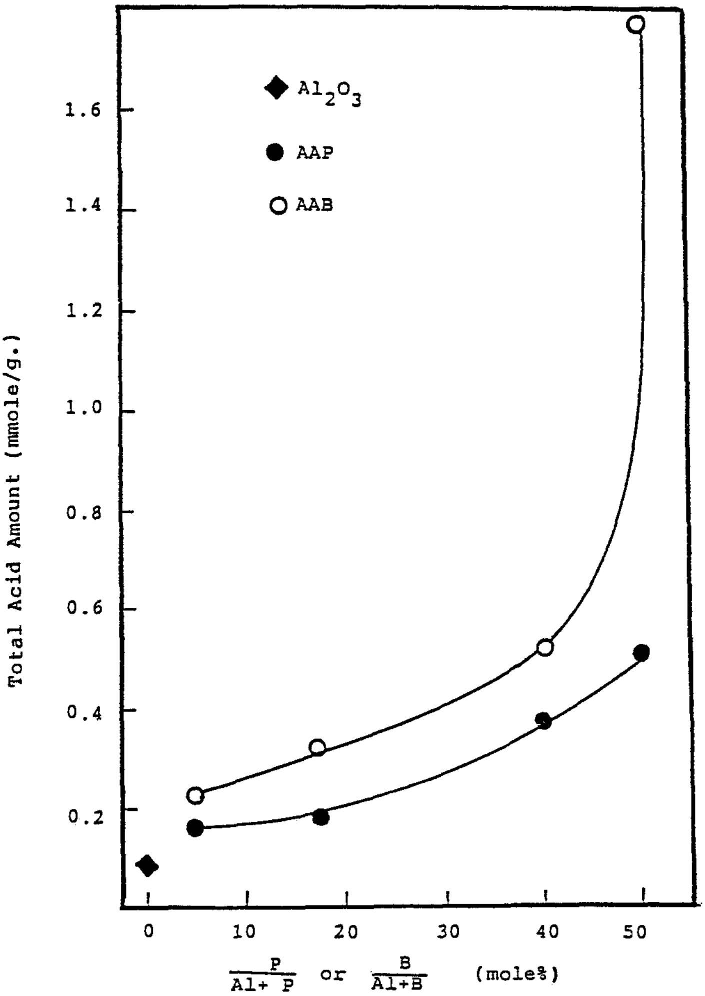

Fig. 3. Acid amount vs. phosphorus content and boron content for AAP and AAB, respectively.

acidic amount is closely related to the phosphorus content and boron content for AAP and AAB, respectively. In addition, under the same aluminum content, the acidic amount of AAB is larger than that of AAP. Campelo et al. [10] reported that the surface acidity of AAP is determined by the degree of crystallinity and Al/P ratio. The higher the phosphorus content, the stronger the acidic strength is. Wendt [11] obtained the same results. In this study, we found that the acidic amount of AAB is increased with the boron content. However, this composition effect has no influence on the acidic strength. No distinction is made between Lewis or Bronsted acid sites with this NH_3 TPD method. Fig. 2 also indicates that the addition of boron, even in a small amount, in the r-alumina system could significantly enhance the acidities of the catalysts.

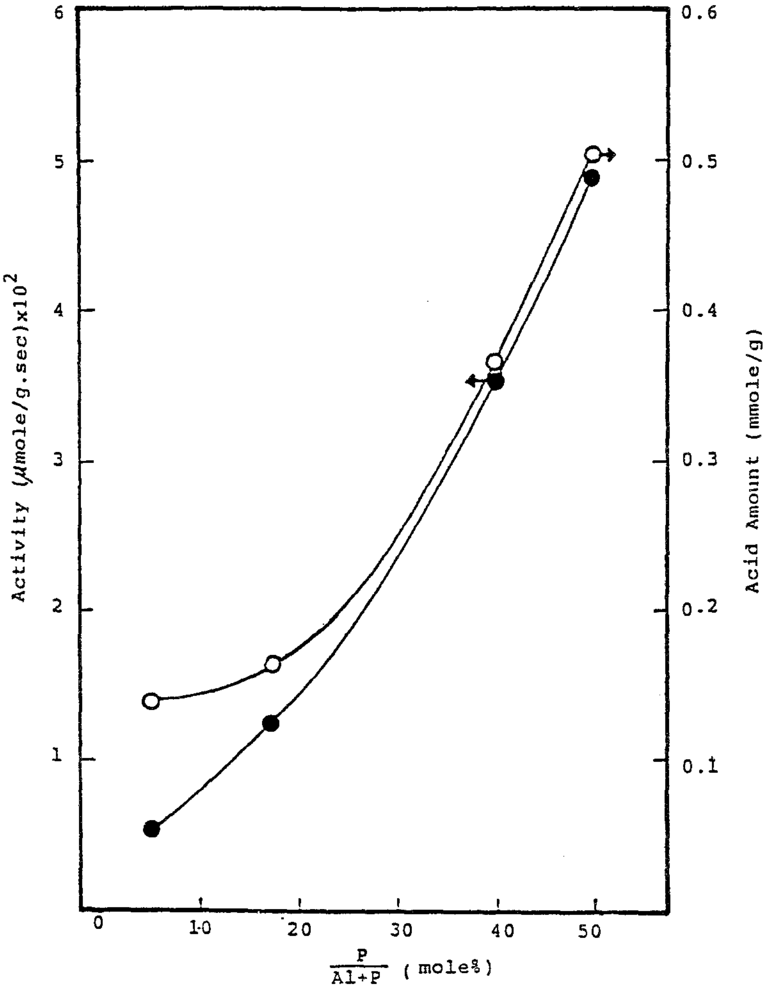

Fig. 4. Isopropanol dehydration activity and acid amount vs. phosphorus content for AAP.

ISOPROPANOL DEHYDRATION REACTION

In the isopropanol catalytic reaction, there are two possibilities. One is the electronic effect of dehydrogenation to produce acetone, the other is the acidic effect of dehydration to produce propene and water [10]. The results indicated that isopropanol proceeds simply by the dehydration reaction on AAP and AAB catalysts, in agreement with the literature data [11]. No acetone was formed over any of these catalysts. Figs. 4 and 5 show the dehydration activities and acid amount of AAP and AAB as a function of phosphorus content and boron content, respectively. The results indicated that the reaction activities are mainly decided by the amount of the acidic sites, not by the acid strength. Murakami et al. [12] also obtained the same results in the acidic cracking reaction over AAP catalysts. Since the increase in the phosphorus content can elevate the concen-

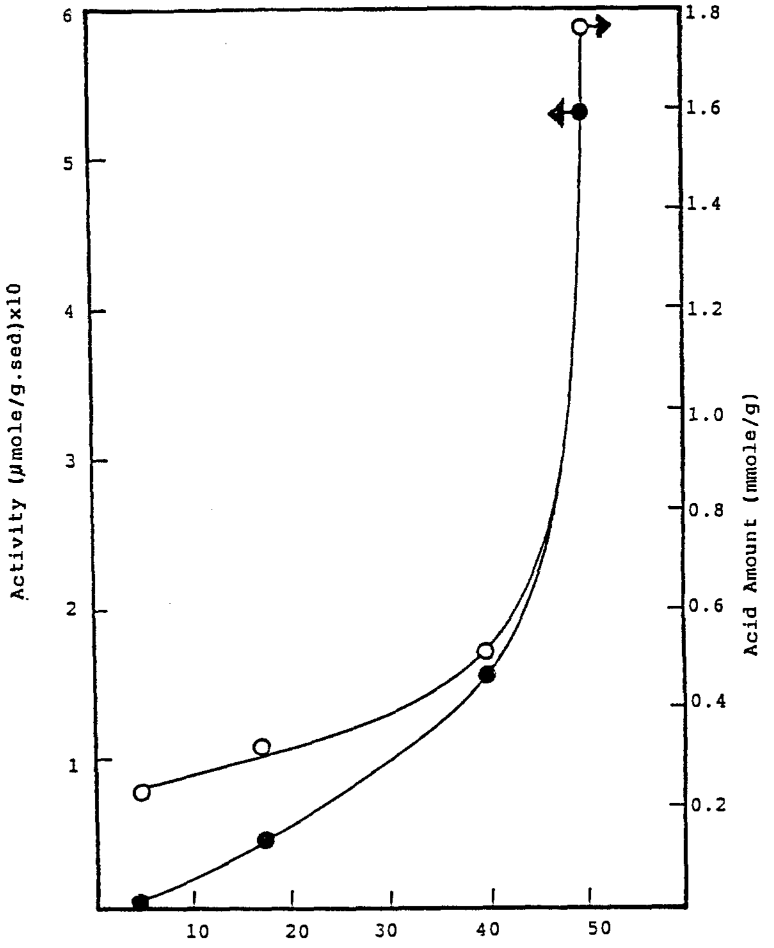

Fig. 5. Isopropanol dehydration activity and acid amount vs. boron content for AAB.

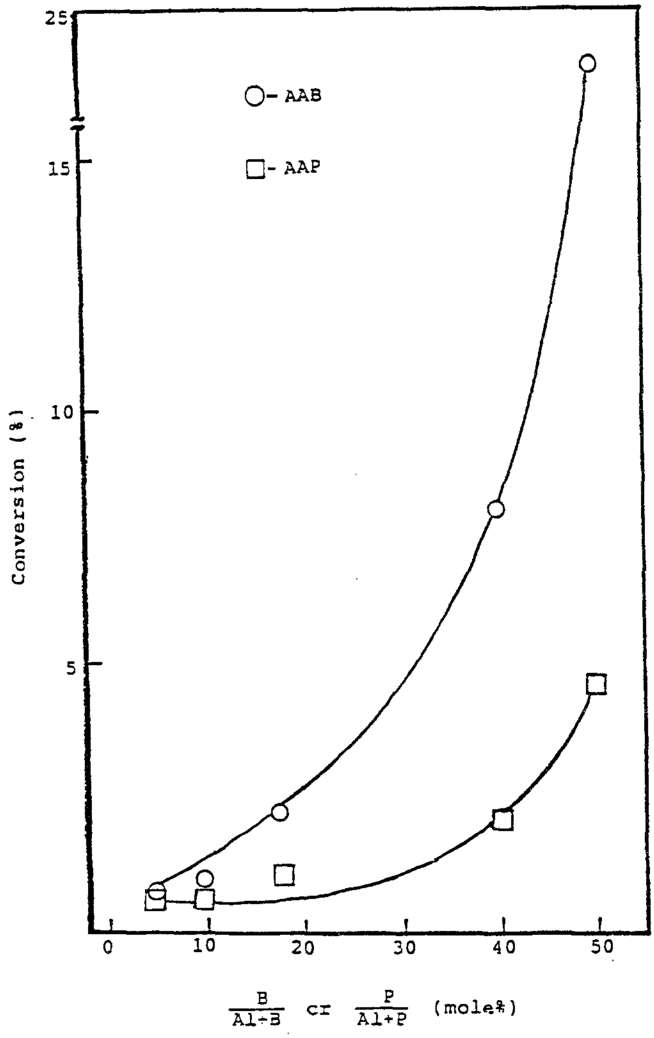

Fig. 6. Isopropanol dehydration activity vs. phosphorus content and boron content for AAP and AAB, respectively.

tration of acidic sites, and this would result in the increase of dehydration activities. Fig. 6 shows that the dehydration activities of AABs are higher than those of AAPs. This again can be attributed to the larger amount of acidic sites in AAB catalysts.

4. Conclusion

A series of AAB catalysts with various Al/B ratios have been prepared via the coprecipitation technique. TPD of NH_3 and isopropanol dehydration reaction have been used to characterize the surface acidities of these catalysts. AAP samples were also included in this study for comparison. TPD of NH_3 results indicated that both AAB and AAP belong to medium strength acids. The number of acid sites is increased with increasing the phosphorus content and boron content, respectively. In addition, the number of the acidic sites of AAP is smaller than that of AAB. The activity of isopropanol dehydration on AAB is higher than that on AAP with the same aluminum content. In addition, the activity of isopropanol on AAB is increased with increasing the boron content. This is essentially due to the different amount of acidic sites, not to the acidic strength of these catalysts.

Acknowledgement

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