Isomerization of 1-Butene on High-Temperature-Chlorinated Alumina

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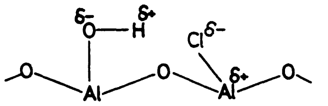
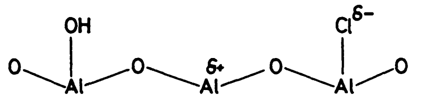
Regarding aluminas chlorinated at 973—1223 K, which have only a Lewis acidic character without hydroxyl groups and basic sites, the IR spectra of the adsorbed 1-butene were measured and the isomerization of 1-butene and *cis*-2-butene was performed at 273—323 K. The obtained results were compared with those for aluminas dehydrated at the same temperatures. The IR spectra of the adsorbed 1-butene well resembled that of *cis*-2-butene, including the absence of peaks due to double-bond and π-allyl carbanion species, observed even after outgassing at 473 K. During isomerization at 273 K, the initial isomerization reaction rates and cis/trans ratios were greater than those for dehydrated alumina. The ratio decreased rapidly with increasing reaction temperature. The specific reaction rates and the ratio were independent of the chlorination temperature. In the isomerization of *cis*-2-butene the most thermodynamically unstable molecule, 1-butene, was formed preferentially. The obtained results could be interpreted by an isomerization mechanism through a doubly bonded intermediate, i.e., the allylic butenyl cation.

A high-temperature treatment of aluminas in air and/or in vacuo removes water molecules from the surfaces, resulting in aluminium cations with unsaturated coordination, isolated hydroxyl groups and oxygen anions on the surfaces. Consequently, Lewis acid, Brϕnsted acid and basic sites are formed.[1-5] On the other hand, it is known that by chlorination with hydrogen chloride, carbon tetrachloride, aluminium trichloride, and gaseous chlorine below 823 K the Lewis and Brϕnsted acid sites on γ and η-aluminas can be enhanced.[6-11] The effects are interpreted in terms of a decrease in the electron density of aluminium atoms which are directly linked to chlorine **I** or in the nearest position to the aluminium atom linked to chlorine **II**.



[I]



[II]

The authors studied the chlorination of γ-aluminas with dry chlorine at 773—1273 K as well as the surface characteristics of treated aluminas.[12] Chlorination effectively removed surface hydroxyl groups and sulfate ions. The obtained alumina surface had chlorine atoms (2—3 nm^{-2}) bonded with the tetrahedral aluminium cation, leading to the formation of strong Lewis acid sites with $H_0 \leqq -14.52$ and yielding intense IR peaks at 1628 and 1453 cm^{-1} in pyridine adsorption. The surface was, however, unable to form carbonate and bicarbonate ions in carbon dioxide adsorption. In the 1,2-epoxypropane isomerization, allyl alcohol promoted by an acid-base bifunctional catalysis was not produced, whereas the abstraction of an oxygen atom from the epoxide molecule by strong Lewis acid site took place in addition to the formation of propionaldehyde and acetone. Even in hydrogen chloride adsorption, there was no evidence for the formation of hydroxyl groups and water molecules.[13] These experimental results undoubtedly indicated that on high-temperature-chlorinated aluminas Brϕnsted acid and strong basic sites were absent; only

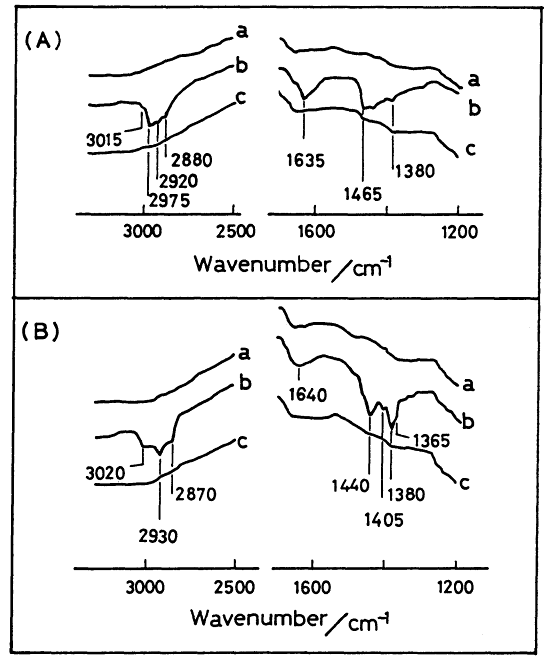


Fig. 1. IR spectra of (A) 1-butene and (B) *cis*-2-butene on alumina (ALO-4) dehydrated at 1073 K. (a) Background; (b) after exposed to 1-butene under 40 Torr for 15 min at room temperature; (c) after outgassing at room temperature for 30 min.

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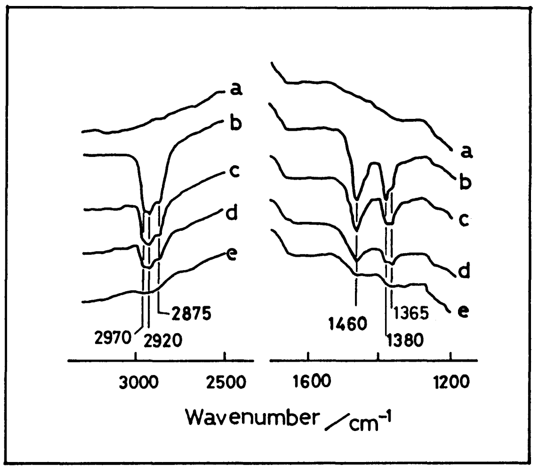


Fig. 2. IR spectra of 1-butene on alumina (ALO-4) chlorinated at 1073 K. (a) Background; (b) after exposed to 1-butene under 40 Torr for 15 min at room temperature; after outgassing for 30 min at (c) room temperature, (d) 373 K, and (e) 473 K.

Lewis acid sites were present. In addition, the strong Lewis acid sites tightly adsorbed benzene to form a π-complex with λ_{max}=294 nm and chloropropanes to the π-allyl cation, respectively, and promoted the isomerization of butane and cyclohexane to 2-methylpropane and methylcyclopentane with 100% selectivity, respectively, at 303 K.[13,14] Consequently, the chlorinated alumina is expected to be a solid Lewis superacid and to be used instead of homogeneous Lewis acids.

In the present work, in order to reveal the catalytic properties of chlorinated alumina, the infrared spectra of adsorbed 1-butene were measured and compared with those for the dehydrated aluminas; also, the isomerization of 1-butene and *cis*-2-butene was carried out. In this paper the 1-butene isomerization mechanism on a pure Lewis acidic surface is also discussed.

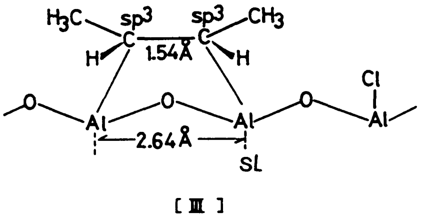
Experimental

Cylindrical γ-alumina JRC-ALO-4 (JRC represents the Japan Reference Catalyst[15]) was first crushed and sieved to obtain 16—32 and 100—150 mesh fractions; these were then washed with pure water and dried. Self-supported disks (13 mmϕ) prepared with the 100—150 mesh fraction were used in IR measurements and the 16—32 fraction in catalytic reactions. Commercial chlorine (Nissan Shoji Co., 99.4%) was purified by vacuum distillation, and 1-butene and *cis*-2-butene (Takachiho Chemicals, 99.0%) were used without special purification.

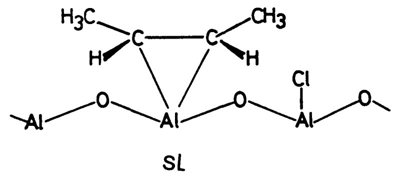
Chlorination of the samples was carried out with 100 Torr (1 Torr≈133.322 Pa) chlorine gas at temperatures between 973 and 1223 K for 1 h and then outgassed. Prior to chlorination, the samples were dehydrated at 773 K for 1 h in vacuo. During chlorination, an IR in situ cell made of a quartz glass tube and a highly pure alumina ceramics tube of 8 mmϕ i.d. (SSA-S, Nippon Ceramics Co.) were used. IR spectra were measured at room temperature using a Hitachi 215 transmission spectrometer. Isomerization reactions of 1-butene and *cis*-2-butene were performed using a fixed bed-closed circular reactor with a volume of about 550 ml. The reactant mixture comprised 1-butene (10 vol%) and helium (99.99% in purity; 90 vol%). The total pressure of the mixture was 300 Torr. The reactor comprised a U-type Pyrex glass tube (4 mmϕ i.d.) and the catalyst (0.1 g) supported by glass wool. The reaction temperature was between 273 and 323 K, and the reactant and product gases were analyzed by a gas chromatograph equipped with a column packed with propylene carbonate (15 wt%/Chromosorb G).

Results and Discussion

IR Spectra. The IR spectra of 1-butene and *cis*-2-butene adsorbed on the alumina dehydrated at 1073 K (Fig. 1). Spectrum b agreed with that on magnesium oxide pretreated at 773 K (reported by Baird and Lunsford[16]). In the spectra of 1-butene, the two peaks at 3015 and 1635 cm^{-1} were assigned to the terminal =C-H and the double-bond stretching vibrations, respectively. For *cis*-2-butene, these peaks appeared at 3020 and 1640 cm^{-1}. The 1405 cm^{-1} peak was due to the C-H deformation vibration of -CH=CH- in the cis configuration. A doublet band consisting of 1380 and 1365 cm^{-1} peaks was assigned to the resonating symmetrical deformation vibration of the C-H bond of two methyl groups in such hydrocarbon molecules as a molecule-like isopropyl group. All of the peaks described above were almost eliminated by outgassing at room temperature for 30 min. Figure 2 shows the IR spectra of the 1-butene adsorbed on alumina chlorinated at 1073 K. The spectra are very similar to that for *cis*-2-butene physically adsorbed on dehydrated alumina, also observed after outgassing at 473 K for 30 min. However, the peaks assigned to the double bond completely disappeared, the 1440 cm^{-1} peak due to the C-H deformation vibration was shifted to 1460 cm^{-1}, and a new 2970 cm^{-1} peak due to the C-H stretching vibration of the methyl group appeared. Further, the intensity ratio of the 1380 to 1460 cm^{-1} peak was 0.6—0.7, which was in accord with that for *cis*-2-butene (Fig. 1). These results indicate that 1-butene was strongly adsorbed on the strong Lewis acid sites to form such adsorbed species as **III** or **IV** via an intermolecular hydrogen-transfer reaction.



[III]



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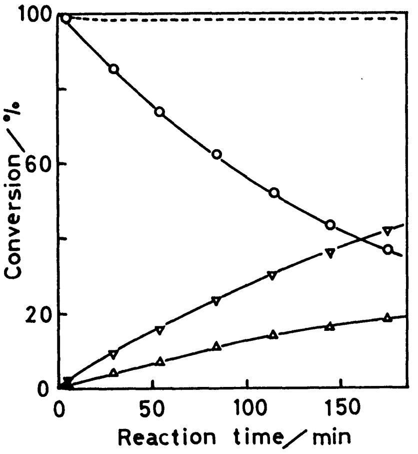

Fig. 3. Isomerization of 1-butene at 323 K on ALO-4 dehydrated at 1073 K. (○) 1-butene; (△) *cis*-2-butene; (▽) *trans*-2-butene; (----) total butenes.

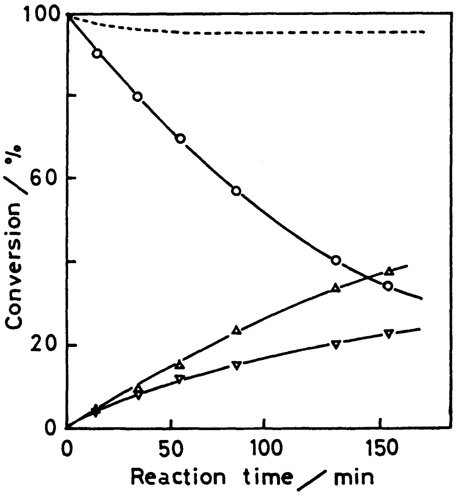

Fig. 4. Isomerization of 1-butene at 323 K on ALO-4 chlorinated at 1073 K. (○) 1-butene; (△) *cis*-2-butene; (▽) *trans*-2-butene; (----) total butene.

Geometrically, form **III** would be favorable, where *sL* indicates a possible strong Lewis acid site enhanced by chlorine bonding to the tetrahedral aluminium cation. In addition, the adsorbed species was likely to be desorbed at a higher reaction temperature, since the clear peaks assigned to oligomers or polymers were not observed. Along with the 1-butene adsorption, a new appearance of OH bands and peaks due to allylic species, which might arise from dissociation of the butene molecule, were undetected. However, on the dehydrated sample a small shift in the OH band to the low-frequency side was observed.

Isomerization of 1-Butene. Table 1 summarizes the initial isomerization reaction rates and obtained cis/trans ratios. The time courses of gas composition when a large conversion of 1-butene was obtained are shown in Figs. 3 and 4. The compositions were far apart from the thermodynamical equilibrium values of butenes: 4.1/70.7/25.2 for 1-butene/*trans*-2-butene/*cis*-2-butene. In every run, a loss in carbon balance was observed. An irreversibly adsorbed amount for 120 min decreased with an increasing reaction time and treatment temperature, being 1—7 and 3—15 mol% of 1-butene for the dehydrated and chlorinated aluminas, respectively. At every reaction temperature, the isomerization rates and cis/trans ratios for the chlorinated aluminas were greater than those for the dehydrated aluminas. Each reaction rate indicated a maximum at a chlorination temperature between 973 and 1073 K. The chlorination temperature dependence was very similar to that of the chlorine content for chlorinated alumina JRC-ALO-2.[12] The surface area decreased as a result of chlorination, as well as with an increase in the chlorination temperature. Consequently, the differences in the reaction rates between the two kinds of treated aluminas became increasingly large with increasing temperature. However, the specific isomerization rates and the cis/trans ratios were almost independent of the chlorination temperature (Fig. 5). Only the specific

Table 1. Initial Reaction Rates and Cis/Trans Ratios in 1-Butene Isomerization on Aluminas (ALO-4) Dehydrated and Chlorinated at High Temperatures above 973 K

Catalyst (0.1 g)	Treatment temperature/K	Initial isomerization rates/mol $(g \cdot s)^{-1}10^7$											
		973			1073			1173			1223		
	Reaction temperature/K	273	296	323	273	296	323	273	296	323	273	296	323
Chlorinated ALO-4	*cis*-2-Butene	2.03	4.39	3.89	2.34	4.17	4.28	1.66	3.30	3.56	0.95	2.79	2.80
	trans-2-Butene	0.34	1.19	2.91	0.38	1.09	2.79	0.26	0.95	2.32	0.15	0.76	1.62
	cis/trans ratio	5.97	3.69	1.33	6.16	3.84	1.53	6.31	3.47	1.53	6.33	3.67	1.73
	Surface area/m^2g^{-1}	139			139			115			88		
Dehydrated ALO-4	*cis*-2-Butene	0.22	0.92	1.31	0.44	1.34	2.15	0.43	0.93	1.64	0.26	1.01	1.33
	trans-2-Butene	0.06	0.51	2.59	0.13	0.62	4.55	0.12	0.35	2.27	0.08	0.38	0.82
	cis/trans ratio	3.57	1.80	0.51	3.47	2.14	0.47	3.50	2.67	0.72	3.37	2.60	1.62
	Surface area/m^2g^{-1}	157			160			152			145		

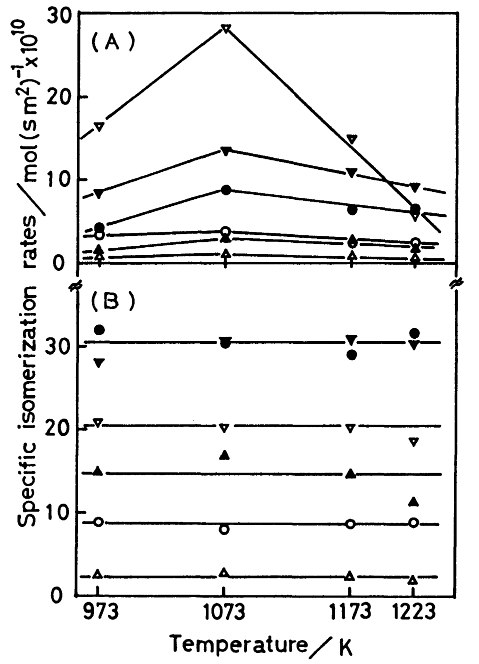

Fig. 5. Treatment temperature dependences of the isomerization reaction rates of 1-butene for (A) dehydrated and (B) chlorinated alumina (ALO-4). Reaction temperatures—273 K (▲ cis, △ trans); 296 K (● cis, ○ trans); 323 K (▼ cis, ▽ trans).

rate to *cis*-2-butene at 273 K varied with the chlorination temperature. This variation seems to reflect an unstable surface state caused by the accumulation of *cis*-2-butene tightly adsorbed in form **III** or **IV**. The number of chlorine atoms per unit surface area was almost constant (2.5 nm^{-2}) and did not depend on the chlorination temperature.[13] This result suggests that 1-butene isomerization is mainly catalyzed by the strong Lewis acid site, "*sL*".

Isomerization of *cis*-2-Butene. The isomerization of *cis*-2-butene was carried out at 273 K under the same reaction conditions as 1-butene (Table 2). The most unstable molecule, 1-butene, among the butenes was formed at 3.2—4.4 times the reaction rates for the dehydrated aluminas. However, the *trans*-2-butene formation rates for the two kinds of catalysts were of the same order. The trans/1 ratios (0.7—1.4) were abnormally small, being smaller than those for the dehydrated aluminas. Such low trans/1 ratios indicate that the rotation of the ^{2}C-^{3}C axis of adsorbed *cis*-2-butene is remarkedly depressed on chlorinated aluminas.

Mechanism. The cis/trans ratio and the trans/1 ratio obtained for dehydrated aluminas were almost in accord with the results reported by Gerberich and Hall and explained by the acid-base bifunctional and geometric isomerization mechanism via allylic butenyl ion intermediate.[17] Basset et al. reported that the π electrons of the double bond were delocalized to yield a dipole intermediate with partially negative and positive charges on ^{1}C and ^{4}C, respectively; they concluded that the repulsion between the positive methyl group and aluminium cation took place to give the high trans/1 ratio in *cis*-2-butene isomerization.[18] In addition, they explained the low trans/1 ratio for carbon tetrachloride-treated alumina by the classical carbonium ion mechanism. However, the cis/trans ratio in the 1-butene isomerization with the carbonium ion mechanism should be close to unity.[17,19] Regarding the chlorinated alumina which Basset et al. employed, oxygen ions with an electron-donor property, weak basic sites and strong Lewis acid sites were present because of adoption of a low chlorination temperature, 473 K.[18] In order to effectively eliminate hydroxyl groups and strong basic sites from the surfaces, a chlorination temperature of at least above 973 K was required.[12] On alumina chlorinated at such temperatures, the strong Lewis acid sites, "*sL*", were enhanced by chlorine bonding to aluminium cations; other weak sites were present. The presence of weak basic sites which would compensate the acidity is not necessarily denied. However, the surface had no ability to adsorb carbon dioxide to form carbonate and bicarbonate ions. In the adsorption of hydrogen chloride, a new OH stretching band at 3700 cm^{-1} and a deformation band of the O-H bond of H$_2$O at 1600 cm^{-1} clearly appeared on the dehydrated sample,

Table 2. Initial Reaction Rates and Trans/1 Ratio in *cis*-2-Butene Isomerization

Catalyst (0.1 g)	Treatment tempertature /K	Reaction temperature /K	Initial rates/mol (g·m^2)$^{-1}$×10^{10}		Trans/1
			trans-2-Butene	1-Butene	
Chlorinated	1073	273	2.45	1.80	1.38
	1173	273	1.91	2.61	0.73
ALO-4		296	6.52	3.84	1.71
		323	19.5	5.30	5.52
	1223	273	2.04	2.84	0.74
Dehydrated	1073	273	2.81	0.56	5.02
	1173	273	1.97	0.59	3.33
ALO-4		296	11.7	1.97	6.00
		323	15.5	2.11	7.49
	1223	273	2.07	0.76	2.74

whereas on the chlorinated sample both bands were entirely undetected.[13] These results indicate the complete absence of oxygen ions and hydroxyl groups having an electron-donor character.

The cis/trans ratios obtained on the Lewis acidic surfaces (Table 1) were very great, being rather similar to those for basic metal oxides.[16,20] Dent and Kokes[21] and Chang et al.[22] studied the isomerization and adsorption of 1-butene on a partially dehydrated zinc oxide and concluded that the cis/trans ratio was 10.5 and the adsorbed butene formed a π-allyl carbanion species, which showed absorption peaks at 1550—1572 cm^{-1}. In addition, they confirmed, along with the π-allyl bands, the appearance of a new OH band at 3587 cm^{-1} arising from the dissociation of adsorbed butene, which was caused by strong basic sites. In the present study, there was no evidence for the formation of the π-allyl species or new OH groups. Thus, a mechanism involving a π-allyl carbanion intermediate is very difficult to justify for isomerization on chlorinated aluminas. Further, although the IR peaks assigned to the π-allyl cation can not be observed in Fig. 2, as well as in the case of more longer-time adsorption, it was ascertained that the adsorption of chloropropanes yielded an intense peak at 1533—1535 cm^{-1} due to the cation.[12] This indicates that the strong Lewis acid site abstracts, as a hydride ion, an allylic hydrogen of propene formed from chloropropanes by dehydrochlorination. Consequently, the high selectivity of 1-butene to *cis*-2-butene, as shown in Table 1, is considered to be illustrated by a mechanism via a doubly bonded intermediate, butenyl cation, similar to that presented by Tanaka and Ogasawara[8] (Fig. 6). The 1-butene molecule can approach very closely to the '"*sL*" site because of the absence of hydroxyl groups and basic oxygen ions with a large electron cloud. The "*sL*" site abstracts the hydrogen atom on allylic carbon and the adjacent Lewis acid site attracts the terminal methylene carbon. When the intermediate **V** shifts to **VI**, the hybrid orbital of ^3C changes from sp^3 to sp^2. At the same time, the methyl group goes away from the surface due to its large electron cloud and the ^2C moves upward. Subsequently, during the shifting of π-electrons, the cis configuration would be completed. The IR spectra of 1-butene adsorbed on the "*sL*" site, coinciding with that of *cis*-2-butene, completely lost its double-bond character. This shows that a hydride shift and a ^2C-^3C axis rotation take place very fast. Intermediate **III**, corresponding to the spectra in Fig. 2, seems to be the most stable configuration of 1-butene and *cis*-2-butene molecules which approach very close to the surface, since two methyl groups on the same side are permitted to move somewhat away from the surface. The butenyl cation mechanism would lead to the high cis/trans ratio. The experimental value was about 6. Similar results were reported by Gerberich and Hall (about 5) regarding fluoridized alumina[17] and Tanaka and Ogasawara (about 6) regarding hydrogen chloride-treated alumina.[8] For *cis*-2-butene isomerization, intermediate **III** is first formed; however, the formation of a ^2C-^3C axis at rotation to give *trans*-2-butene is more difficult than a hydride shift from ^1C to ^3C, since the interaction between the "*sL*" site and the *cis*-2-butene molecule is very strong. The lower trans/1 ratios therefore seem to have been obtained. At high reaction temperatures, doubly bonded intermediate **III** would become easy to shift to a singly bonded *s*-butyl cation, i.e., trans configuration. Consequently, with increasing reaction temperature, the cis/trans ratio and the trans/1 ratio seem to decrease and increase, respectively.

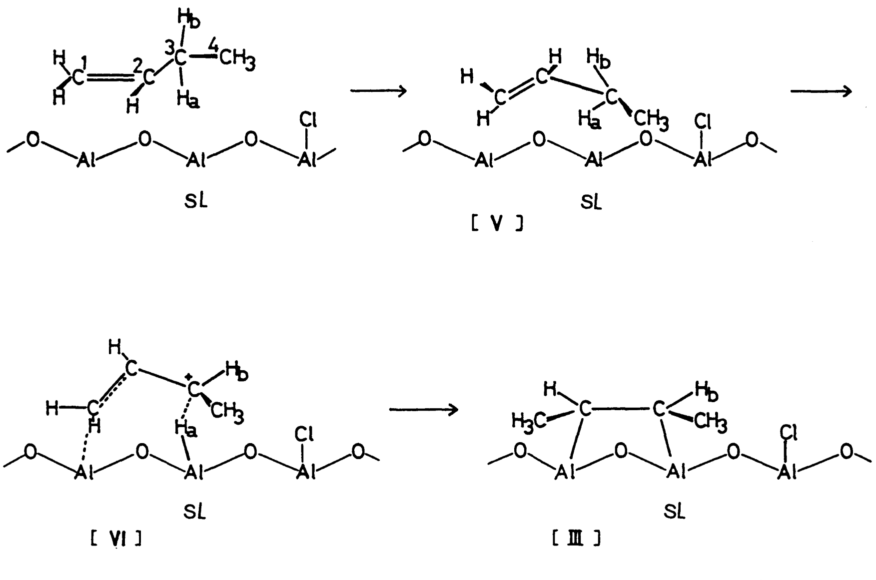

Fig. 6. Possible isomerization mechanism on the chlorinated aluminas. The *sL* represents a possible strong Lewis acid site.

References

1) E. Parry, *J. Catal.*, **2**, 371 (1963).

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

3) J. B. Peri, *J. Phys. Chem.*, **69**, 231 (1965).

4) C. Morterra, S. Coluccia, A. Chiorino, and F. Boccuzzi, *J. Catal.*, **54**, 348 (1978).

5) "Kinzoku Sanka-butsu to Sono Shokubai Sayo," ed. by T. Seiyama, Kodan-sha-VHC, Tokyo (1979), p. 106.

6) J. B. Peri, *J. Phys. Chem.*, **70**, 1482 (1965).

7) M. Tanaka and S. Ogasawara, *J. Catal.*, **16**, 157 (1970).

8) M. Tanaka and S. Ogasawara, *J. Catal.*, **16**, 164 (1970).

9) A. Melchor, E. Garbowski, M. V. Mathieu, and M. Primet, *J. Chem. Soc., Faraday Trans. 1*, **82**, 1893 (1986).

10) E. Garbowski and M. Primet, *J. Chem. Soc., Faraday Trans. 1*, **83**, 1469 (1987).

11) M. Marczewski, M. Derewinski, and S. Malinowski, *Can. J. Chem. Eng.*, **61**, 93 (1983).

12) A. Ayame, G. Sawada, H. Sato, G. Zhang, T. Ohta, and T. Izumizawa, *Appl. Catal.*, **48**, 25 (1989).

13) A. Ayame, T. Izumizawa, and H. Kakizaki, Proceedings of Acid-Base Catalysis Intern. Symp., ed. by K. Tanabe, Kodan-sha-VHC, Tokyo (1989), p. 371.

14) A. Ayame and T. Izumizawa, *J. Chem. Soc., Chem. Commun.*, **1989**, 645.

15) The Committee on Reference Catalysts (Catal. Soc. Jpn.), *Shokubai*, **22**, 410 (1980).

16) M. J. Baird and J. H. Lunsford, *J. Catal.*, **26**, 440 (1972).

17) H. R. Gerberich and W. K. Hall, *J. Catal.*, **5**, 99 (1966).

18) J. Basset, F. Figueras, M. V. Mathieu, and M. Prettre, *J. Catal.*, **16**, 53 (1970).

19) K. Tanabe, "Shokubai no Hataraki," Kagaku-dojin, (1979).

20) T. Okuhara and M. Misono, *Shokubai*, **25**, 279 (1983).

21) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **75**, 487 (1971).

22) C. C. Chang, W. C. Conner, and R. J. Kokes, *J. Phys. Chem.*, **77**, 1957 (1973).