Effect of preparation method on the acidities of Al–B–O_x mixed oxides

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Received 8 December 1992; accepted 11 March 1993

A series of Al–B–O_x metal oxides with various Al/B ratios were prepared with impregnation and coprecipitation methods. 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 130–260°C under atmospheric pressure. The results of TPD of ammonia indicated that the surface acidity of Al–B–O_x material is medium-strong. The acidic strengths are approximately the same for all the Al–B–O_x samples, regardless of its preparation method. In addition, their acid strengths are much stronger than that of pure alumina. However, the acid concentration is increased with decreasing the Al/B atomic ratio of the catalyst. The dehydration activities of these catalysts are increased with decreasing the Al/B atomic ratios of the samples. The results also indicated that the addition of boron on alumina, no matter what preparation method is used, could significantly enhance the acidities of the catalysts. A compensation effect was observed in isopropanol dehydration reaction over these catalysts. The preexponential factor decreases and activation energy increases with increasing Al/B ratio of the catalyst. The results can be interpreted in terms of the acidity of the catalyst.

Keywords: Al–B–O_x metal oxide; isopropanol dehydration; solid acid catalyst; characterization (temperature-programmed desorption of ammonia)

1. Introduction

The applications of binary oxides such as silica–alumina, alumina–aluminum phosphate, alumina–aluminum borate, and iron oxide–iron phosphate, to catalyze dehydration, isomerization, and alkylation have been widely reported [1–11]. One important result of the reported mixed-oxide work is the knowledge that some of these materials can function as strong acid solids, some even behaving as superacids [8].

Al–B–O_x mixed oxide has been reported to be a good catalyst and a good cata-

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lyst support material for various reactions. Pine [7] employed alumina–boria on hydrocarbon conversion process. Sato et al. [8] reported that alumina–boria is a good catalyst for the Beckmann rearrangement of cyclohexanone oxime. Peil et al. [9] and Wang and Chen [5] have shown that Al–B–O_x binary metal oxide prepared with coprecipitation method is highly acidic. Tsai et al. [12] have shown that Al–B–O_x is a good support for hydrodesulfurization catalysts. In a previous paper [13], the authors have reported that it is a good support for liquid phase hydrogenation catalysts.

It has been shown that the surface acidities are affected by the preparation methods of the mixed oxide [1]. Most of the researchers used the incipient-wetness impregnation method to prepare Al–B–O_x catalysts. Here we report a study of the effect of preparation methods on the acidities of Al–B–O_x metal oxides as determined by temperature-programmed desorption of ammonia. We also studied the dehydration reaction of isopropanol in order to understand the correlation with the acidic properties. Previous reported results [5] are also included just for comparison.

2. Experimental

2.1. CATALYST PREPARATION

Al–B–O_x oxides were prepared by the impregnation and coprecipitation methods. The impregnated catalyst was obtained by impregnating γ-alumina (24–60 mesh granules) with aqueous boric acid followed by calcination at 500°C. The coprecipitated catalyst was prepared from common solutions of aluminum nitrate and boric acid using an ammonium hydroxide solution as a precipitant. 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 throughout the precipitation process. The resulting precipitate was then filtered, washed with distilled water, dried overnight at 120°C, and then calcined at 500°C for 12 h. The Al / B atomic ratios of the catalysts were varied from 1 to 20 by altering the relative amounts of aluminum nitrate and boric acid.

2.2. CHARACTERIZATION

The Al to B atomic ratios were obtained by an inductively coupled plasma-atomic emission spectrophotometer (Herarus CHN-O-Rapid). Materials were first dissolved by aqua regia and then diluted to a concentration of about 1000 ppm for measurement. The specific surface areas and pore diameters of the samples were determined by adsorption of nitrogen at −197°C using a Micromeritics 2600 surface area analyzer.

2.3. NH_3 TPD

In a typical experiment, 100 mg of sample in a U-shaped quartz tube was activated with He at 300°C for 3 h. After cooling to room temperature, high purity ammonia (99.99%) was adsorbed. The temperature was raised and held at 120°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 trapped in a buffer solution of boric acid and autotitrated with sulfamic acid using the Radiometer RTS822 automatic titrator. The total acid amount of the sample can be read in the automatic titrator.

2.4. ISOPROPANOL DEHYDRATION

The catalytic experiments were carried out in a flow system. A stream of helium (30 cm^3/min) was used as a carrier for the isopropanol (Merck reagent, water content $<0.1\%$), which was contained in a bubbler maintained at 25°C. The carrier gas was passed through a purifier (Matheson 6406) to remove traces of oxygen. In a typical experiment 100 mg of sample, fixed with 200 mg quartz wool in a U-tubed silica reactor, was reactivated at 300°C for 3 h. The temperature in the furnace containing the reactor could be controlled to within ±0.1°C. A thermal couple located in the thermowell of the reactor confirmed isothermal operation. Several millimeters of glass wool were placed at each end of the reactor to avoid entrance and exit effects. The product was sampled by a six-port valve and analyzed by a Shimadtzu gas chromatograph (GC-8A) with a thermal conductivity detector. The column was a 6 m long and packed with Carbopack in 80–100 mesh SP-1000 at 100°C. The areas of GC peaks were determined with a Shimadtzu CR3 A integrator. In order to prevent any condensation of reactants and products in the apparatus, all connections from the saturator to the chromatograph were heated by heating tapes at 50°C. The precision or repeatibility of the conversion data was in the range of ±3%.

3. Results and discussion

3.1. PHYSICAL PROPERTIES

Table 1 summarizes the surface areas and pore diameters of the Al–B–O_x mixed oxides prepared for this study. Examination of the results for impregnated samples shows that the surface area is increased and the pore diameter is decreased with increasing the Al/B ratio of the catalyst. This is possibly due to the plugging of small pores of alumina by impregnation. However, the boron content had little effect on either the specific surface area or the pore diameter of the coprecipitated

Table 1
The pore structure of Al–B–O_x catalysts

Sample	Al/B ratio	Surface area (m^2/g)	Average pore diameter (Å)
Al_2O_3		225	154
impregn. Al–B–O_x	1.0	172	78
	1.5	183	93
	5.0	194	120
	10.0	212	142
	20.0	218	154
coprecip. Al–B–O_x	1.0	182	120
	1.5	268	88
	5.0	308	78
	10.0	298	84
	20.0	212	101

samples, in agreement with our previous results [5] and those reported in the literature [9].

3.2. NH_3 TPD

The acidities of Al–B–O_x mixed oxides with various Al/B ratios were measured by temperature-programmed desorption (TPD) of ammonia. The ammonia desorption temperature and the amount of ammonia evolved are considered to be an index of acid strength and acid amount, respectively [14]. Fig. 1 shows the TPD spectra of the impregnated catalysts. All demonstrate a mono dispersed distribution of acid sites. Heterogeneity of Al–B–O_x surface causes a wide range of adsorption energy for ammonia. This would result in a broad TPD peak existing on the profile. In a previous paper [5], one of the authors has shown the same patterns for the coprecipitated samples. No matter what preparation method is used, the maximum desorption temperatures (T_{max}) of ammonia on Al–B–O_x oxides are in the range of 280–300°C, indicating that these catalysts belong to medium strength acids. This increase in acidity is not uncommon in mixed-alumina systems, where the presence of divalent ions or tetrahedral inclusions is known to result in increased acidity [1]. Tanabe et al. [15] have reported that the acid sites on binary metal oxides are formed by an excess of a positive or negative charge in the mixed oxides. It is mainly determined by the coordination number of the minor cation, in this case, boron. Peil et al. [9] reported that the acidity of the precipitated Al–B–O_x is closely related to the relative concentration of BO_4. Since boron has a higher electronegativity than aluminum, B–OH would be more acidic than Al–OH.

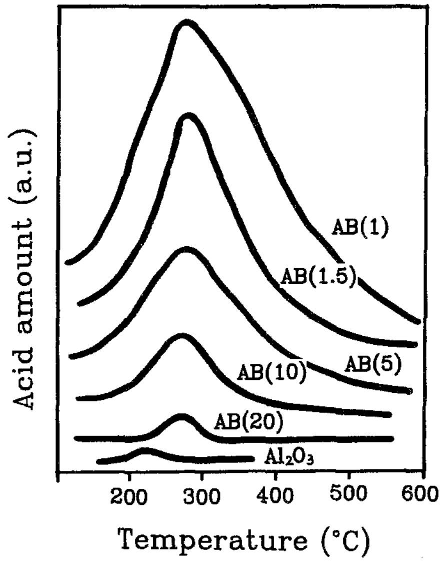

Fig. 1. NH_3 TPD of impregnated Al–B–O_x catalysts.

Fig. 2 shows the T_{max} of TPD NH_3 for the impregnated catalysts versus the B/Al atomic ratio. The effect of boron on the relative strength of the acid sites is very pronounced. In going from alumina to an Al–B–O_x material with a B/Al ratio of 0.05, the acid strength is increased dramatically. However, further increase in B content did not increase the acid strength of the catalyst. The precipitated catalysts gave the same results as reported in the previous paper [5].

Fig. 3 demonstrates that the total acidic amount is closely related to the boron content of Al–B–O_x catalyst. In addition, under the same boron content, the acid amount of the coprecipitated catalyst is larger than that of the impregnated one.

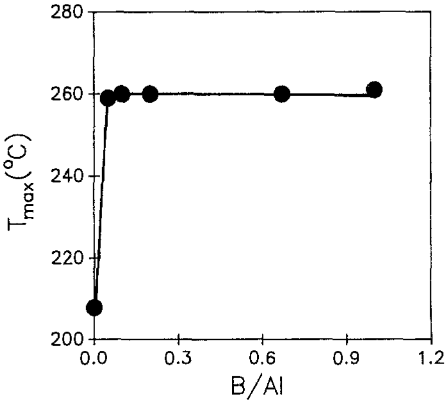

Fig. 2. T_{max} of TPD NH_3 versus B/Al atomic ratio of the impregnated catalysts.

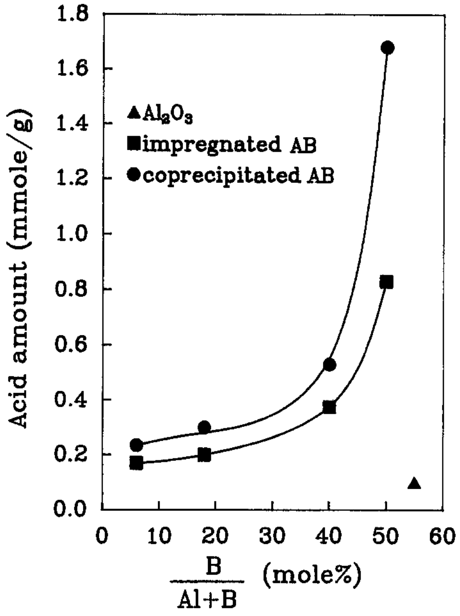

Fig. 3. Acid amount versus boron content for Al–B–O_x catalysts.

3.3. ISOPROPANOL DEHYDRATION REACTION

In the isopropanol catalytic reaction, there are three possibilities: (i) monomolecular dehydration to propylene and water, (ii) dehydrogenation to ketone and hydrogen, and (iii) bimolecular dehydration to diisopropyl ether and water. The results of this study indicated that isopropanol proceeds simply the monomolecular dehydration reaction to propylene and water on Al–B–O_x catalysts. Only trace amount of other products were detected over these catalysts. Fig. 4 shows the dehydration conversions of Al–B–O_x catalysts. The results clearly show that all the Al–B–O_x catalysts are much more active than the pure alumina. The coprecipitated catalyst is more active than the impregnated one, provided the boron content is the same. In addition, the dehydration activity is increased with decreasing the Al/B atomic ratio of the catalyst. The increase of activity with boron content is possibly due to a high degree of boron dispersion on the support surface [16]. Since boron has a higher electronegativity than aluminum, B–OH would be more acidic than Al–OH.

The reaction data at 160°C were replotted in fig. 5 for comparison. However, it holds the same trend even at other reaction temperatures. Fig. 5 shows that the dehydration activity is increased sharply with increasing the boron content of the catalyst no matter what preparation method is used. Murakami et al. [17] also obtained the same results in the acidic cracking reaction over aluminum phosphate catalysts. The increase in the boron content can increase the concentration of

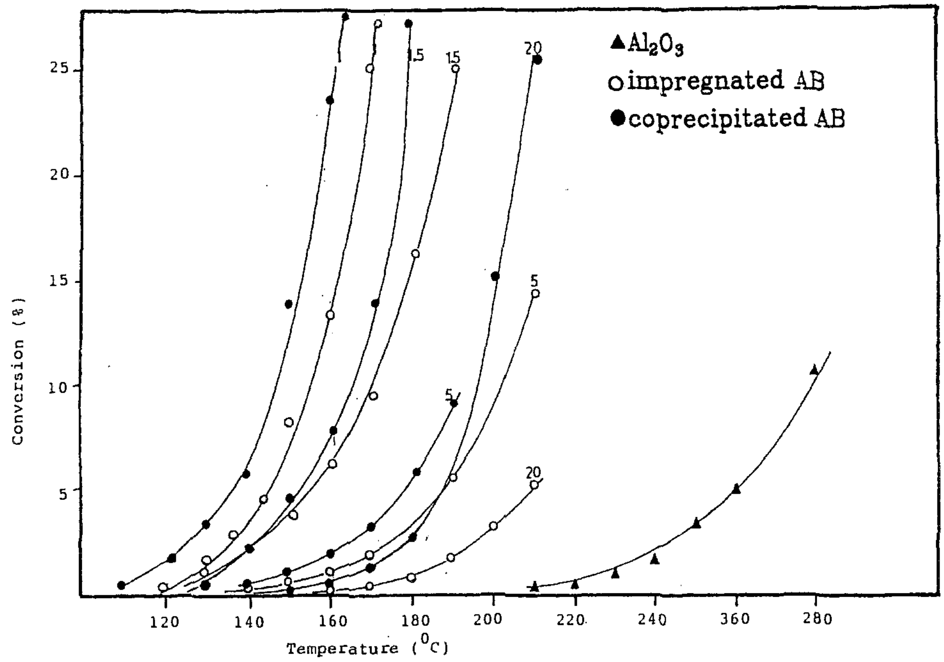

Fig. 4. Isopropanol dehydration conversion of Al–B–O_x catalysts. (The number on the line is the Al/B atomic ratio.)

acidic sites, and this would result in the increase of dehydration activities. It should be noted that the dehydration of isopropanol is not a very demanding reaction when it comes to acid strength [9]. Even in pure Al_2O_3 some activity for dehydration of isopropanol is evident at 160°C.

Activities, activation energies, and preexponential factors were based on the expression

$$r = A_0 \, e^{-\Delta E/RT} P_{\mathrm{IPA}} , \qquad (1)$$

where r is the activity, A_0 the preexponential factor, and ΔE the activation energy for isopropanol conversion. Table 2 shows that the preexponential factor and activation energy increase with each other, i.e. the two values change in the same sign. This is the well-known compensation effect which is probably due to the existence of reaction intermediates (activated complex) so that the differences of entropy and enthalpy change in the same sign [18].

The preexponential factor is generally related in surface reactions to the number of collisions occurring on the surface; this number is dependent upon the density of active surface sites. The observed variations in A_0 with variations in Al/B ratio could be due to changes in the relative amount of acid sites. Indeed this is consistent with the observations in fig. 3 of increasing acid amount with decreasing Al/B ratio.

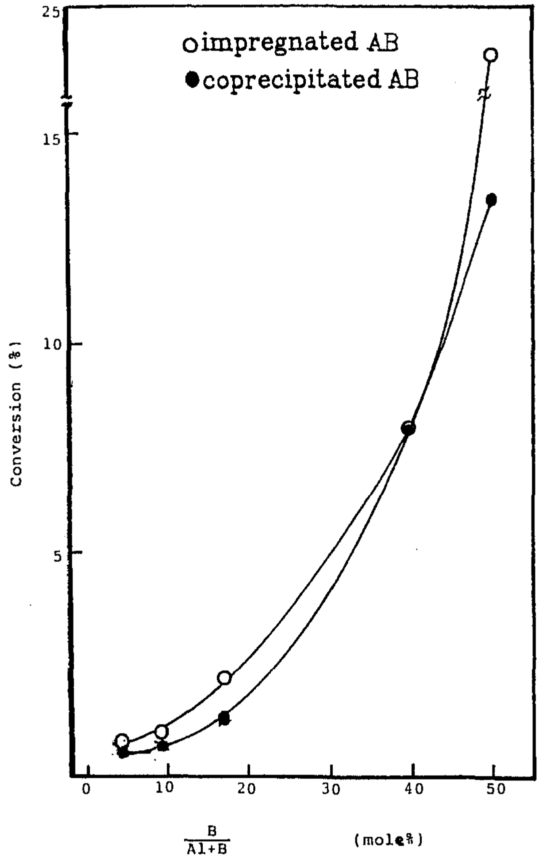

Fig. 5. Isopropanol dehydration activity versus boron content for Al–B–O_x catalysts. (Reaction temperature: 160°C.)

The activation energy is related to the changes in binding energy from reactants to the transition-state complex. It is a measure of the binding energy of reactants involved in the rate-determining step. The observed changes in activation energy with addition of boron might be explained by changes in the electronic structure induced by the inclusion of boron into alumina. This explanation is supported by the higher acid strength of Al–B–O_x compared to that of pure alumina.

4. Conclusion

A series of Al–B–O_x catalysts with various Al/B atomic ratios have been prepared via the impregnation and precipitation techniques. TPD of NH_3 and isopropanol dehydration reaction have been used to characterize the surface acidities of these catalysts. TPD of NH_3 results indicated that Al–B–O_x catalysts

Table 2
Kinetic parameters of isopropanol dehydration on Al–B–O_x catalysts

Catalyst	Al/B ratio	A_0 [a]	ΔE [b] (kJ/mol)
Al_2O_3		0.0156	30.0
impregn. Al–B–O_x	1.0	0.0500	20.3
	1.5	0.0440	23.3
	5.0	0.0300	24.0
	10.0	0.0220	25.0
	20.0	0.0210	28.9
coprecip. Al–B–O_x	1.0	0.0495	22.6
	1.5	0.0445	23.2
	5.0	0.0298	27.5
	10.0	0.0290	27.3
	20.0	0.0220	29.4

[a] Preexponential factor.
[b] Activation energy.

are medium strength acids. The amount of acid sites is increased with decreasing the Al/B ratio of the catalyst. In addition, the activity of isopropanol on Al–B–O_x is increased with decreasing the Al/B ratio of the catalyst. A compensation effect is observed in isopropanol dehydration reaction. The preexponential factor decreases and activation energy increases with increasing Al/B ratio of the catalyst. The results can be interpreted in terms of acid characteristics of the catalyst.

Acknowledgement

This work was supported by the National Science Council, Taiwan, ROC, under contract number NSC-81-0402-E008-12.

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