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NOTES

Catalytic Properties of BF_3-treated Aluminas

III. Influence of Precalcination Temperature on the Product Selectivity in 1-Butene Isomerization and n-BuOH Dehydration

Boron trifluoride-treated oxide catalysts present a remarkable activity for various acid-catalyzed reactions (*1–5*). Recently, Rhee and Basila described in detail the chemisorption of BF_3 on a few oxide surfaces by means of infrared spectroscopy (*6*). Although numerous works on a catalyst promotion with BF_3 appeared in literatures, little work has been done to clarify the nature of the acid sites on catalyst surface. In our previous works (*7–8*), we reported on the relationship between the butylamine acidity and the catalytic activities in a series of BF_3-treated alumina catalysts. It was conclusively suggested that the remaining hydroxyl groups may well be strong Bronsted centers by promotion with BF_3. A spectrophotometric study of chemisorbed triphenyl chloride and an ESR study of adsorbed perylene were made, and the results were discussed in relation to the butylamine acidity. In the present study, to obtain further information concerning the nature of acid sites, the activity and product selectivity in 1-butene isomerization and in dehydration reaction of *n*-butyl alcohol were examined for BF_3- treated alumina catalysts and other solid acids.

A series of BF_3-treated alumina samples were prepared as follows. Aluminas were made by the thermal decomposition of aluminum hydroxide, which was consisted of well crystallized bayerite. The calcination of alumina was done at various temperatures ranging from 300 to 1000°C. Boron trifluoride was adsorbed by charging through a fixed bed of alumina at room temperature. Silica–alumina (SA, 13% alumina) and solid phosphoric acid (SPA) employed in this study were commercial products. Alumina–boria catalyst (AB) was prepared by the Izumi and Shiba procedure (*11*). The isomerization of 1-butene was performed in a closed circulating system. Each catalyst was first heated at 300°C *in vacuo* at a pressure of $10^{-4} \sim 10^{-5}$ Torr for 1 hr and then cooled to reaction temperature. Initial pressure of 1-butene of 99% purity was 250 mmHg. The catalytic activity for the dehydration of *n*-butyl alcohol was studied by a usual gas flow fixed-bed reactor at atmospheric pressure.

The observed activity and product selectivity for the isomerization of 1-butene and dehydration of *n*-butyl alcohol for the catalysts are listed in Table 1. The rate constants for 1-butene isomerization were derived by assuming as a first order reaction and product selectivities (*cis*-2-butene/*trans*-2-butene) calculated for each samples were obtained by extrapolation at zero conversion. A significant influence of precalcination temperature on the isomerization activity and product selectivity was revealed at Fig. 1. When alumina was dehydrated in approximately 450°C prior to BF_3-adsorp-

TABLE 1

ACTIVITY AND PRODUCT SELECTIVITY FOR 1-BUTENE ISOMERIZATION AND n-BUTYL ALCOHOL DEHYDRATION OVER VARIOUS SOLID ACIDS

		Isomerization of 1-butene at 30°C			Dehydration of n-BuOH at 270°C			
						Composition of n-C_4H_8		
Catalyst[a]	Surf.[b] area (m^2/g)	Activity k (min^{-1} g^{-1})	Product selectivity (*cis*/*trans*)	E_a (kcal/mole)	Conv. (%)	1-Butene	2-Butene	*cis*/*trans*
BA-400	192	0.203	0.94		98.3	24.4	75.6	0.71
BA-500	158	0.175	0.85	6.0	98.1	26.2	73.8	0.79
BA-600	134	0.079	1.00		83.8	27.7	72.3	0.92
BA-700	130	0.089	1.70		81.0	25.7	74.3	0.93
BA-800	119	0.102	2.06	7.5	71.1	30.1	69.9	1.10
BA-900	111	0.083	1.80		56.3	37.3	62.7	1.27
SPA-350	185				92.0	18.2	81.8	0.79
SA-500	449	0.070	0.93		100	21.5	78.5	0.81
AB-700	286				100	21.7	78.3	0.85
A-500	233	0.063[c]	5.40	16.8	89.8	72.3	27.7	1.72
BA-500-P					87.0	24.6	75.4	0.85
BA-900-P					40.1	15.6	84.4	0.98

[a] Each catalyst was precalcined at indicated temperatures (°C).

[b] By nitrogen adsorption.

[c] Activity observed in a reaction at 130°C.

tion (BA-450), maximum activity was obtained for both reactions examined in this work. The same results were also illustrated in cumene cracking and other reactions over BF_3-treated aluminas (7). The ratio between the two butenes produced in the reaction falls in a range of 0.85 to 2.06. The values were markedly varied in accordance with the calcination temperature. Whereas the initial ratio of *cis*-2-butene to *trans*-2-butene was found to be near unity for the low temperature-precalcined BF_3–alumina catalysts (e.g., BA-400), a considerable increase of *cis*-distribution was indicated for the sample of BA-900. The observed temperature dependence would estimate the activation energies for the isomerization of 1-butene over pure alumina of 16.8 kcal/mole, and of 6.0 ~ 7.5 kcal/mole for the BF_3-treated aluminas (Table 1).

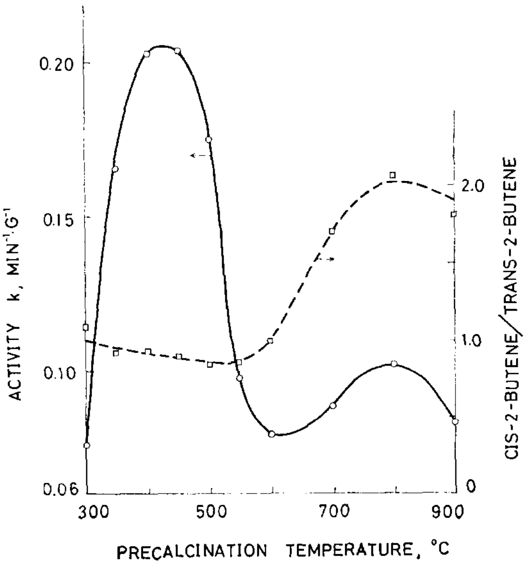

FIG. 1. Influence of precalcination temperature on activity and product selectivity of 1-butene isomerization over BF_3–alumina catalysts.

The composition of product butenes for the n-butyl alcohol dehydration over these catalyst samples appreciably changed depending on their respective precalcination temperature. In general, the isomeric 2-butenes were formed selectively in the case of the BF_3-treated samples as indicated in BA-400 and BA-500, and some other solid acids (SPA-350 and SA-500) in which the active centers are believed to be mainly of the Bronsted type. On the other hand, the samples obtained at higher precalcination temperatures (e.g., BA-900) gave relatively small ratios of 2-butene with a large distribution of the *cis*-isomer, which is considerably close to the experimental result with pure alumina (A-500), as reported by Pines and Haag (*12*). When the BA-900 was saturated with perylene (BA-900-P), the composition of the produced 1-butene showed a remarkable decrease, as compared with that in the case of BA-900. It is of interest that there is but a little difference in 1-butene composition between BA-500 and BA-500-P. This fact might be caused by the difference in the acid type of the catalyst concerned.

Although the mechanisms of *n*-butene isomerization and of *n*-butyl alcohol dehydration over solid acids appear not to be clear, these catalyst-dependent selectivities have been found to be quite general on most oxides (*13*, *14*). It is noticeable that the experimental observations in the above reactions are relatively well explained by correlating each acidity composition described in the previous work (*8*), in which it was assumed that both the Bronsted and Lewis acidity composition change with the precalcination temperature, although it becomes to be practically doubtful that strong Lewis sites removes chloride ions from triphenyl chloride, as discussed by Hirschler and Hudson (*9*) and Wu and Hall (*10*). With all such uncertainty above mentioned in determining Lewis sites on the catalysts studied, it may be concluded that the strong Bronsted sites, as described by Antipina and Vinokurora (5), would be expected to exist on the surface of the samples precalcined at relatively low temperatures up to 600°C, but when precalcined above 700°C, the composition of Lewis sites would be important in total acidity.

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