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Catalytic Properties of BF_3-treated Aluminas. IV. The Effect of BF_3 Adsorption on the Acidic Properties of Aluminum Oxides

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An account was given of the surface acidic properties of a series of BF_3-treated aluminum oxides, ranging in their precalcination temperature up to 1000°C. It was concluded that all aluminum oxides dehydrated over 300°C were converted to solid acids with new strong acid centers of $H_0 \leqq -8.2$ by adsorption with BF_3. This new acid centers would be certainly of the Brönsted type. Their catalytic activities in some carbonium ion type reactions are well correlated with the *n*-butylamine acidity in the presence of Hammett's indicators, and the maximum number of acid centers was observed in catalyst samples precalcined at 450 and 800°C respectively. The present study also suggests that the acid centers developed on the surface of aluminum oxides are somewhat different in nature depending upon their precalcination temperatures. Since there was a good correlation between the amount of the remaining hydroxyl groups and that of the absorbed BF_3, the surface hydroxyl groups, in addition to the aluminum atoms serving as the Lewis centers, which are not fully coordinated, were discussed as the most important factors in the formation of such acid centers.

It is well known that BF_3-treated acidic oxides are effective for catalysis in some hydrocarbon conversion reactions. Some studies of catalysts activated with BF_3 have been published in the literature;[1–5] however, little work has been done to clarify the effect of BF_3 adsorption on the nature of the acid centers responsible for catalytic activity. Recent results reported by Antipina and Vinokurora[5] have indicated that the treatment of aluminum oxide with HF or BF_3 does not greatly increase the strength of the acid centers on the surface, but is accompanied by the formation of a certain number of new, relatively weak centers. Since BF_3 is believed to react with the surface hydroxyl groups, it can be accepted that the activity and stability of activated aluminum oxide depend substantially upon the surface properties of the initial alumina.

Pure aluminum oxide has intrinsic acidic properties and thus has been widely employed as a catalyst or as a catalyst support. It is now well established that the acid center of pure alumina can generally be characterized as a Lewis type. On the other hand, there are very little consideration of the presence or absence of Brönsted acid centers on the surface. When aluminum hydroxide is calcined at various temperatures up to 1000°C, it may be expected that the alumina formed will have a great variety of acidity and activities corresponding to the respective surface properties. For example, Peri[6] has demonstrated that several acidic types of hydroxyl groups exist on the surface of dehydrated alumina; it is considered that such surface properties are strongly affected by BF_3 treatment.

Accordingly, we have attempted to clarify the nature of the acid centers developed by such a treatment, and to find whether these centers are of the Brönsted and/or the Lewis type. In this study, we selected a series of aluminum oxides ranging in precalcination temperature from 130°C to 1000°C as adsorbents and investigated the effect of BF_3 treatment on the acidic properties after modification.

Experimental

Materials. The alumina (A-) used in this work was obtained by the thermal decomposition of bayerite. The aluminum hydroxide was prepared by the hydrolysis of aluminum isopropoxide with water. The product was washed with distilled water, kept standing overnight at 130°C, and finally calcined at various temperatures for 3 hr a stream of dry nitrogen. The boron trifluoride was a commercial product of the Hashimoto Kasei Co. (Osaka), with a purity of 99.5%. All the chemicals, cumene, toluene, *o*-xylene, and benzene, were the reagent-grade commercial products. They were dried over metallic sodium and then distilled. The propylene was used after purification by distillation. The ethylmagnesium bromide used for the determination of the hydroxyl content was prepared by mixing ethyl bromide with a magnesium ribbon in di-*n*-butyl ether at 30°C. The Hammett's and arylmethanol indicators for the determination of the acidity distribution are

TABLE 1. HAMMETT AND ARYLMETHANOL INDICATORS

Indicator	p*K*	H_2SO_4 Concn (wt%)
Hammett indicators:		
p-Dimethylaminoazobenzene	+3.3	3×10^{-4}
4-Phenylazodiphenylamine	+1.5	2×10^{-2}
Dicinnamalacetone	−3.0	48
Benzalacetophenone	−5.6	71
Anthraquinone	−8.2	90
Arylmethanol indicators:		
4,4′,4″-Trimethyltriphenylmethanol	−4.0	36
Triphenylmethanol	−6.6	50
Diphenylmethaonl	−13.3	77

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1) C. J. Plank, U. S. 2428741 (1947).

2) Y. M. Paushkin and Y. U. Lipatov, *Dokl. Akad. Nauk SSSR*, **76**, 547 (1951).

3) a) T. V. Antipina and E. H. Avdonika, *Zh. Fiz. Khim.*, **33**, 192 (1959); b) T. V. Antipina and E. M. Cherednik, *ibid.*, **35**, 836 (1961); c) V. A. Chernov and T. V. Antipina, *Kinet. Katal.*, **4**, 595 (1963).

4) G. L. Herbert and C. B. Linn, U. S. 3114785 (1963).

5) T. V. Antipina and E. B. Vinokurora, *Kinet. Katal.*, **9**, 199 (1968).

6) J. B. Peri, *J. Phys. Chem.*, **69**, 220 (1965).

listed in Table 1, together with the pK_a and pK_r values.

Apparatus and Procedure. The adsorption of BF_3 was carried out at room temperature under atomospheric pressure by exposing the dehydrated aluminum oxides for 5 min or less; then immediate evacuation was done to remove any residual vapors. Differential thermal analysis was carried out under atomospheric pressure. The water loss of alumina with heating was determined gravimetrically on a silica spring balance, as has been reported elsewhere.[7] The X-ray data were obtained using nickel-filtered Cu-$K\alpha$ radiation, a Geiger-counter X-ray spectrometer of the Toshiba Electric Co. The specific surface area (BET) was measured with nitrogen as the adsorbate. The micropore volume was determined by a method proposed by Benesi.[8] The surface hydroxyl content was determined by the technique of Satoh *et al.*[9] The butylamine acidity was determined in the way described by Benesi.[10] All the catalyst sample, screened to 100—200 mesh particles, were evacuated by a high vacuum technique at 300°C for 3 hr before the measurement of their acidity. The catalytic activity for cumene cracking, *o*-xylene isomerization, and toluene disproportionation were studied using an all-glass, fixed-bed-flow reactor system. Each reactant mixture was fed in continuously by means of a gas-syringe drive. The reaction products were analyzed by glpc using a column packed with 5% silicon DC-550. Propylene polymerization was carried out in a closed apparatus, as has been described by Tamele.[11]

Results

Aluminum Oxides as Adsorbents. The characteristics of the various aluminum oxides used in this work are summarized in Table 2. Thermograms of a starting hydroxide are shown in Fig. 1. The main residual water is shown to have a sharp endothermic peak at around 350°C, which is believed to be characteristic of bayerite or gibbsite. The water loss of hydrous alumina at several dehydration temperatures is shown in Fig. 2. It is shown that a rapid decline in the water content occurred between 200 and 400°C, while above 600°C only a little loss of weight was detectable. These results are in good agreement with those of the endothermic heat change shown in Fig. 1.

Table 2. Surface properties of aluminum oxides

Calctn. temp. (°C)	Surf.[a] area (m^2/g)	Pore[b] volume (m*l*/g)	Av. pore dia (Å)	Hydroxyl content (OH/g × 10^{-20})	X-Ray diffraction pattern
A-130					bayerite
A-300	256	0.34	27	—	some *eta*
A-400	250	0.39	31	11.4	some *eta*
A-450	238	0.42	34	10.2	essentially *eta*
A-500	233	0.43	37	7.7	essentially *eta*
A-600	213	0.41	39	6.5	*eta*
A-700	183	—	—	5.8	*eta*, some *theta*
A-800	166	0.43	52	4.5	*eta* and *theta*
A-900	124	—	—	2.8	*theta*
A-1000	78	0.30	77	1.8	*theta* and *alpha*

a) by nitrogen adsorption (BET)
b) by a method described by Benesi[9]

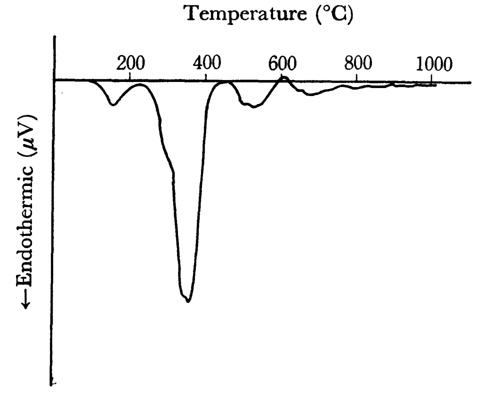

Fig. 1. Differential thermal analysis. (Heating rate: 10°C/min)

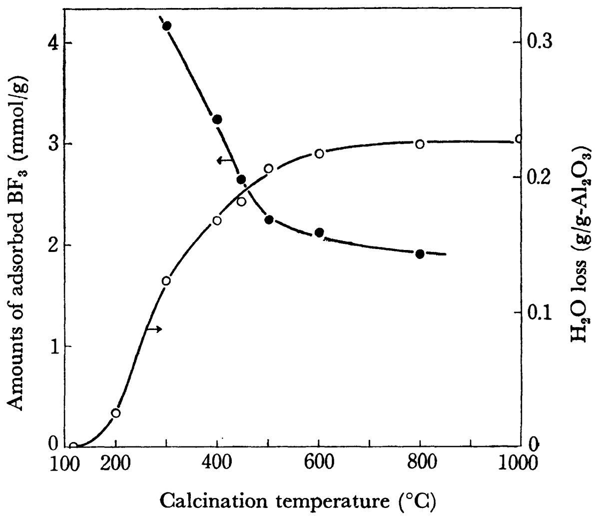

Fig. 2. Water loss with calcination temperature *vs.* amount of adsorbed BF_3 on aluminum oxides.

The specific surface area gradually decreases with the increase in calcination temperature. This diminution is appreciable after the elimination of the residual water shown in the endothermic peaks. The total pore volume of aluminum oxides increases as the heating temperature is raised, and they become simultaneous in pores of 18 to 77 Å. The maximum volume in the micropore is exhibited at around 500°C, indicating that the materials are obviously highly porous at this temperature.

The X-ray diffraction pattern of the original hydrate indicated a well-crystallized bayerite containing a trace of boehmite. As far as was determined by X-ray diffraction, no major phase transformations took place between 300° to 600°C, and the usual transformation to *theta* and *alpha* alumina was found above 600°C. It was indicated that when this material was heated at 400° to 500°C, it became a highly porous solid showing an X-ray pattern characteristic of relatively poorly crystallized *eta* alumina. This is possibly of great interest from the point of view of their catalytic action.

The acidic properties of a series of aluminum oxides

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[7] D. S. MacIver, H. H. Tobin, and R. T. Barth, *J. Catal.*, **2**, 485 (1963).

[8] H. A. Benesi, R. U. Bonnar, and C. F. Lee, *Anal. Chem.*, **27**, 1963 (1955).

[9] M. Satoh, T. Kanbayashi, K. Kobayashi, and Y. Shima, *J. Catal.*, **7**, 342 (1967).

[10] H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

[11] M. W. Tamele, *Discuss. Faraday Soc.*, **8**, 270 (1950).

Table 3. *n*-Butylamine acidity of aluminum oxides

Catalyst[a]	Acidity within intervals of pK_a (meq/g)				
	-8.2	$-8.2 \sim -5.6$	$-5.6 \sim -3.0$	$-3.0 \sim +1.5$	$+1.5 \sim +3.3$
A(B)-300	0.25	0.06	0.09	00.0	0.01
A(B)-400	0.49	0.04	0.01	0.01	0.07
A(B)-500	0.56	0.01	0.02	0.01	0.03
A(B)-600	0.47	0.01	0.08	0.03	0.05
A(B)-700	0.44	0.03	0.02	0.03	0.03
A(B)-800	0.36	0.05	0.05	0.02	0.01
A(B)-900	0.19	0.02	0.05	0.02	0.03
A(B)-1000	0.06	0.01	0.16	0.00	0.00
A(G)-500	0.37	0.00	0.11	0.01	0.01
A(G)-800	0.06	0.03	0.14	0.00	0.00

a) A(B)=bayerite as a starting material.
A(G)=gibbsite as a starting material.

were determined by *n*-butylamine titration using Hammett's indicators. The concentrations and strengths of the surface acid centers are demonstrated in Table 3. It is shown that some aluminas had a certain number of acid centers (~0.56 meq/g at $H_0 \leq -8.2$). It was also observed that the acidity at any acid strength varied remarkably with the increase in the dehydration temperature, which had its maximum at 500°C. Since these dehydrated aluminum oxides have such different surface properties, the appearance of an interesting surface behavior both for acidity and activity possibly resulted from their modification with BF$_3$.

Surface Properties of Aluminum Oxides after BF$_3$ Adsorption. The characteristics of a series of BF$_3$-treated aluminum oxides are summarized in Table 4. The adsorption of BF$_3$ was studied on various aluminum oxides, ranging in precalcination temperature from 300 to 1000°C. It was found that the amount of BF$_3$ adsorbed on the adsorbents dehydrated below 500°C decreases markedly with the increase in preheating temperature. However, the difference in the amount was negligibly small above approximately 600°C. When the results in Table 2 are compared with those in Table 4, it is clear that there is a good correlation between the remaining hydroxyl content and the amount of adsorbed BF$_3$.

Table 4. Surface properties of BF$_3$-treated aluminas

Catalyst and precalcination temperature (°C)	Surf. area (m^2/g)	Pore volume (ml/g)	Av. pore dia. (Å)	Amount of adsorbed BF$_3$ (wt%)	Amount of adsorbed BF$_3$ (mmol/g)
BA-300	200	0.22	25	21.9	4.1
BA-400	192	0.23	22	17.6	3.2
BA-450	190	0.30	31	15.2	2.6
BA-500	158	0.29	35	12.8	2.2
BA-600	134	0.29	43	12.5	2.1
BA-700	130	—	—	—	—
BA-800	119	0.25	41	11.7	1.9
BA-900	111	—	—	—	—
BA-1000	67	0.17	51	6.0	1.0

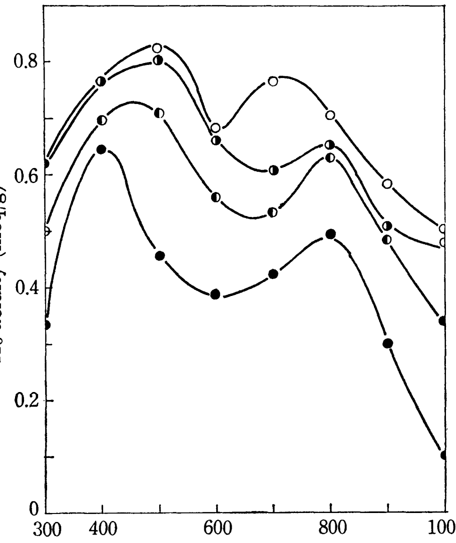

Fig. 3. *n*-Butylamine acidity of BF$_3$-treated aluminas at various temperatures.
-○-: p$K_a \leq +3.3$, -◑-: p$K_a \leq -3.0$, -◐-: p$K_a \leq -5.6$, -●-: p$K_a \leq -8.2$

The acidity of the BF$_3$-treated aluminum oxides was also determined by butylamine titration using two types of indicators, Hammett's and arylmethanol indicators. The distribution of the acid centers at diferent strengths is shown in Table 5 and Fig. 3. The following conclusions were obtained:

Table 5. *n*-Butylamine acidity of BF$_3$-treated aluminas

Catalyst	Total acidity within intervals of pK (meq/g)							
	pK_a					pK_r		
	-8.2	$-8.2 \sim -5.6$	$-5.6 \sim -3.0$	$-3.0 \sim +1.5$	$+1.5 \sim +3.3$	-13.3	$-13.3 \sim -6.6$	$-6.6 \sim -4.0$
BA-300	0.33	0.16	0.12	0.00	0.00	0.41	0.04	0.02
BA-400	0.64	0.05	0.06	0.00	0.01	0.70	0.14	0.02
BA-500	0.45	0.25	0.09	0.01	0.00	0.66	0.11	0.03
BA-600	0.38	0.17	0.11	0.00	0.01	0.61	0.09	0.04
BA-700	0.42	0.12	0.06	0.06	0.10	0.58	0.06	0.07
BA-800	0.49	0.14	0.02	0.05	0.00	0.61	0.07	0.03
BA-900	0.30	0.18	0.02	0.01	0.07	0.53	0.01	0.01
BA-1000	0.10	0.24	0.14	0.00	0.02	0.25	0.05	0.01

a) BF_3-treated aluminas had an appreciable number of acid centers at a strength of $H_0 \leq -8.2$ ($\sim$0.64 meq/g), but none or little acidity was observed in relatively weak centers ($H_0 > -3.0$). This does not coincide with the results of Antipina and Vinokurora.⁵⁾

b) As the precalcination temperature is raised from 300 to 1000°C, there is a remarkable difference in overall acidity; namely, the number of strong acid centers at $H_0 \leq -8.2$ reaches a maximum in the catalysts dehydrated at about 400 and 800°C. The catalyst obtained at 600°C indicated a considerably low acid number as is shown in Fig. 3.

c) All of the aluminum oxides, after treatment with BF_3, convert some arylmethanol indicators to the corresponding acid forms. On the other hand, initial pure aluminas do not change any H_r indicators to the acid form. This is evidently due to the difference in the nature of the surface acid centers.

As will be shown in the later part of this paper, such differences in acid number among several aluminum oxides are related to the results on the catalytic activity of various carbonium ion type reactions. The results for acidities shown in Table 5 enable us to differentiate the H_0 from the H_r acidity. BA-300 to BA-500 in Table 5 have large number of acid centers in both indicators. BA-800 to BA-1000, on the other hand, have relatively small H_r acidities but, more overall acidity exists.

TABLE 6. ACTIVITY FOR VARIOUS MODEL REACTIONS

Catalyst	Cumene^a) cracking 365°C (mol%)	*o*-Xylene^a) isomerzn. 350°C (mol%)	Toluene^b) disproptn. 500°C (mol%)	Propylene^c) polymerzn. 200°C *k*
BA-300	56.0	41.0	6.6	4.57
BA-400	77.3	77.0	13.5	7.13
BA-450	—	—	—	8.44
BA-500	74.9	67.0	12.9	6.54
BA-600	65.5	58.0	11.7	4.38
BA-700	76.1	57.1	—	5.38
BA-800	83.5	69.0	13.6	8.15
BA-1000	73.2	37.0	9.4	2.04
A-600	0.0	0.0	0.0	0.00
SA-500	85.8	49.5	18.5	—
SPA-350	19.6	—	0.0	—

a) SV=2.16 hr^{-1}, b) SV=0.4 hr^{-1}, c) P_0=360 mmHg; k= $min^{-1} \times g^{-1}$

Catalytic Activity. The comparative catalytic activities for some acid-catalyzed reactions are examined. The results are shown in Table 6. It was generally concluded that all of the catalytic activities of BF_3-treated alumina were much higher than those of non-treated alumina; the latter indicated no activity for any conversion reactions examined under the present experimental conditions. The BF_3-treated samples of BA-450 and BA-800 indicated a maximum conversion for all reactions, and BA-600 showed a quite low conversion. This activity profile shows a good fit the acid-site distribution shown in Fig. 3. The activity for *o*-xylene isomerization in Table 6 is plotted against the number of relatively strong acid centers. The plots with $H_0 \leq -5.6$ lie on a comparatively good straight line, as is shown in Fig. 4. Therefore, it seems likely that the acid centers having a strength of $H_0 \leq -5.6$ are responsible for the reactions studied in this paper.

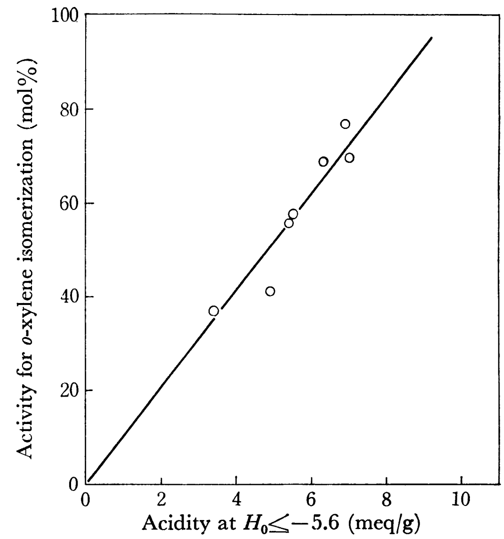

Fig. 4. Acidity at $H_0 \leq -5.6$ *vs.* activity for *o*-xylene isomerization at 350°C.

Discussion

Mainly in view of the acidic behavior of aluminum oxides before and after BF_3-treatment, the difference in surface properties due to the variation of their dehydration temperatures was studied, and it was demonstrated that the surface acidity of the activated catalysts depended, at least in part, on the initial properties, such as the hydroxyl content and the crystallinity.

Table 6 shows the catalytic activities with some other solid acids. It was found that the BF_3-treated aluminas, especially those precalcinated at around 450 and 800°C, indicated nearly the same high activity as the silica-alumina catalyst. However, non-treated pure alumina showed no activity for any of the reactions in this work. The catalytic action of BF_3-treated aluminas is assumed to be due to the formation of new Brönsted centers. As may be seen in Tables 2 and 4, it has already been described that the concentration of the surface hydroxyl groups of aluminum oxides decreases gradually as the dehydration temperature is raised to 1000°C, and there is a proportional relationship between the hydroxyl content and the amount of BF_3 adsorbed. Since all of the BF_3-treated aluminum oxides converted the arylmethanol indicators to their respective acid forms, it has generally been suggested that the appearance of Brönsted acid centers in the case of alumina activated with BF_3 is associated with the hydroxyl groups of the initial alumina. Accordingly, it may be considered that the hydroxyl concentration has an effective influence upon the catalytic action after the treatment with BF_3. According to Rhee and Basila,¹²⁾ hydrogen-bonding interactions similar to those in the BF_3-aliphatic alcohol complexes¹³⁾ may occur on the surface

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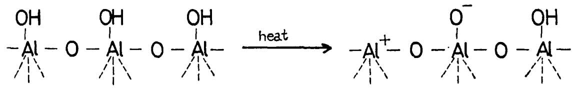
12) K. H. Rhee and M. R. Basila, *J. Catal.*, **10**, 243 (1968).

13) K. Nakamoto and M. Margoshes, *J. Phys. Chem.*, **77**, 6480 (1955).

of alumina. A similar interaction between adjacent surface hydroxyl groups, which is promoted by the BF_3 complex formation, seems to be strongly affected at higher concentrations. Thus, it is possible that the most effective sites for all reactions in the present work result from the coordination of BF_3 with the remaining hydroxyl group, which varies gradually in its concentration and acidic property with the heating temperature of the initial aluminum oxide.

On the other hand, other higher conversions were observed with the catalyst samples of BA-800 or BA-900, although relatively small hydroxyl contents were found at such higher precalcination temperatures (Table 2). Though either of the O atoms in the Al-O-Al, Al-O^- or surface OH group on the dehydrated aluminas was regarded as the adsorption site of BF_3, it was demonstrated that a greater part of the BF_3 adsorbed on the surface OH group to form Brönsted acid centers. However, it can also be assumed from the results shown in Table 5 that BF_3 generally coordinates with the O atoms in Al-O^- or Al-O-Al to strengthen the Lewis acidity on the surface, especially on the alumina dehydrated over 700°C. It is believed that Brönsted centers on alumina, if present at all, are of a very low acid strength. The Lewis acid centers of the dehydrated alumina can be best explained by not-fully-coordinated aluminum atoms, and their formation during calcination can be pictured by the model suggested by Hindin and Weller:[14]



$$-\overset{\mathrm{OH}}{\underset{/|\backslash}{\mathrm{Al}}}-\mathrm{O}-\overset{\mathrm{OH}}{\underset{/|\backslash}{\mathrm{Al}}}-\mathrm{O}-\overset{\mathrm{OH}}{\underset{/|\backslash}{\mathrm{Al}}}- \xrightarrow{\text{heat}} -\underset{/|\backslash}{\mathrm{Al}}^{+}-\mathrm{O}-\overset{\mathrm{O}^-}{\underset{/|\backslash}{\mathrm{Al}}}-\mathrm{O}-\overset{\mathrm{OH}}{\underset{/|\backslash}{\mathrm{Al}}}-$$

As to the effect of the surface properties of alumina, such factors as the number of Lewis acid centers, besides the concentration and acidic behavior of each remaining surface hydroxyl group, must be causes of the difference in the catalytic activities with the aluminum oxides promoted by BF_3 complex formation, as is shown in Table 6.

As has been mentioned above, in the effective sites of a series of BF_3-treated aluminum oxides there are a considerable number of Brönsted centers and a small number of Lewis centers, and these acid centers are responsible for the acid-catalyzed reactions in this work. These catalytic activities correspond well to the *n*-butylamine acidity in the presence of a Hammett indicator rather than an arylmethanol indicator. Although some arylmethanol indicators are believed to be converted to their respective acid forms on Brönsted acid centers, as has been discussed by Hirschler,[15] it is an open question whether their butylamine titers are equal to the number of Brönsted centers; the Lewis center, if present, should also be taken into consideration, as should other adsorption sites of the amine. It is also demonstrated that the activity and product selectivity in the isomerization of 1-butene differ considerably depending upon their respective precalcination temperatures. This is largely due to the difference in the nature of active centers, as was described in a recent work.[16]

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14) S.G. Hindin and S.W. Weller, *J. Phys. Chem.*, **60**, 1506 (1956).

15) A.E. Hirschler, *J. Catal.*, **2**, 428 (1963).

16) K. Matsuura, A. Suzuki, and M. Itoh, *ibid.*, in press.