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The Nature of Active Sites on Aluminum Phosphate for the Isomerization of Butenes

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The nature of active sites on aluminum phosphate for the isomerization of *n*-butenes was investigated by means of a tracer study which consisted of isomerization over deuterated catalyst and co-isomerization of light and perdeuterated butene. There exist three kinds of active sites, Brönsted acid sites, Lewis acid sites where intermolecular hydrogen transfer occurs (L-inter sites), and Lewis acid sites where intramolecular hydrogen transfer occurs (L-intra sites). Their contributions to *n*-butene isomerization, which were quite dependent on the thermal treatment of the catalyst, were calculated for different evacuation temperatures. At low evacuation temperature, Brönsted acid sites and L-inter sites are the main active sites, while L-intra sites become prominent at high evacuation temperature. L-intra sites are characteristically active for *cis–trans* rotation.

The adsorption state of butene molecules was also examined. From the isotopic distributions of butene isomers, it was concluded that secondary butyl carbenium ion intermediates on Brönsted acid sites and L-inter sites were adsorbed weakly, and all bonds of the intermediates rotated freely. Over L-intra sites, the isomerization may be initiated by the abstraction of H^- at the vinyl hydrogen of butene.

INTRODUCTION

Most metal phosphates are known to be solid acid catalysts and to catalyze several reactions such as the polymerization of olefins (*1*), the dehydration of alcohols (*2*), the hydration of olefins (*3*), the amination of alcohols (*3*), and the decomposition of 4,4-dimethyl-*meta*dioxane (*4*, *5*). Aluminum phosphate shows similar cracking activity and selectivity to those of silica–alumina (*6*) and shows a good correlation between its acidity and its activity for the dehydration of 2-propanol (*7*). Shima and Ohta (*8*) reported that acid phosphate showed activity in the polymerization of butenes but orthophosphate did not show the activity. They concluded that the hydrogen of the P–OH acted as an acid and the reaction proceeded via a butyl carbenium ion. On the other hand, Tada *et al.* (*9*) found that orthophosphate showed acidity on thermal treatment and anhydrous phosphate showed little acidity. They postulated that the vacant orbital occurred by removal of the bonding water, which acted as a Lewis acid, and the hydrogen of the bonding water became protonic by the electron induction effect of the metal ion and acted as a Brönsted acid. Peri (*10*) investigated the nature of the acid sites by an ir study and demonstrated that both Lewis and Brönsted acid sites existed on aluminum phosphate. The reaction mechanisms and the adsorbed states of the reactant on aluminum phosphate, however, have not been studied so extensively.

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In this study, the nature of the active sites on aluminum phosphate for the isomerization of *n*-butenes is investigated by means of a tracer study using deuterium as a tracer, which was developed by Hightower and Hall (*11*, *12*). The reaction mechanisms are also studied in connection with the nature of the active sites.

EXPERIMENTAL METHODS

Catalyst preparation. A mixture of 500 g of $AlCl_3 \cdot 6H_2O$ and 230 g of 85% H_3PO_4 in 500 g of water was subjected to hydrolysis at 0°C by dropwise addition of 930 g of 14% ammonium hydroxide over 2 hr with continuous stirring followed by the addition of 500 g of water. After standing overnight, the precipitate was filtered (filtrate was pH 5.5), washed with 1000 g of water and filtered again. Finally it was washed with 1000 g of 90% isopropyl alcohol and dried at 120°C for 10 hr in air. The resulting material, sieved into 20–34 mesh, was calcined in a Pyrex tube at 400°C for 3 hr in air and stored after sealing the tube.

Reactant. 1-Butene and *cis*-2-butene were purified after vacuum distillation by passing through 4A molecular sieves kept at −78°C. A mixture of equivalent amounts of light and perdeuterated *cis*-2-butene was purified by vacuum distillation and used for the co-isomerization reaction. Perdeuterated butenes were prepared by the exchange reaction of butene with D_2 over MgO. The mixtures of *n*-butenes and D_2 (1:4) were recirculated for several hours at room temperature over MgO which had been activated by evacuation at 550°C. Partly exchanged butenes were trapped in liquid N_2, and the gas phase was replaced by fresh D_2. This procedure was repeated more than seven times. Finally butenes were isomerized at 400°C after removing D_2 in order to increase the fraction of 1-butene and *cis*-2-butene in the mixture. Each butene was collected by a liquid N_2 trap after separation by gas chromatography. The isotopic purity was more than 99.6%, that is 97% of d_8 and 3% of d_7.

Reaction procedure. One gram of catalyst was placed in a quartz reactor and evacuated at 400°C for 1 hr. Surface OH was replaced by OD at 400°C by exposure to 10 Torr (1 Torr = 133.3 N m^{-2}) of D_2O followed by evacuation. This process was repeated three times. Finally the catalyst was evacuated at 400 or 600°C or cooled to 200°C under D_2O vapor and evacuated at 200°C for 1 hr. For the co-isomerization experiment, the catalyst was treated with the mixture containing equal amounts of D_2O and H_2O instead of D_2O. Between each run, the catalyst was regenerated by evacuation at 400°C followed by the same treatment with D_2O or the mixture of D_2O and H_2O as described above.

A microcatalytic reactor was used and the reactions were carried out primarily at 140°C. Helium carrier gas, purified by passage through 13X molecular sieves at −195°C, flowed over the catalysts. Different conversions could be obtained by varying the flow rate of carrier gas from 20 to 120 ml/min. In some experiments, reaction temperature was lowered to obtain an appropriate conversion. Measured amounts of *n*-butenes consisting of about 40 μmol were introduced into the helium stream ahead of the catalyst. Products from each slug were collected in a −195°C trap before being flash evaporated into a 10-m chromatographic column (30% propylene carbonate on Celite) kept at 0°C. The separated isomers were trapped at −195°C for mass spectral analysis. All mass spectral analyses were performed on a Hitachi mass spectrometer RUM-2 using low energy electrons (12–13 eV). As fragmentation was very low (less than 1% of the parent peak), parent peaks were measured and corrected for naturally occuring carbon-13 isotopes.

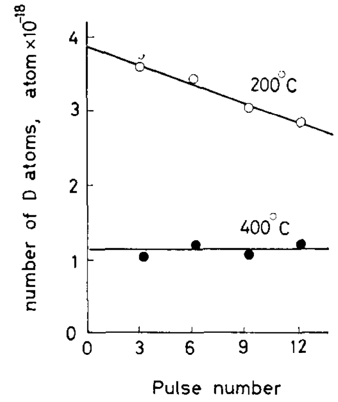


FIG. 1. Number of D atoms in the effluent butene mixture against pulse number for the isomerization of *cis*-2-butene at 140°C over deuterated aluminum phosphate evacuated at 200°C (○) and 400°C (●).

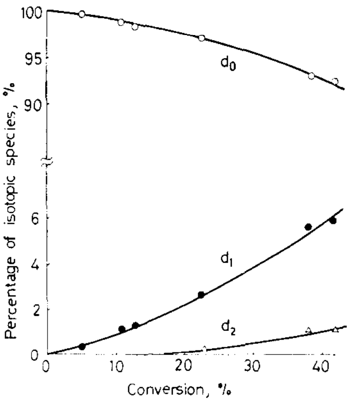


FIG. 3. Isotopic distribution of effluent 1-butene for 1-butene isomerization at 140°C over deuterated aluminum phosphate evacuated at 200°C.

RESULTS

Specific surface areas of the catalysts evacuated at 200, 400, and 600°C were 70.1, 78.6, and 71.8 m^2/g, respectively.

In Fig. 1, the number of D atoms picked up by butenes is plotted as a function of the pulse number when successive pulses of 40 μmol of *cis*-2-butene were passed over the deuterated catalyst without redeuteration between each pulse. In this experiment, series of three pulses were collected together and the mixture of butene isomers was subjected to mass spectral analysis without separation into each isomer. Conversions were about 10% for each pulse. Over the catalyst evacuated at 200°C, the number of D atoms picked up decreased gradually from 3.6×10^{18} atoms for the first three pulses to 2.8×10^{18} atoms for the fourth series of three pulses. Over the catalyst evacuated at 400°C, these were 1.1×10^{18} atoms for all series of three pulses.

On varying the pulse size from 20 to 80 μmol in the conversion range of 6–9%, the ϕ values were almost constant for both catalysts evacuated at 200 and 400°C. (The

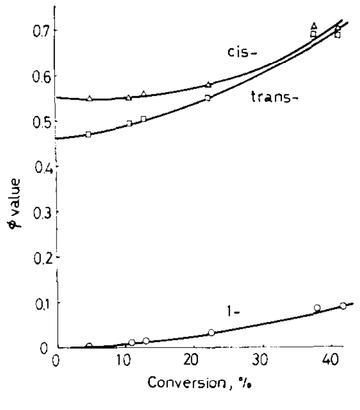


FIG. 2. ϕ Values of butene isomers against conversion for the isomerization of 1-butene at 140°C over dueterated aluminum phosphate evacuated at 200°C. (○), 1-Butene; (□), *trans*-2-butene; (△), *cis*-2-butene.

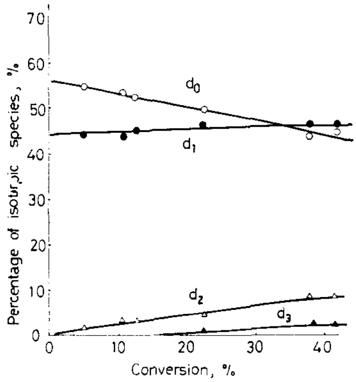


FIG. 4. Isotopic distribution of *trans*-2-butene for 1-butene isomerization at 140°C over deuterated aluminum phosphate evacuated at 200°C.

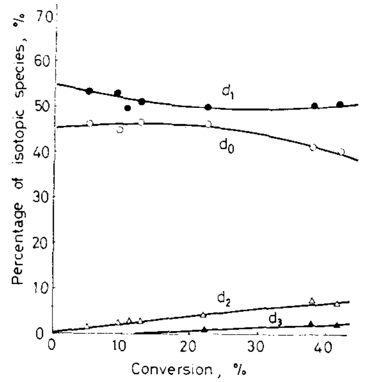


FIG. 5. Isotopic distribution of *cis*-2-butene for 1-butene isomerization at 140°C over deuterated aluminum phosphate evacuated at 200°C.

ϕ value is the average number of D atoms contained per molecule, represented as $\sum_i i \cdot d_i$, where d_i is the fraction of molecules containing i D-atoms.)

In Fig. 2 are shown ϕ values of butene isomers plotted against conversion in the isomerization of 1-butene over the deuterated catalyst evacuated at 200°C. Extraporation of ϕ values to zero conversion (ϕ_0) gave 0.55 and 0.46 for *cis*-2-butene and *trans*-2-butene, respectively. Small initial gradients of ϕ values of all butenes indicate that the rate of the exchange reaction is slow compared with that of the isomerization reaction.

The change in isotopic distribution of 1-butene with the conversion of 1-butene by isomerization is shown in Fig. 3. At low conversion, 1-butene-d_0 was the main species and a small amount of 1-butene-d_1 was the only species which contained D atoms. Isotopic distributions of *cis*- and *trans*-2-butene for 1-butene isomerization are shown in Figs. 4 and 5, respectively. At the initial stage of the reaction, products were limitted to about equal amounts of d_0 and d_1 species.

Similarly, ϕ values are plotted against the conversion for 1-butene isomerization over the 400°C evacuated catalyst in Fig. 6 and for *cis*-2-butene isomerization over deuterated catalysts evacuated at 200 and 400°C in Figs. 7 and 8, respectively. In all these figures, it is observed that the ϕ_0 values of the products are not unity, that the ϕ values of the products increase with the conversion, and that initial gradients of the ϕ values of the reactants are small. Results are summarized in Table 1.

In the isomerization of *cis*-2-butene, the number of D atoms in *cis*-2-butene was about the same as that in *trans*-2-butene. For example, the numbers of D atoms in *cis*- and *trans*-2-butene at 10% conversion were 7×10^{17} atoms per pulse over the catalyst evacuated at 200°C and 1.4×10^{17} and 1.6×10^{17} atoms per pulse, respec-

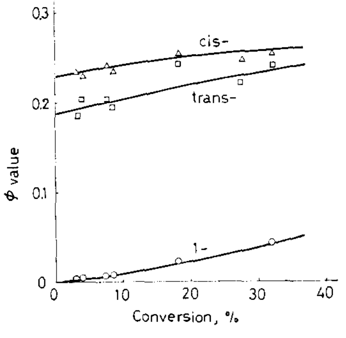


FIG. 6. ϕ Values of butene isomers for 1-butene isomerization at 140°C over deuterated aluminum phosphate evacuated at 400°C.

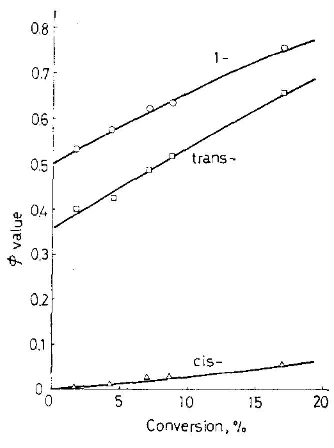


FIG. 7. ϕ Values of butene isomers for *cis*-2-butene isomerization at 140°C over deuterated aluminum phosphate evacuated at 200°C.

tively, over the catalyst evacuated at 400°C.

When the reaction was carried out over the catalyst evacuated at 600°C, deuterium was not introduced into any butene isomers over the range of reaction temperatures from 45 to 140°C. The activity and the selectivity of the 600°C evacuated catalyst were quite different from those of 200 and 400°C evacuated catalysts. As summarized in Table 2, the 600°C evacuated catalyst was very active for the isomerization of *cis*-2-butene and showed a high ratio of *trans*-2-butene to 1-butene. For the isomerization of 1-butene, however, it was not so active. These results imply that the active sites on the 600°C evacuated catalyst were specifically active for the *cis–trans* rotation.

The isotopic distributions of butene isomers in the co-isomerization of *cis*-2-butene (d_0/d_8) are listed in Table 3. The fractions of d_1 and d_7 in 1-butene formed over the catalysts evacuated at 200 and 400°C were large. The number of H (or D) atoms exchanged per molecule (AEM) (*11*) were above 0.44 on both catalysts. Since the d_1–d_7 fractions were produced by the intermolecular H (or D) transfer and the AEM value would not exceed 0.5, which is expected when the reaction involves only intermolecular H (or D) transfer without an isotope effect, the formation of 1-butene over the catalysts evacuated at 200 and 400°C, therefore, involve mainly intermolecular hydrogen transfer.

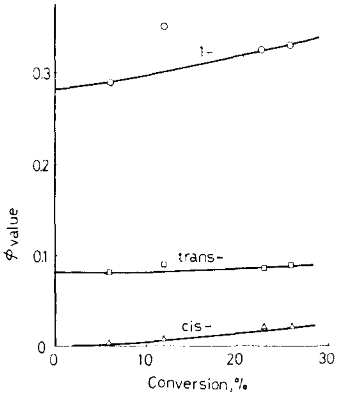


FIG. 8. φ Values of butene isomers for *cis*-2-butene isomerization at 140°C over deuterated aluminum phosphate evacuated at 400°C.

The fractions of mono-exchanged d_1 and d_7 isotopic species in *trans*-2-butene were always smaller than those in 1-butene and decreased on raising the evacuation temperature. To determine whether the formation of *trans*-2-butene involves intramolecular H transfer from the distribution of D atoms, the degree of free rotation of the C_{II}–C_{III} bond should be taken into account, which will be discussed later. Over the catalyst evacuated at 600°C, the negligible amounts of d_1 and d_7 indicate that only intramolecular hydrogen transfer

TABLE 1

φ Values and Ratios of Products in the Isomerization of 1-Butene and *cis*-2-Butene over Deuterated Aluminum Phosphate

Reactant	Pretreatment temperature (°C)	Product	φ Value[a]	Ratio of products[a] (S_0)
1-Butene	200	*cis-*	0.55	1.3 (*cis-*/*trans-*)
		trans-	0.46	
1-Butene	400	*cis-*	0.23	1.2 (*cis-*/*trans-*)
		trans-	0.19	
cis-2-Butene	200	1-	0.50	1.0 (*trans-*/1-)
		trans-	0.36	
cis-2-Butene	400	1-	0.29	2.7 (*trans-*/1-)
		trans-	0.07	

[a] The values were obtained by extrapolation to zero conversion.

TABLE 2

Activity and Selectivity of Aluminum Phosphate Evacuated at Different Temperatures

Reactant	Pretreatment temperature (°C)	Flow rate (ml/min)	Reaction temperature (°C)	Conversion (%)	Ratio of products[a]
cis-2-Butene	600	60	140	59.2	27
	600	60	100	34.4	137
	600	60	45	4.6	228
	400	60	140	6.0	3.0
	200	60	120	4.3	1.1
1-Butene	600	60	140	18.8	0.77
	600	60	100	3.2	0.59
	400	60	140	8.7	1.1
	200	60	140	10.6	1.2

[a] The ratios of *trans*-2-butene to 1-butene for *cis*-2-butene isomerization and *cis*-2-butene to *trans*-2-butene for 1-butene isomerization.

is involved in the reaction. As d_0 comes from light *cis*-2-butene and d_8 from perdeuterated *cis*-2-butene, an isotope effect is shown by the ratio of the d_0 fraction to the d_8 fraction. The large isotope effect of 4.96 indicates that the cleavage of a C–H bond is involved in the rate-determining step over the 600°C evacuated catalysts.

DISCUSSION

In the reaction of butenes over deuterated catalyst, the exchange reaction between surface D and H in the reactant occurs as well as the isomerization. There may be two types of exchange reaction. The first one may proceed via a secondary butyl carbenium ion intermediate which is a common intermediate for the isomerization over acid catalyst. The second one may be independent of the isomerization. The initial gradients of the curves for the reactants in Figs. 2, 6, 7, and 8 show the ratios of the isomerization rate to the exchange rate.

TABLE 3

Isotopic Distributions of Product Isomers in Co-isomerization of *cis*-2-Butene d_0/d_8

Pretreatment temperature (°C)	Reaction temperature (°C)	Conversion (%)	Ratio of *trans*-/*cis*-	Product	(Isotopic distribution (%))							AEM[a]	$\mathrm{IE_m}$[b]	$\mathrm{IE_s}$[c]
					d_0	d_1	d_2	d_3–d_5	d_6	d_7	d_8			
200	140	2.22	0.95	1-	37.8	23.1	0.2	—	0.8	20.1	18.0	0.452	1.57	1.43
				trans	32.0	16.0	—	—	0.1	18.4	33.5	0.346	0.92	1.02
400	140	3.29	2.07	1-	36.7	21.7	0.1	—	0.3	21.6	18.6	0.441	1.41	1.48
				trans	49.7	10.5	—	—	0.3	12.0	27.5	0.131	1.51	1.64
600	50	4.16	100	1-	—	—	—	—	—	—	—	—	—	—
				trans	83.2	0	—	—	0	0.7	16.1	0.007	4.96	—

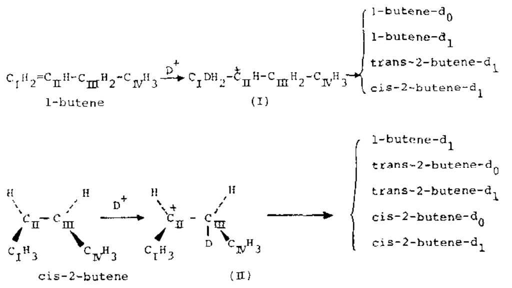
[a] Calculated from $\sum_{i=0}^{4} i \cdot d_i + \sum_{i=5}^{8} (8 - i) \cdot d_i$.

[b] Calculated from $(\sum_{i=0}^{3} d_i + d_4/2)/(\sum_{i=5}^{8} d_i + d_4/2)$.

[c] Calculated from $(d_0 + d_7 + 2 \cdot d_6 + 3 \cdot d_5 + 2 \cdot d_4)/(d_8 + d_1 + 2 \cdot d_2 + 3 \cdot d_3 + 2 \cdot d_4)$.

Small initial gradients observed here over all the catalysts evacuated at 200 and 400°C in both 1-butene and *cis*-2-butene isomerizations indicate that the rates of the exchange are slow compared with those of the isomerization.

In the isomerization of *n*-butenes over the deuterated catalysts, the inclusion of D atoms into butene isomers is limited to the case that D atoms on the catalyst surface act as active sites. The reactions over the surface D atoms would occur as follows.



In 1-butene isomerization, surface D adds to C_I to form a secondary butyl carbenium ion intermediate, I. The abstraction of H^+ from C_{III} produces *trans*- or *cis*-2-butene which necessarily contains one D atom per molecule. The abstraction of H^+ from C_I produces 1-butene which contains one D atom. In this case only an exchange reaction is observed. In the *cis*-2-butene isomerization, a secondary butyl carbenium intermediate, II, is formed by the addition of D^+ to C_{III} and by the abstraction of H^+ from C_I to produce 1-butene containing one D atom. *Trans*-2-butene is produced by the abstraction of H^+ or D^+ from C_{III}. If the species II is adsorbed so tightly that a C_{II}–C_{III} bond could not rotate freely, *trans*-2-butene would be formed only by the abstraction of H^+ and should contain one D atom per molecule. If a C_{II}–C_{III} bond could rotate freely, *trans*-2-butene could be formed by the abstraction of D^+ as well as H^+. In this case, the average number of D atoms in *trans*-2-butene per molecule becomes $\frac{1}{2}$, providing there is no isotope effect, and approaches zero as an isotope effect becomes large. Furthermore, the number of D atoms in *cis*-2-butene is equal to that in *trans*-2-butene regardless of the value of the isotope effect. This is the observed result over the catalysts evacuated at 200 and 400°C.

As shown in Table 1, ϕ_0 values of double-bond shifted isomers were not unity. In the case that the amount of active D atoms on the catalyst surface is so small compared with that of the reactant molecules that one active site participates several times at one pulse, ϕ_0 would not become unity even if only Brönsted sites are active. However, ϕ did not change with pulse number or pulse size and did not decrease with conversion. These facts exclude the possibilities that one Brönsted site participates several times at one pulse and that the diffusion of D from the bulk to the surface and/or the migration of D on the surface to the active sites occur between each pulse. Therefore, it is concluded that Brönsted acid sites are not the only kind of active sites.

As mentioned previously, Peri (*10*) reported on the basis of an ir study that Brönsted and Lewis acid existed on aluminum phosphate prepared by Kearby's method (*6*) and oxygen did not act as a base. Furthermore, NH_3 poisoned the activity completely (*13*). Therefore, the active sites other than Brönsted acid sites are probably Lewis acid sites.

The isotopic distributions of product isomers in co-isomerization show the behavior of hydrogen during the isomerization reaction. If the isomerization involved only intramolecular hydrogen transfer, only non-exchanged d_0 and d_8 isotopic species would be formed. On the other hand, if the reaction involved intermolecular hydrogen transfer, mono-exchanged d_1 and d_7 isotopic species would be produced in addition to d_0 and d_8. The isotopic distribution of 1-butene is a function of two kinds of isotope effects. One is the ratio of the reactivity of the d_0 reactant to that of the

d_8 reactant (IE_m) and the other is the ratio of the reactivity of surface H to that of surface D (IE_s). The probabilities of the formation of isotopic species in 1-butene in the co-isomerization of *cis*-2-butene become (*14*)

$$P_{d_0} = \frac{IE_m \cdot IE_s}{(1 + IE_m)(1 + IE_s)},$$

$$P_{d_1} = \frac{IE_m}{(1 + IE_m)(1 + IE_s)},$$

$$P_{d_7} = \frac{IE_s}{(1 + IE_m)(1 + IE_s)},$$

$$P_{d_8} = \frac{1}{(1 + IE_m)(1 + IE_s)},$$

where P_{d_i} represents the probability of the formation of 1-butene containing i D atoms. If there were no isotope effect, equal amounts of four isotopic species would be produced and the fraction of d_0 and that of d_8 would increase and decrease, respectively, as the isotope effects become large. In the case of the formation of *trans*-2-butene, as mentioned in the former section, the degree of rotation of a C_{II}–C_{III} bond in the intermediate (II) must be taken into account. The probabilities of the formation of each isotopic species in *trans*-2-butene become

$$Q_{d_0} = \frac{IE_m \cdot IE_s + (1 - \alpha) IE_m}{(1 + IE_m)(1 + IE_s)},$$

$$Q_{d_1} = \frac{\alpha \cdot IE_m}{(1 + IE_m)(1 + IE_s)},$$

$$Q_{d_7} = \frac{\alpha \cdot IE_s}{(1 + IE_m)(1 + IE_s)},$$

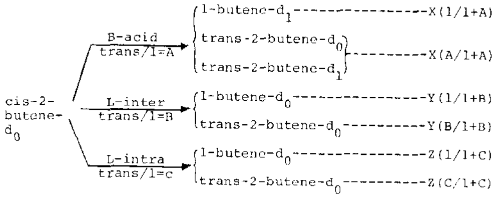
$$Q_{d_8} = \frac{1 + (1 - \alpha) IE_s}{(1 + IE_m)(1 + IE_s)},$$

where Q_{d_i} represents the probability of the formation of *trans*-2-butene containing i D atoms. In those expressions, α is the correction factor for the degree of free rotation of a C_{II}–C_{III} bond, and in the case that a C_{II}–C_{III} bond cannot rotate, α is equal to 1.0 and in the case that a C_{II}–C_{III} bond can rotate freely, α is equal to $\frac{1}{2}$. The fractions of d_0 and d_8 become large as the degree of free rotation become large. Since the C_{II}–C_{III} bond is considered to rotate freely at least in the secondary butyl carbenium ion state as described in the previous section, α should be close to $\frac{1}{2}$. The secondary butyl carbenium ions on aluminum phosphate are different from those on SiO_2–Al_2O_3 which was reported by Hightower and Hall to be restricted in the rotation of the C_{II}–C_{III} bond (*15*).

For the formation of 1-butene over the catalyst evacuated at 200 and 400°C, AEM values were 0.452 and 0.441, respectively. These values are very close to 0.481 and 0.484 which are expected when the isotope effects in Table 3 are taken into account. This result shows that the isomerization (at least the formation of 1-butene) takes place intermolecularly over the Lewis acid sites of the catalyst evacuated at 200 or 400°C. On the other hand, the reaction involves intramolecular H transfer over the Lewis acid sites of the catalyst evacuated at 600°C. Therefore, there are two types of Lewis acid sites, one where intermolecular hydrogen transfer occurs (L-inter sites) and the other where the intramolecular hydrogen transfer occurs (L-intra sites). Over SiO_2–Al_2O_3 it was reported that a proton was provided to butene from butene molecules adsorbed on Lewis acid sites to form secondary butyl carbenium ion and isomerization involved intermolecular H transfer (*16*). Analogous sites could be adopted as L-inter sites on the aluminum phosphate. All the active sites on 600°C evacuated catalyst are L-intra sites as shown in Table 3, and these are especially active for *cis–trans* rotation.

Intramolecular hydrogen transfer is usually observed over basic catalysts where the reaction was initiated by the abstraction of a proton to form a π-allyl anion as an intermediate (*17*, *18*). Since the π-allyl anion is in such a state that the rotation of a C_{II}–C_{III} bond is restricted, the rate of the isomerization between *cis*-2-butene and *trans*-2-butene is slow. On the other hand, the intramolecular hydrogen transfer over a Lewis acid is considered to be initiated by the abstraction of H^- at the allyl or vinyl hydrogen. If allyl H were abstracted, the double-bond migration would easily occur. This was not observed. If vinyl H were abstracted, the *cis–trans* rotation would easily occur because *cis*-2-butene may lose its double-bond character by the abstraction of its vinyl H and rotate relatively freely around a C_{II}–C_{III} bond. This was in coincidence with observed result.

The fractional contribution of the three kinds of active sites to the total activity was calculated for various evacuation temperatures. The isomerization of *cis*-2-butene over the deuterated catalyst proceeds as follows.



The right-side terms are the relative amounts of each isomer produced on each active sites. X, Y, and Z represent the fractional contribution of Brönsted acid sites, L-inter sites, and L-intra sites to the total activity, respectively. The relation of X, Y, and Z is

$$X + Y + Z = 1 \tag{1}$$

A, B, and C represent the ratios of *trans*-2-butene to 1-butene produced on these sites.

The observed ratio of *trans*-2-butene to 1-butene, S_0, becomes

$$S_0 = \frac{X[A/(1+A)] + Y[B/(1+B)] + Z[C/(1+C)]}{X[1/(1+A)] + Y[1/(1+B)] + Z[1/(1+C)]}. \tag{2}$$

Since the 1-butene which is isomerized on Brönsted acid sites necessarily contains one D atom per molecule but those isomerized on L-inter and L-intra sites do not contain D atoms, the ϕ_0 values of 1-butene, $\phi_{0,1}$, becomes

$$\phi_{0,1} = \frac{X(1+A)}{X(1+A) + Y(1+B) + Z(1+C)}. \tag{3}$$

Since the reaction over L-inter sites likely proceeds via the secondary carbenium ion intermediate, it is assumed that B is close to A. As L-intra sites are specifically active for *cis–trans* rotation compared to double-bond migration, C must be very large. By assuming that $A = B$ and $C = \infty$, Eqs. (1)–(3) are solved for X, Y, and Z.

$$X = \phi_{0,1} \cdot (1 + A)/(1 + S_0),$$
$$Y = (1 - \phi_{0,1}) \cdot (1 + A)/(1 + S_0),$$
$$Z = (S_0 - A)/(1 + S_0).$$

The variations of X, Y, and Z are plotted as a function of A in Fig. 9. The values of $\phi_{0,1}$ and S_0 are taken from Table 1. With an increase in the evacuation temperature, the contributions of Brönsted acid sites and L-inter sites decreased and the contribution of L-intra increased.

In the case of the isomerization of 1-butene, the reaction proceeds as follows.

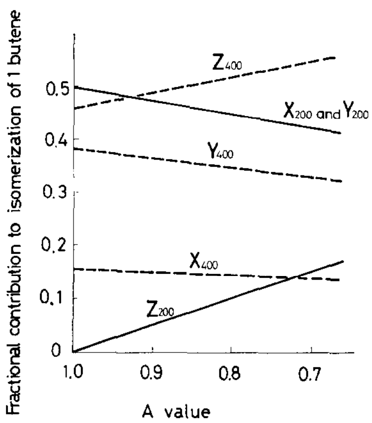
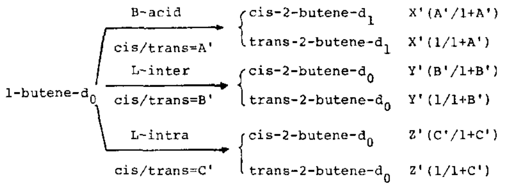


FIG. 9. Fractional contribution of Brönsted acid sites (X), L-inter sites (Y), and L-intra sites (Z) to the total activity as a function of A value (the ratio of *trans*-2-butene to 1-butene produced over Brönsted acid sites). Solid lines, 200°C evacuated catalyst; broken lines, 400°C evacuated catalyst.



X', Y', and Z' represent the fractional contribution of Brönsted acid sites, L-inter sites, and L-intra sites to the total activity, respectively, and their relation is

$$X' + Y' + Z' = 1 \tag{4}$$

A', B', and C' represent the ratios of *cis*-2-butene to *trans*-2-butene produced on these sites. The observed ratio of *cis*-2-butene to *trans*-2-butene, S'_0 and the ϕ_0 value of *cis*-2-butene, $\phi_{0,cis}$ are expressed

$$S'_0 = \frac{X'[A'/(1+A')] + Y'[B'/(1+B')] + Z'[C'/(1+C')]}{X'[1/(1+A')] + Y'[1/(1+B')] + Z'[1/(1+C')]} \tag{5}$$

and

$$\phi_{0,cis} = \frac{X'[A'/(1+A')]}{X'[A'/(1+A')] + Y'[B'/(1+B')] + Z'[C'/(1+C')]}. \tag{6}$$

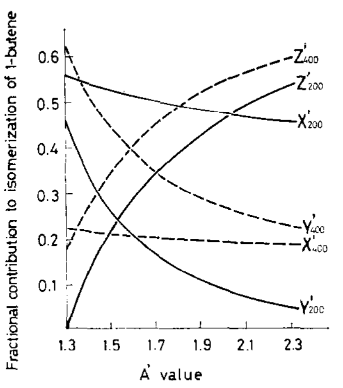


FIG. 10. Fractional contribution of Brönsted acid sites (X'), L-inter sites (Y'), and L-intra sites (Z') to the total activity in the isomerization of 1-butene as a function of A' value (the ratio of *cis*-2-butene to *trans*-2-butene produced over Brönsted acid sites). Solid lines, 200°C evacuated catalyst; broken lines, 400°C evacuated catalyst.

By assuming $A' = B'$, the Eq. (4)–(6) are solved for X', Y', and Z'.

$$\begin{aligned} X' &= \phi_{0,cis}\cdot S'_0(A'+1)/A'(1+S'_0) \\ Y' &= (A'+1)(S'_0 - C')/(A' - C') \\ &\quad \times(1+S'_0) - \phi_{0,cis}\cdot S'_0(A'+1)/ \\ &\qquad A'(1+S'_0) \\ Z' &= (A' - S'_0)(1+C')/(A' - C') \\ &\quad \times(1+S'_0). \end{aligned}$$

The variations of X', Y', and Z' are plotted as a function of A' in Fig. 10. S'_0 and $\phi_{0,cis}$ values are taken from Table 1 and C' is assumed to be 0.8 which is close to the value of 0.77 observed at the 18.8% conversion level (Table 2).

The contributions of the L-inter and L-intra sites vary greatly with the A' value while the contribution of Brönsted acid sites does not change so much. As in the case of the isomerization of *cis*-2-butene, the contribution of Brönsted acid sites decreased with the increase in the evacuation temperature.

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