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n-Butene Isomerization on HCl-Treated Alumina

MASAKO TANAKA AND SADAO OGASAWARA

Department of Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama, Japan

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Interconversion of *n*-butene was studied on HCI-treated alumina by using both closed circulation system and microcatalytic technique. In former experiments, the reaction rate obeyed the Elovich equation and the stereoselectivity to *cis*-2-butene on 1-butene isomerization was much higher than the selectivity to *trans*-2-butene. In later experiments, active sites were blocked by the irreversible adsorption of butenes. On the deuterated catalyst, D atoms transferred from the surface were mainly found in the product butenes. However, the concentration of deutero products was much lower than that estimated by considering that the active sites were only Brönsted type. It is concluded from all results obtained that the isomerization proceeds directly on Lewis acid sites and Brönsted acid sites which were produced by adsorbed HCl rather than on butene "residue."

Although several reaction mechanisms for the isomerization of *n*-butene on solid acid catalysts have been proposed (*1–5*), considerable problems still remain unsolved because of the coexistence of Lewis acid sites and Brönsted acid sites on silica–alumina surface and of uncertainty of the role of each kind of acid sites. Especially, the catalysis of surface Brönsted acid sites for the isomerization has not been so far studied since a solid catalyst which has only Brönsted acid sites has been difficult to obtain. On the other hand, the catalysis of liquid Brönsted acid for the isomerization has been investigated in detail and explained in terms of the hydrogen switch mechanism (*6*).

Previous work has shown that the new OH groups produced by the adsorption of HCl on alumina showed Brönsted acidity and the isomerization proceeded by transferring protons between butenes and these acidic OH groups (*9*). In this paper, we shall deal with the isomerization kinetics for *n*-butenes on HCl-treated alumina in a closed circulation system and also the results of tracer studies on deuterated catalysts obtained by microcatalytic technique.

EXPERIMENTAL METHOD

1. Materials

The γ-alumina aerogel was the same sample as the previous samples. *n*-Butenes from commercial cylinders were used without further purification. Hydrogen chloride (HCl) and deuterium chloride (DCl) were obtained and purified as described previously.

2. Procedure

The pretreatments of alumina powder and HCl adsorption were identical with those in previous studies. The deuteration of alumina, as required, was performed by using heavy water.

The volume of the apparatus, employed for the reaction in the closed circulation system, corresponded to 180 ml at 25°C and the sampling device for analysis was 1 ml. Two kinds of catalysts were prepared and used in the closed circulation system; one was used for the reaction after 30 min from the admittance of HCl on alumina where HCl was completely adsorbed, and the other was prepared by exposing to about 30 mm Hg of HCl for 16 hr and the residual gas removed with a liquid nitrogen trap just before the reaction. Product compositions were examined at intervals by gas chromatographic analysis.

The reactor (8 mm i.d.) employed for the microcatalytic experiments was connected through a stopcock to a vacuum system and HCl or DCl was admitted to the reactor through the same stopcock. After the catalyst preparation as before, dry hydrogen carrier gas was flowed over the catalyst. Products from each slug were collected in a trap at −195°C and transferred into the gas chromatographic doser for analysis. In the tracer studies, the separated products were individually trapped at −195°C for mass spectral analysis which were performed using low energy (10 V) electrons. It was confirmed that the hydrogen carrier gas did not affect the deuterium content of isomerization products.

RESULTS

1. Isomerization of n-Butene in Closed Circulation System

Kinetics for isomerization of *n*-butene. The catalytic activity of HCl-treated alumina (HCl-alumina) was 4 times larger than that of pure alumina at the initial state when 0.1 ml (STP) of HCl was adsorbed, while the activity rapidly decreased during the course of the reaction. The rate of isomerization for three isomers (as reactants) could be expressed as the following Elovich equation rather than the first order rate law which usually holds on pure alumina.

$$\text{rate} = be^{-\alpha v} \qquad (1)$$

where b and α were constants, v was the volume of product butenes at a given reaction time. It should be noted that b corresponds to the initial rate. The typical results of isomerization from each of the three n-butenes are shown in Fig. 1 and Table 1. The initial rate, b, was independent of initial pressure in the range of 30–90 mm Hg when the starting materials were 1-butene and *cis*-2-butene, as given in Table 1. It is probably constant for *trans*-2-butene under the same range of initial pressure. Consequently, it seemed that the order of the initial rate in butenes was zero.

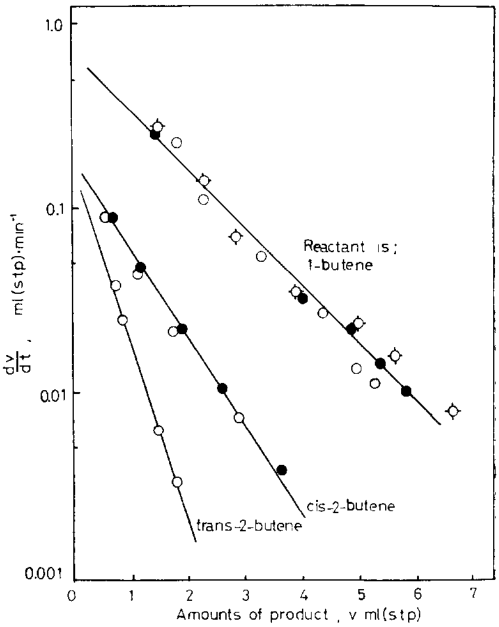
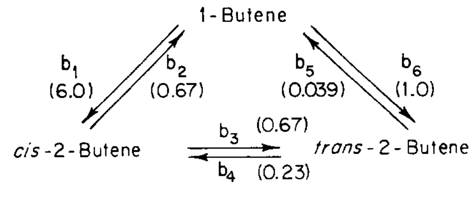


FIG. 1. Elovich plots of isomerization rates: Conditions: 0.1 g of alumina, 1.2 ml (STP) of HCl adsorbed, catalysts were used 16 hr after HCl adsorption, reaction temperature, 50°C. Initial pressure of reactants (mm Hg): 1-butene: ○, 31.6; ●, 50.0; -◇-, 86.1; *cis*-2-butene: ●, 54.0; ○, 69.0; *trans*-2-butene: ○, 90.0.

Initial ratios of the products given in Table 1 were obtained in zero conversion by the extrapolation of ratios. The results showed that isomerizations were not a consecutive reaction, because none of these ratios were zero. By assuming the Scheme 1 and that first order rate law holds at the initial state of the reaction, six relative initial rates, b_1–b_6, were calculated from two initial product ratios in Table 1, *cis/*



SCHEME 1. Relative six initial rates of n-butene interconversion on HCl-treated alumina. Data in Table 1 were used.

TABLE 1
ISOMERIZATION OF *n*-BUTENE OVER HCl-TREATED ALUMINA[c] IN CLOSED CIRCULATION SYSTEM

Reactant	Initial pressure (mm Hg)	Reaction temp. (°C)	Initial rate, *b* (ml/min)	α	Initial product ratio	Adsorption amount of HCl [ml (STP)/g]
1-Butene[a]	31.6	50	0.72	0.80	*cis/trans* 6.0	12
	50.0	50	0.66	0.71	*cis/trans* 6.0	12
	86.1	50	0.66	0.67	*cis/trans* 6.0	12
cis-2-Butene[a]	54.0	50	0.17	1.1	*trans*/1 1.0	12
	69.0	50	0.17	1.1	*trans*/1 1.0	12
trans-2-Butene[a]	90.0	50	0.13	2.1	1/*cis* 0.25	12
1-Butene[b]	57.0	25		0.46	*cis/trans* 6.0	9.6
	50.0	25	0.60	0.30	*cis/trans* 10	6.9
	50.0	25	0.25	0.30	*cis/trans* 5.0	3.6
	50.0	25	0.09	0.30	*cis/trans* 6.0	1.5

[a] The catalysts were used to the reaction after 16 hr from HCl adsorption.
[b] The catalysts were used to the reaction after 30 min from HCl adsorption.
[c] Alumina, 0.1 g.

trans, *trans*/1, and rate constant ratios obtained from the equilibrium composition of linear butenes, $k_1/k_2 = 25.0/2.8$, $k_3/k_4 = 72.2/25.0$, $k_5/k_6 = 2.8/72.2$ at 50°C. The value of these initial rates are given in Scheme 1. It is interesting to note that b_1 is very large in comparison with other acidic oxides.

Figure 2 shows the correlation of initial rates for 1-butene, *b*, on the adsorption amount of HCl on alumina at 25°C. Activation energies were obtained from the temperature dependency of initial rates and plotted against the adsorption amount of HCl, as shown in Fig. 3. Although initial rates increased with amounts of HCl, activation energies were constant at about 6 kcal/mole. This fact strongly suggests that the increase of initial rates with amounts of adsorbed HCl may be attributed to the increase of active sites.

The α varied slightly with reaction temperature, amounts of adsorbed HCl, and initial pressure, as given in Table 1. A few percent of *n*-butane and iso-butane were detected in the products.

Adsorption of butenes during isomerization. Since a large pressure fall of butene mixture was observed during isomerization on HCl–alumina in comparison with that on pure alumina, the rate of adsorption

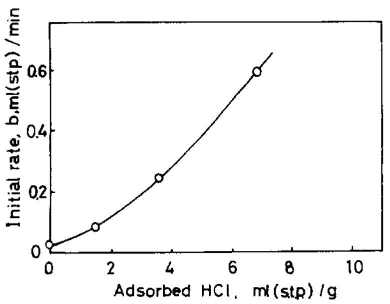


FIG. 2. Dependence of initial rate, *b*, on the adsorption amount of HCl at 25°C.

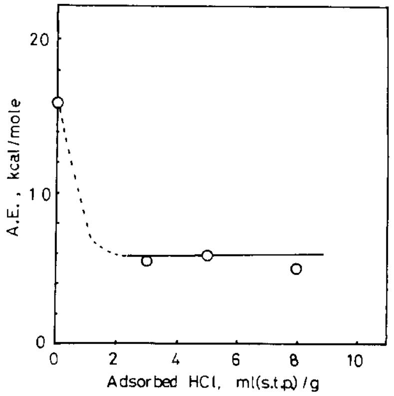


FIG. 3. Dependence of activation energy at initial stage on the adsorption amount of HCl.

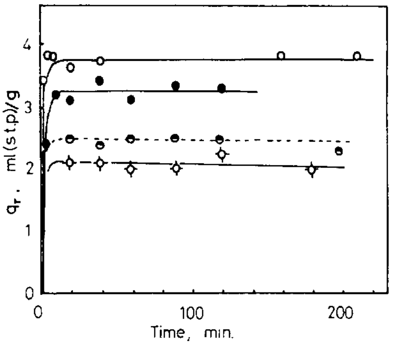


FIG. 4. Reversible adsorption of butene during isomerization at 25°C; reactant was 1-butene, 1.0 g of alumina were used: ○, on alumina; ●, on 1.0 ml (STP) HCl-treated alumina; -◇-, on 5.0 ml (STP) HCl-treated alumina; ◓, on 5.0 ml (STP) HCl-treated alumina, used as a catalyst 16 hr after HCl adsorption.

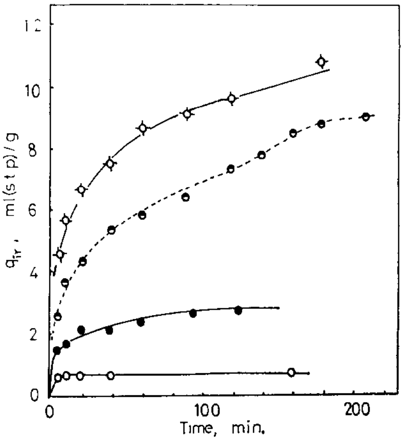


FIG. 5. Irreversible adsorption of butene during isomerization. Conditions and marks are the same as in Fig. 4.

and the possibility of polymerization as a side reaction were examined. The amounts of adsorbed butene isomerization were divided for convenience in two portions to be measured; one was designated as the reversible adsorption, denoted as q_r, which was the amount of desorbed butene on evacuation by a liquid nitrogen trap for 3 min at reaction temperature, and the other irreversible adsorption, denoted as q_{ir}, which was obtained by subtracting the reversible adsorption from total adsorption. The irreversible adsorption designated here could correspond to the "residue" mentioned by Hightower and Hall (*5*).

In this experiment, 1–10 ml (STP) of HCl were adsorbed on 1 g of alumina. After 1-butene was admitted to the catalyst, the pressure fall was measured periodically. The reactions were carried out at 25°C and the results are shown in Figs. 4 and 5. The reversible adsorption q_r in Fig. 4 was constant during the reaction, and decreased with increasing the amounts of adsorbed HCl. When the amounts of adsorbed HCl were 10 ml (STP), q_r decreased to zero. On the other hand, the irreversible adsorption q_{ir} increased during the reaction as shown in Fig. 5, and the increase of q_{ir} was in parallel with the increase of the amounts of HCl. The rate of irreversible adsorption was found to obey the Elovich equation for the first 2 hr, and then deviated increasingly. The amounts of q_{ir} exceeded over the amounts of adsorbed HCl, even at the initial stage of isomerization and after 48 hr, reached 18 ml (STP) on the catalyst treated with 5 ml of HCl. This value is larger than the amount of monolayer adsorption of butene, 9 ml (STP), which is estimated by assuming that the cross-sectional area of n-butene is equal to that of n-butane at 0°C. It is thus supposed that the irreversible adsorption q_{ir} includes polymerized butene.

Although the reversible and irreversible adsorption were defined conveniently in this experiment and so were given only as the relative amounts, Figures 4 and 5 show that the sites for reversible adsorption are located independently from that of the irreversible adsorption and are probably not yet covered by HCl, and that the sites for the isomerization would be included in the sites for irreversible adsorption.

The strongly adsorbed species could be better extracted from the catalyst surface into a polar solvent such as ethanol, rather than nonpolar solvent such as cyclohexane. The infrared spectra of the extracts were similar to that of liquid paraffin. After the catalyst disk was exposed to 1-butene in the infrared cell for 16 hr and followed to the evacuation of butenes in gas phase for 30 min at room temperature, the spectra

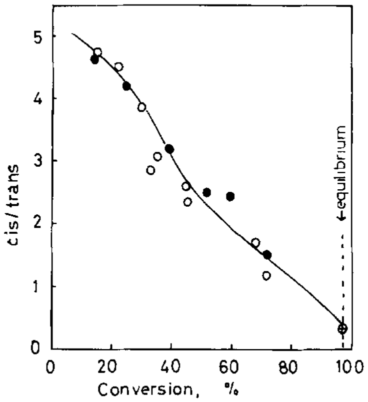


FIG. 6. *cis/trans* on isomerization of 1-butene at 25°C: ○, in closed circulation system, 0.1 g of alumina, 1.0 ml (STP) of HCl, 50 mm Hg of 1-butene; ●, in microreactor, 0.1 g of alumina, 0.8 ml (STP) of HCl, 0.1 ml (STP) of 1-butene in a slug.

of adsorbed species on the catalyst were recorded. There were two bands at 2980 and 2840 cm^{-1} due to saturated hydrocarbon species, but no band at the region of vinyl groups. When the catalyst was exposed to the atmosphere after isomerization, it gradually produced a lavender color. While the color was stable in cyclohexane for a month, it was so unstable in ethanol as to disappear rapidly. These results are believed to show that the adsorbed species was a kind of polymer or polymeric cation. It is interesting that the lavender color was the same one which was found on the adsorbed olefin on silica–alumina (7).

2. *Microcatalytic Experiments*

First experiments by microcatalytic technique were performed using 0.1 g of alumina treated with 0.8 ml of HCl and the flow rate of the carrier gas was about 70 ml/min at 25°C. Each sample size for the reaction was 0.2 ml of 1-butene. As expected from the results of adsorption experiment in the closed circulation system, 70% of the first slug and a significant fraction of the second slug remained on the catalyst, and the catalytic activity decreased markedly with slug numbers. Figure 6 shows the dependence of the ratio of *cis/trans* in products on conversion of 1-butene. The ratios obtained in the experiments with the closed circulation system are also given in Fig. 6 for comparison. It was found that both ratios fall on the same line. Since the butenes are in adsorption equilibrium in the closed circulation system, Fig. 6 must indicate that they were also in adsorption equilibrium in the flow system studied. It also indicates that the product ratio at a given conversion was not affected by the extent of poison, because butene "residue" was little at low conversion in the closed circulation system, whereas the low conversion means much poisoning in the flow system. Therefore, it is concluded that the isomerization proceeded on the surface not covered by irreversibly adsorbed butenes, but such surface area of the catalyst could decrease with reaction time.

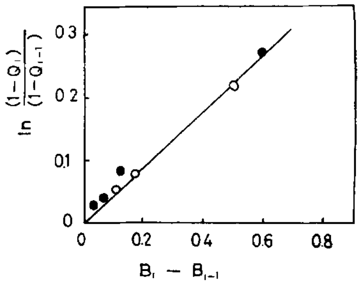


FIG. 7. Dependence of the extent of reactivity lowering on the amounts of "residue."

If the catalyst was poisoned by adsorbed butenes of the preceding slugs and the true rate law of isomerization on unpoisoned sites was the first order, where the rate constant was proportional to the number of active sites, the rate equation for each slug should be as follows;

$$-\ln(1 - Q_1) = aB_0 \quad \text{for first slug,} \qquad (3)$$

$$-\ln(1 - Q_2) = aB_1 \quad \text{for second slug,} \qquad (4)$$

$$-\ln(1 - Q_i) = aB_{i-1} \quad \text{for } i\text{th slug,} \qquad (5)$$

where Q_1 was the conversion of isomerization on ith slug, a was a constant including the contact time and B_0 was the number of active sites originally present and B_{i-1} the number of sites still remained unpoisoned for ith slug. Subtracting the $(i - 1)$th equation from the ith equation,

$$\ln(1 - Q_i)/\ln(1 - Q_{i-1}) = a(B_{i-1} - B_i), \qquad (6)$$

$(B_{i-1} - B_i)$, the number of sites poisoned by ith slug only, should be proportional to the amount of butenes adsorbed on the surface by the ith slug. Accordingly, $\ln (1 - Q_i)/(1 - Q_{i-1})$ is expected to linearly relate to the ith adsorption amount of butenes. This is shown in Fig. 7.

Other experiments by the microcatalytic method were undertaken to evaluate the deuterium contents of butenes in isomerization on deuterated catalyst. Each 0.5 ml (STP) of 1-butene flowed on deuterated alumina treated with 1.6 ml (STP) of DCl or HCl at 25°C. Conversion was controlled by changing the flow rate of carrier gas. Results obtained are presented in Table 2. The kinetic isotope effect was not observed on the isomerization of 1-butene and *cis*-2-butene. From the fact that deuteriums transferred from the catalyst were concentrated in the products even at high conversion, as shown in the next to last column in Table 2, it is evident that the step of deuterium transfer between butenes and the catalyst was involved in process of isomerization. Results obtained over the deuterated alumina adsorbing HCl (HCl–alumina-OD) indicated that OD groups originally present on the surface were able to transfer on the isomerization step, if no hydrogen exchange occurred between adsorbed HCl and OD groups of alumina.

The total amount of product 2-butene and deutero 2-butene calculated as C_4H_7D are plotted against the contact time in Fig. 8. The rates of the formation of 2-butene and the rates of the appearance of deutero 2-butene were obtained by drawing tangents to each curve in Fig. 8 at any contact time. The results are shown in Fig. 9. It illustrates that the ratio of those rates was constant through the course of isomerization and average numbers of D atoms picked up from the catalyst to one mole-

TABLE 2

MICROCATALYTIC EXPERIMENTS ON HCl-TREATED ALUMINA[a]

Expt. no.	Catalyst	Flow rate (ml/min)	Product (%) 1-butene		Each isotopic species (%)				D atom calculated as C_4H_7D ($\times 10^{-2}$ ml; STP)	Total recovery (%)
			trans	*cis*	d_0	d_1	d_2	d_3		
1	DCl–	800	92.7		99.8	0.25	—	—	0.070	
	Alumina-OD		2.3	5.0	80.2	16.2	2.0	1.0	0.51	60
2		167	75.5		99.8	0.31	0.15	0.15	0.23	
			11.0	13.5	83.8	14.0	1.7	0.46	1.27	55
3		70	23.7		87.9	4.7	—	—	1.00	
			36.7	39.6	81.4	16.8	1.8	—	3.94	54.5
4	HCl–	1000	96.4		99.8	0.25			0.08	
	Alumina-OD		0.8	2.8	89.4	8.0	2.6	—	0.16	67
5		273	67.5		100.	tr.	—	—	—	
			11.7	20.8	94.3	5.0	0.74	—	0.57	55.0
6		70	24.8		98.1	1.9	—	—	0.12	
			33.1	42.1	93.6	6.1	0.3	—	1.25	68.0
7[b]	DCl–	70	4.8		81.3[c]	16.3	2.4	—	2.40	
	Alumina-OD		43.2	52.0	89.0[d]	9.6	1.4	—	1.53	47.5

[a] Conditions: 0.2 g of alumina, adsorption amount of HCl (DCl) was 0.16 ml (STP), 0.5 ml (STP) of butene in each slug, reaction temperature was 25°C.

[b] The reactant was *cis*-2-butane.

[c] 1-Butene + *trans*-2-butene.

[d] *cis*-2-Butene.

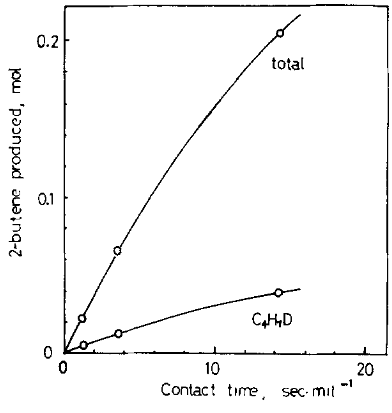


FIG. 8. Relationship between the rate of total 2-butene formation and that of deutero 2-butene.

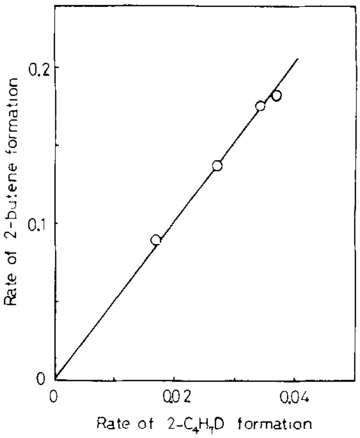


FIG. 9. Isomerization of 1-butene over deuterated catalyst in microreactor: 0.2 g of deuterated alumina, 1.6 ml (STP) of DCl, 0.5 ml (STP) of 1-butene in each slug, 25°C.

cule was only 0.2. Under these experiments the ratio of adsorbed DCl and 1-butene supplied was about 3.

Similar results were obtained in the modified flow method without carrier gas, in which given amounts of reactants passed through the catalyst bed in a moment and then the reaction products were directly collected in a liquid nitrogen trap. Those results were given in Table 3. The ratio of the amount of adsorbed DCl to 1-butene used was about unity in this experiment. As shown in fifth column in Table 3, it should be noted that the ratio of the rate of isomerization and of the appearance of deutero 2-butene was constant during the reaction, and approximately equal to the value observed in microcatalytic experiments.

DISCUSSION

It is evident from Figs. 2 and 3 that the active sites for the isomerization are caused by the adsorbed HCl. Recently, Ozaki and Kimura (*3*) and Hightower and Hall (*5*) suggested that the active sites of isomerization are not surface acid sites itself, but adsorbed olefin on acid sites, which formed carbonium ion to catalyze the reaction by supplying a proton to the reactant. The above suggestion, however, cannot explain our results. According to our results from microcatalytic experiments, it should appear that the reaction

TABLE 3

MICROCATALYTIC EXPERIMENTS WITHOUT CARRIER GAS[a]

Expt. no.	Catalyst	Product (%) 1-butene 2-butene	Each isotopic species (%) d_0	d_1	d_2
1	DCl–	83.0	99.3	0.7	—
	Alumina–OH	17.0	86.2	12.1	1.7
2		65.0	98.7	1.3	—
		35.0	87.2	11.2	1.6
3		11.4	86.6	11.4	2.0
		88.6	84.8	13.3	1.9
4	HCl–	87.0	99.0	1.0	—
	Alumina–OD	13.0	96.5	3.5	—
6		28.8	~100	—	—
		71.2	89.8	6.0	4.2

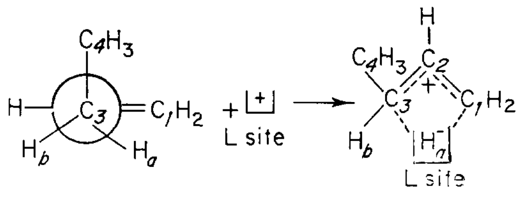
[a] Conditions: 0.35 g of alumina, 0.3 ml (STP) of adsorbed HCl (DCl), reaction temperature was 25°C.

occurred immediately on surface acid sites. As shown in Fig. 7, the adsorbed butenes poisoned the surface active sites quantitatively and led to retardation of the reaction. Simultaneously, some fraction of adsorbed butene polymerized on the same sites. The decrease of active sites with reaction time is believed to lead to Elovich type reaction rate, as interpreted theoretically by Landsberg in respect to adsorption rate (*8*).

From the results of the infrared study in the preceding report (*9*), it was shown that these active sites were known to involve acidic OH groups and they easily exchanged with butenes on the rate proportional to that of isomerization. Similar results were also obtained from the microcatalytic tracer study as follows; (i) a large fraction of surface D atoms exchanged with butene during isomerization and appeared in product butenes, (ii) the rate of isomerization was linearly related to that of exchange reaction, as shown in Fig. 9. These results suggest that all D atoms in product were picked up in the course of isomerization, in other words, the new OH groups produced by adsorbed HCl participated in the reaction as Brönsted acid sites. However, if it is allowed to postulate that the 1-butene isomerization of deuterated catalyst proceeds through the first slow step of surface D^+ addition to the adsorbed butene to form classical carbonium cation and then is followed by the second step of releasing H^+ from the cation to produce deutero 2-butene-d_1, the concentration of deutero 2-butene in products should be observed to be near 100% at the initial stage of the reaction. Moreover, the deuterium concentration in the product would rapidly decrease as the reaction proceeds because the surface deuterium was diluted by the substituted hydrogen, unless the amount of surface deuterium was large enough compared with the amount of butene. Experimental results do not agree with these postulates. It is shown from mass spectrometric analysis in Table 3 that deuterium contents in products are approximately only 16% even at initial stage of the reaction and constant during the reaction. These phenomena could be explained by the following mechanism in which products were formed by two different routes; one is the main reaction without surface proton, probably inter- or intramolecular hydrogen transfer mechanism on Lewis acid sites, and the other is the catalysis by surface protonic OH groups. The rate of the former is five times faster than that of the latter from the fact that the average deuteration was 0.2.

Another possibility is that after a butene molecule has consumed a deuterium on an active site, this site isomerizes approximately five molecules until a deuterium is supplied from other sites by surface migration. This, however, should not be acceptable because it is difficult to consider such a surface migration of hydrogen at room temperature, and consequently, the constancy of deutero 2-butene concentration in the products cannot be explained.

It is impossible to determine only from the above data which hydrogen transfer (intermolecular or intramolecular) occurs on Lewis acid sites. Furthermore, studies using deutero butene are required for a solution of this problem. Nevertheless, it seems reasonable to suppose that the intramolecular mechanism mainly proceeds on Lewis acid sites of HCl–alumina, since it is considered that adsorbed species did not promote the reaction. The intermediate of this reaction is likely butenyl cation similar to the one described before by Leftin and Hermana (*4*). If the adsorbed 1-butene has a preference for the following limited configuration, locating the methyl group at the longest distance from the catalyst surface, to form butenyl cation,



H_a would be easier to move to C_1 than H_b for its shorter distance to C_1. According to this model, the intramolecular mechanism would lead to larger selectivity for *cis*-2-butene. Experimental value of the initial ratio of *cis* to *trans* was above 5. Similar large selectivity for *cis*-2-butene was obtained by Hall and co-workers (*10*) on HF-treated alumina. Thus, it seems that the large initial *cis/trans* ratio is characteristic for halogen coated alumina. Taking account that this ratio is usually in the range of 1.5–2.5 on silica–alumina which has been interpreted statistically, and that this is about 2 on alumina, the surface structure of Lewis acid sites on halide-treated alumina would be considerably different from those on silica–alumina or pure alumina, on which surface the adsorbed species would be fixed in the specific configuration. In the case of homogeneous catalysis, intramolecular mechanism, $C_3 \rightarrow C_1$ hydrogen shift, has been found in isomerization by palladium complex catalysts (*11*).

The formation of Brönsted acid sites by adsorbed HCl is also evidenced by high activity for polymerization. Infrared spectra of polymerized species indicate the possibility of cyclization. This fact should be interesting in respect to the action of surface proton, in comparison with the result obtained by Deno (*12*) that olefins form cycloalkenyl cation and its polymers in a suitable concentration of sulfuric acid.

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REFERENCES

1. PINES, H., AND HAAG, W. O., *J. Am. Chem. Soc.* **82,** 2488 (1960).
2. LUCCHESI, P. J., BAEDER, D. L., AND LONGWELL, J. P., *J. Am. Chem. Soc.* **81,** 3235 (1959).
3. OZAKI, A., AND KIMURA, K., *J. Catalysis* **3,** 395 (1964).
4. LEFTIN, H. P., AND HERMANA, E., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* **2,** 1064 (1965).
5. (a) HIGHTOWER, J. W., AND HALL, W. K., *J. Am. Chem. Soc.* **89,** 778 (1967); (b) HIGHTOWER, J. W., AND HALL, W. K., *J. Phys. Chem.* **71,** 1014 (1967).
6. TURKEVICH, J., AND SMITH, R. K., *J. Chem. Phys.* **16,** 446 (1948).
7. LEFTIN, H. P., *Advan. Catalysis* **14,** 115 (1963).
8. LANDSBERG, P. T., *J. Chem. Phys.* **23,** 1079 (1955).
9. TANAKA, M., AND OGASAWARA, S., *J. Catalysis* **16,** 157 (1970).
10. HIGHTOWER, J. W., GERBERICH, H. R., AND HALL, W. K., *J. Catalysis* **7,** 57 (1967).
11. HARROD, J. F., AND CHALK, A. J., *J. Am. Chem. Soc.* **88,** 3491 (1966).
12. DENO, N. C., *Progr. Phys. Org. Chem.* **1,** 134 (1963).