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Active Sites of Solid Acidic Catalysts

I. Chemisorption of Ammonia and Its Effect on the Isomerization of 1-Butene on Alumina[1]

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The chemisorption of ammonia and the isomerization of 1-butene on alumina have been studied in an attempt to obtain more detailed information on the nature of active sites. The temperature-programmed desorption of ammonia revealed two types of chemisorption: weaker chemisorption which occurred at room temperature and stronger chemisorption which took place at 250°C or higher. With the aid of infrared spectroscopy, the stronger type has been explained as NH_2 species adsorbed on exposed Al ions on the surface, and the weaker type as molecular ammonia adsorbed probably on strained oxide ions.

On the basis of the above results, the isomerization of 1-butene was carried out with preadsorbed ammonia as a poison. Ammonia chemisorbed in the stronger form blocked the isomerization efficiently and linearly while weakly chemisorbed ammonia had little effect on the reaction. Also, the catalyst activity was proportional to the amount of butene chemisorbed on sites I of alumina which had been found by us to be responsible for the chemisorption of olefins. On the other hand, other chemisorptive sites, sites II, also found previously were found not to be responsible for isomerization. The present results could be explained by a proton donor–acceptor mechanism postulated by Ozaki and Kimura [*J. Catal.* **3**, 395 (1964)] with butene chemisorbed on Lewis acid centers acting as proton donor. Those Lewis centers are sites I, and it appears that sites I are a pair or triplet of exposed Al ions, while sites II are isolated Al ions associated with hydroxyl groups.

INTRODUCTION

During recent years the mechanism of *n*-butene isomerization over alumina has been studied extensively by using various techniques (*1–9*) including infrared spectroscopy (*1*), coisomerization with perdeutero butenes (*5*), isomerization in the presence of perdeutero propylene (*3*) with further determination of hydrogen position by microwave spectroscopy (*7*), and the reaction with selectively deuterated butenes (*8, 9*). Active sites of alumina responsible for the isomerization have also been the subject of investigation (*10–17*). Various vapors were used in an attempt to poison the active sites selectively: ammonia (*11, 14*), triethylamine (*13*), sulfur dioxide (*14, 17*), carbon dioxide (*14, 15*), methyl mercaptan (*17*) and hydrogen sulfide (*16, 17*). Geometrical factors of molecule were also found important for the isomerization of olefins (*18*). It seems to be agreed upon that the upper limit of active sites thus obtained on γ-alumina is $3\text{–}5 \times 10^{13}/\text{cm}^2$ (*11, 16, 17*). In spite of these numerous works, however, more information is yet to be obtained to clarify the mechanism of reaction and the nature of active sites in particular.

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We have found two distinctive active centers on alumina, sites I and II, which are responsible not only for the chemisorption of olefins (*19*) but for the polymerization (*20*) and the hydrogenation (*21, 22*) of ethylene. Recently, Rosynek *et al.* (*14, 15*) found by using carbon dioxide as a poison that CO_2 poisoned alumina for the exchange of hydrogen atoms of olefins with D_2 but not for the isomerization of olefins, and they postulated E and I sites responsible for exchange and isomerization, respectively, in addition to two adsorption sites, A and B. A and B sites apparently correspond to sites I and II found by us. In view of this, we carried out the isomerization reaction of 1-butene on alumina with ammonia as a poison to confirm the isomerization sites, and the results are reported in this paper.

Basic vapors have been used to poison or measure acid centers on solid acidic catalysts, and they seem to be suitable for the study of isomerization reaction whether it takes place on protonic sites or Lewis acid centers. One of the difficulties in using these vapors, however, is the fact that physical and chemical adsorption both occur on high area surface materials such as alumina. Usually, physically adsorbed gas is removed by pumping at a temperature, but the selection of temperature is rather arbitrary. The effect of basic vapors on the isomerization of olefin is not conclusive either. Peri (*11*) reported that a small amount of ammonia adsorbed at 400°C covered most of the isomerization sites on γ-alumina, while Rosynek *et al.* (*14*) observed only very small effect on the isomerization when ammonia and pyridine were adsorbed at room temperature.

The adsorption of ammonia on alumina and its effect on ethylene chemisorption were earlier studied by us using a temperature-programmed desorption (TPD) technique (*23*), but the effect of adsorption temperature was not studied extensively. Therefore, the chemisorption of ammonia was studied prior to the isomerization reaction mainly by TPD and varying adsorption temperature over a wide range. Results obtained by the aid of infrared spectroscopy are also discussed in this paper.

EXPERIMENTAL METHODS

Materials

Alumina catalyst used in this study was an η-alumina kindly supplied by Exxon Co. A typical analysis by emission and atomic absorption spectroscopy showed 34 ppm of metallic impurity (Cu and Fe), 45 ppm of Si and 75 ppm of Mg. An amount of 0.205 g of 24 mesh particles was taken in the reactor, calcined with air for 1 hr at 600°C and finally evacuated for 3 hr at the same temperature before use. After this treatment, the surface area was 234.7 m^2/g by BET with nitrogen. The same sample of catalyst was used for all reaction and TPD experiments in this study. A wafer of catalyst for infrared spectroscopy was prepared from the same batch of alumina. The fine powder of the alumina was pressed into a wafer of 19 mm diameter and its density was 17.8 mg/cm^2.

Anhydrous ammonia (99.99%), research grade 1-butene and *cis*-2-butene were all degassed thoroughly by condensing with liquid nitrogen. Perdeuterobutene (2-butene-d_8) was purchased from Merck Sharp & Dohme of Canada, and it contained 19.5% *trans*- and 80.5% *cis*-2-butene but no 1-butene. The only isotopic impurity found by mass spectroscopy was 7.2% of C_4H_7D. Helium used as the carrier gas of TPD was Matheson's ultrahigh purity grade (99.99%). It was used after passing through a molecular sieve tower to remove a trace of water and carbon dioxide.

Apparatus and Procedure

The apparatus consisted of three systems: a closed recirculation system for isomerization reaction; a static adsorption system; and a TPD system. The three systems were combined with a common reactor of jacketed type (*24*) so that the same sample of catalyst was used for all experiments without risking a change of surface conditions. The total volume of reaction system was 130 ml including the reactor (20 ml), while the adsorption system had a volume of 33 ml for more accurate measurement of adsorption. The reaction system was equipped with a stainless steel bellows circulation pump rated 6.2 liters/min (max). Varying its speed in a range used in the present experiments did not change the observed rate of isomerization. A sample of gas (about 2% of the total gas in the system) was taken to a gas chromatograph for analysis at proper intervals of time during reaction. The whole system could be evacuated to 10^{-6} Torr. The temperature-programmed desorption has been described elsewhere (*24*).

The isomerization reaction was started with or without preadsorbed ammonia by circulating a known amount of 1-butene through the reactor, and the pressure was recorded with a capacitance pressure transducer. The pressure decreased at first by adsorption, but it was stabilized usually within 5 min. The first order rate constant, k, was obtained according to the equation

$$\ln (1 - x_e)/(x_t - x_e) = kt, \qquad (1)$$

where x_t and x_e are the fractions of 1-butene at time t and at equilibrium, respectively. The plot of the left side of Eq. (1) against t fell well on a straight line mostly up to 80% of conversion which corresponded to about 90 min of reaction time on a clean surface. x_e was calculated from a thermochemical table (*25*).

Usually TPD was carried out up to 600°C after each reaction. The catalyst was then treated with about 300 Torr (1 Torr = 133.3 N m^{-2}) of dry air circulated through a trap at liquid nitrogen temperature for 1 hr at 600°C to remove a trace of hydrocarbon or carbon which might be still remaining on the surface. Finally the catalyst was evacuated for 1 hr at 600°C for the next reaction. This procedure was sufficient to keep the catalyst activity constant throughout a series of about 70 experiments. The surface area decreased only by 2% during the experiments.

The cell used for infrared spectroscopy was an inverse T-shape cell made of quartz. The catalyst wafer held in a quartz holder could be raised by an outer magnet to the upper part of the cell where it was treated at 600°C similarly to the catalyst for reaction. The system was all glass with UHV flanges and metal valves so that the contamination by grease and mercury was avoided. A routine pressure of 10^{-8} Torr was easily obtained and after bakeout the pressure became in the 10^{-9} Torr range. Spectra were recorded with a Beckman IR4230 spectrophotometer at a spectral slit width of 4 cm^{-1}. After spectra were taken, the catalyst wafer was raised to the furnace position again and the temperature was increased linearly with a proportional programmer-controller, while the pressure of desorbed gas was detected and recorded by a mass spectrometer either in total or partial pressure mode. This temperature-programmed desorption carried out under high vacuum (10^{-6} to 10^{-7} Torr) was not used for the quantitative discussion of TPD but for the identification of molecules observed by infrared spectroscopy with those found by TPD.

RESULTS AND DISCUSSION

I. CHEMISORPTION OF AMMONIA

1. Temperature-Programmed Desorption

Some typical TPD spectra of ammonia are shown in Fig. 1. Various amounts of ammonia were admitted to the reactor at 450, 250°C or room temperature (starting temperature). The temperature was kept for 1 hr and then cooled to room temperature at which ammonia was removed from the reactor before TPD. When a small amount of ammonia was adsorbed at 250°C (curve a in Fig. 1), it showed a single peak at high temperatures with the top of the peak between 250 and 350°C. Beyond this amount TPD started to give an additional peak that desorbed at lower temperatures (b and c), but the size of the high temperature peak stayed almost constant when the peak height was adjusted for the overlapping tail of the low temperature peak. Therefore, the curve a shows approximately the saturation by the stronger chemisorption of ammonia at about 1.1×10^{14} molecules/cm^2.

Curve d was obtained by adsorbing ammonia at room temperature, and it lacked the high temperature peak. An experiment in which a much larger amount of ammonia was admitted at room temperature and the temperature was finally cooled to -35°C gave a very large peak in TPD between 0 and 50°C with a shoulder whose temperature (120°C), height and tail were the same as d in Fig. 1. Although it is not sure whether the large peak that appeared at 0–50°C is a still weaker chemisorption or physical adsorption, the chemisorption that takes place at room temperature was saturated in curve d, the amount of which was about 2.1×10^{14} molecules/cm^2.

When ammonia was adsorbed at 450°C (e in Fig. 1), the peak at 250–350°C decreased and a third peak appeared at about 550°C. It appears that strongly chemisorbed ammonia decomposed at this high temperature. However, a trap cooled by liquid nitrogen and inserted between the reactor and the detector of TPD removed all peaks indicating that the peak at 550°C was also condensable. Infrared spectra of ammonia adsorbed at 450°C did not show any difference from those at 250°C. Also, a mass spectrometric search during the TPD after infrared spectroscopy could not detect any H_2, N_2, or CO_2 in spite of the fact that the TPD showed similar high temperature peak at about 550°C.

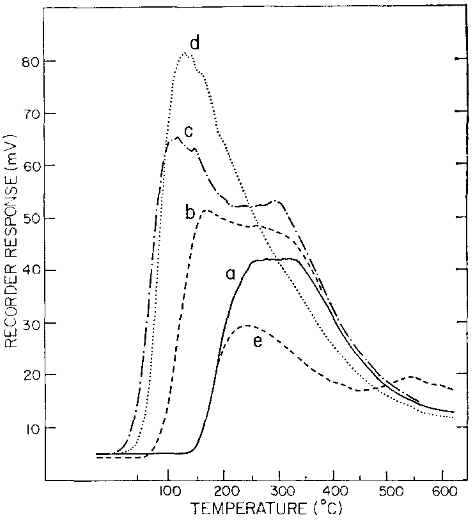

FIG. 1. TPD spectra of ammonia. Starting temperature of adsorption and the amount (molecules/cm^2) desorbed by TPD were: (a) 250°C, 1.13×10^{14}; (b) 250°C, 1.67×10^{14}; (c) 250°C, 2.20×10^{14}; (d) 23°C, 2.09×10^{14}; (e) 450°C, 1.12×10^{14}.

Although the adsorption at 450°C is not fully understood at this stage, the results of TPD revealed that two different types of chemisorption of ammonia take place on the alumina surface, one is a weaker chemisorption occurring at room temperature and the other is a stronger chemisorption requiring a greater activation energy of adsorption.

2. *Infrared Spectroscopy*

The present density of catalyst wafer (17.8 mg/cm^2) was necessary to obtain reasonable intensities of absorption bands, but it made transparency poor in the region between 4000 and 3000 cm^{-1} in particular. Therefore, the alumina was deuterated with deuterium gas at 600°C and ND_3 was used as adsorbate for spectroscopy in the region of 3000–2000 cm^{-1}, while NH_3 was used on the undeuterated surface between 2000 and 1100 cm^{-1}. The objective of the spectroscopy was to find differences in the adsorbed state, if any, between the weak and strong chemisorption of ammonia found by TPD. Therefore, TPD of adsorbed gas was carried out after each spectroscopic observation, as described in the Experimental Methods section, to confirm the type of chemisorption.

The two types of chemisorbed ammonia were again confirmed by TPD although the peaks were somewhat broader than those shown in Fig. 1. Probably the heating of catalyst would not have been uniform on the 19 mm diameter disk suspended in a high vacuum. Ammonia adsorption on the walls of the apparatus might also be a reason for the broadening in spite of the fact that the wall and flanges of cell, and vacuum manifold were all kept at about 100°C. Some representative absorption spectra are shown in Figs. 2 and 3. TPD after spectra a and b in both figures gave only the high temperature peak, while d in Fig. 2 and e in Fig. 3 gave only the low temperature peak as expected.

The spectra shown in Figs. 2 and 3 are generally consistent with the results obtained by Peri (*11*) except for the bands in the 1130–1300 cm^{-1} region. Therefore, the only results relevant to those of TPD are discussed. No detectable shift of frequency with the adsorbed amount was observed for the all N–D stretching vibrations in Fig. 2. In Fig. 3, on the other hand, bands at 1620 and 1506 cm^{-1} both started to shift towards lower frequencies after spectrum c at which the surface concentration slightly exceeded the saturation of stronger chemisorption and TPD started to show the lower temperature peak as well. A plot of the absorbance of the 1506 cm^{-1} band as a function of surface concentration showed that the absorbance increased with the amount adsorbed at 270°C up to 8×10^{13} molecules/cm^2 but it remained unchanged after that. This amount is again close to the saturation of stronger chemisorption (1.1×10^{14}) indicating that the surface species of this type of chemisorption is NH_2. With other bands, the absorbance either increased monotonously or it was hard to obtain any definite correlation with the adsorbed amount.

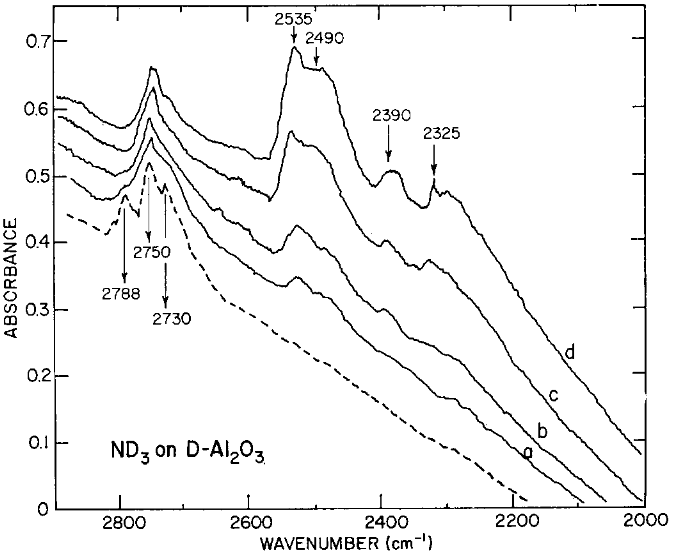

FIG. 2. Infrared spectra of adsorbed ND_3 on deuterated alumina. (– –) Catalyst. Starting temperature of adsorption and the adsorbed amount (molecules/cm^2) were: (a) 270°C, 4.1×10^{13}; (b) 270°C, 8.4×10^{13}; (c) 270°C, 1.6×10^{14}; (d) 23°C, 1.9×10^{14}.

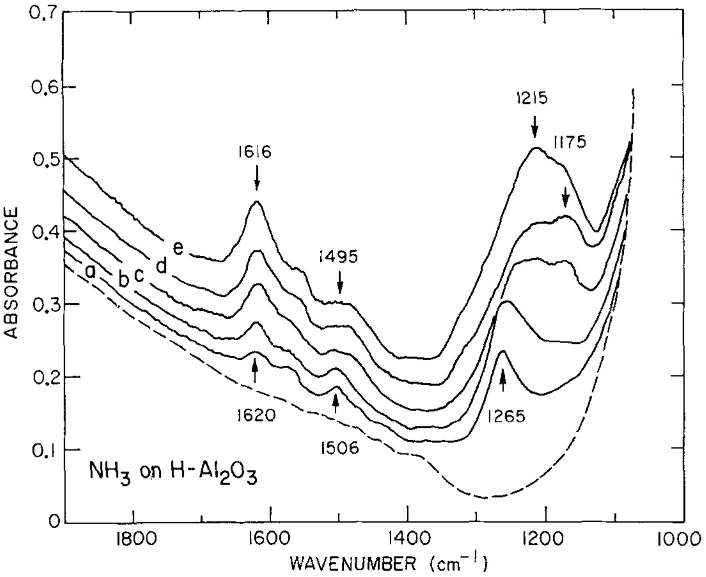

FIG. 3. Infrared spectra of adsorbed NH_3 on undeuterated alumina. (– –) Catalyst. Starting temperature of adsorption and the adsorbed amount (molecules/cm^2) were: (a) 260°C, 4.1×10^{13}; (b) 270°C, 7.9×10^{13}; (c) 270°C, 1.4×10^{14}; (d) 270°C, 1.8×10^{14}; (e) 23°C, 1.9×10^{14}. Spectra in Figs. 2 and 3 were obtained with different attenuation.

Not too many reports are found about the bands in the 1130–1300 cm^{-1} region for ammonia adsorption. Primet *et al.* (*26*) observed two bands at 1220 and 1190 cm^{-1} as well as other bands at higher frequencies on the adsorption of ammonia on titanium oxides, and they assigned the bands to the ν_2 vibration of ammonia adsorbed on the sites of different strength of acidity. The bands at 1215 and 1175 cm^{-1} in Fig. 3 could also result from similar mode of vibration, while the band at 1265 cm^{-1} may be ascribed to NH_2 species. However, a definite assignment of these bands is impossible at this moment. Also, the reason for the disappearance of the 1265 cm^{-1} band from the spectra c and d in Fig. 3 is not clear yet, although the overlap of the lower frequency bands may make this band less conspicuous to some extent.

As already mentioned, the present results are consistent with those of Peri (*11*), and his interpretations also seem applicable to our results without conflicting with the TPD results. Thus ammonia chemisorbs strongly at 250°C or higher on exposed aluminum ions on the surface with one hydrogen atom interacting with an adjacent oxide ion, while at room temperature ammonia chemisorbs as molecules probably on strained oxide ions. At 450°C, ammonia dissociates more completely as NH_2^- + OH^-, and in TPD, water is formed at high temperature giving a condensable peak at 550°C. No band was observed near 1400 cm^{-1} indicating the absence of ammonium ion within the detection limit.

II. ISOMERIZATION OF 1-BUTENE

1. *Poisoning by Ammonia*

Recovery of *n*-butenes after the reaction including butenes from the catalyst surface by TPD was better than 99.5%, and no isobutene was found by gas chromatography during the reaction. No other reactions than *n*-butene isomerization therefore occurred to an appreciable extent.

The results obtained are shown in Fig. 4, where the first order rate constant, *k*, is

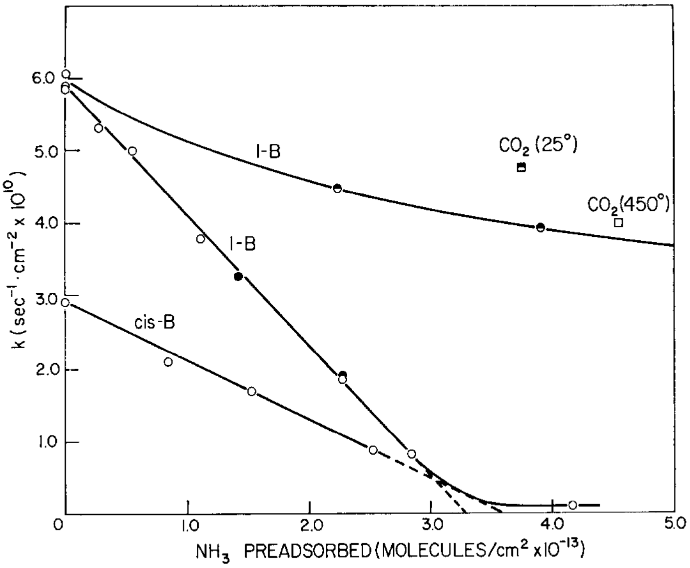

FIG. 4. Effect of preadsorbed ammonia on the isomerization of butenes. The pressure of butenes was 85 ± 2 Torr, and reaction temperature was 19.0°C for 1-butene (1-B) and 19.5°C for *cis*-butene (*cis*-B). The temperature of NH_3 preadsorption was 250°C (○); 23°C (◓); and 450°C (●). The temperature of CO_2 preadsorption is indicated.

plotted as a function of the surface concentration of ammonia preadsorbed as a poison. Ammonia was adsorbed at various temperatures before reaction, but the amounts were all so small that the residual pressure became 10^{-3} Torr or less. The isomerization, therefore, followed without evacuation of the reactor.

Figure 4 shows that ammonia preadsorbed at 250°C (open circles) poisons the catalyst efficiently and in a linear manner, while the weaker form of ammonia adsorbed at room temperature (half-filled circles) is much less effective. Indeed, a large amount of ammonia preadsorbed at room temperature at a concentration of 1.2×10^{14} molecules/cm^2 still left 15% of the original activity. On the other hand, ammonia adsorbed at 450°C (filled circles) was as effective as that at 250°C. The upper limit of the active sites for isomerization was obtained as 3.3×10^{13} sites/cm^2 by extrapolation of the linear portion of the curve in the figure. The isomerization of *cis*-2-butene was also carried out for comparison, with ammonia adsorbed at 250°C, and the results are included in Fig. 4. The poisoning effect is also linear and the extrapolation falls on the same site density as for 1-butene within experimental error, suggesting that the double bond migration and *cis–trans* isomerization reactions take place on the same sites. The site density (3.3×10^{13}/cm^2) obtained here is in reasonable agreement with those obtained by other workers with hydrogen sulfide and methyl mercaptan (*16, 17*). The activation energy of 1-butene isomerization obtained on unpoisoned surface between 0 and 42°C was 11.5 kcal/mole.

Figure 4 also includes some results obtained with CO_2 as poison (squares). Carbon dioxide adsorbed at 450°C seems slightly more effective than that at room temperature, but in any case it has little poisoning effect in agreement with Rosynek *et al.* (*14, 15*). They also reported that ammonia had little effect on the isomerization (*14*), but they did not adsorb ammonia at high temperatures. On the other hand, Peri (*11*) found by infrared spectroscopy that only 5% of a monolayer of ammonia adsorbed at 400°C covered 90% of the isomerization sites on γ-alumina. This coverage corresponds to about 3×10^{13} molecules/cm^2 according to the surface area of his alumina, and it agrees quite well with our results.

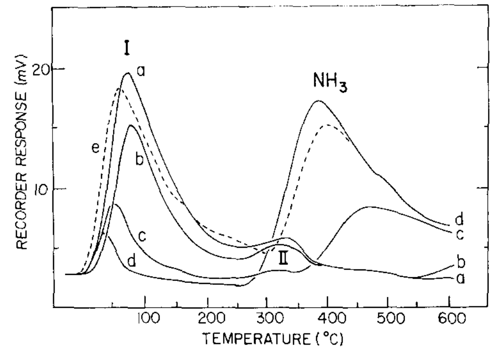

Fig. 5. TPD spectra after isomerization reactions. Preadsorption temperature of ammonia was 250°C (b, c, and d); and 23°C (e). Amount of ammonia (molecules/cm^2): (a) 0; (b) 5.4×10^{12}; (c) 2.3×10^{13}; (d) 4.2×10^{13}; (e) 3.9×10^{13}.

2. TPD of Butene

After the final gas sample was taken to the gas chromatograph (60–90 min), butenes in the reactor were removed at 19°C by condensing in the trap for 15 min, and TPD was carried out subsequently to see the gas remaining on the surface. Some of the results thus obtained are shown in Fig. 5. A TPD spectrum obtained on unpoisoned catalyst (curve a) shows two peaks of butene, I and II, in agreement with the butene peaks previously found on γ-alumina (*19*, *24*), although the ratio of the sizes of peaks I to II is much larger on the present alumina. Chemisorptive sites corresponding to peaks I and II were referred to as sites I and II, respectively (*19*, *24*). In the case of ammonia poisoning, an ammonia peak appeared at higher temperatures but it was well separated from the peak I of butene. It should be noted here that, when the amount of ammonia becomes smaller, the peak appears at higher temperature, sometimes above 600°C as a part of the rear end of the saturation peak shown in Fig. 1. Therefore, the peak height of ammonia in Fig. 5 is not necessarily proportional to the amount. Note also that the ordinate scale is quite different between Figs. 1 and 5.

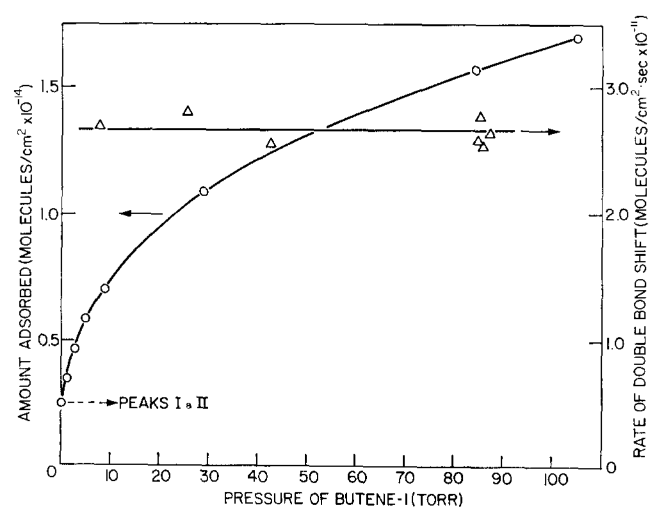

Fig. 6. Isotherm of butene at room temperature and the pressure effect on the net rate of 1-butene isomerization at 19°C.

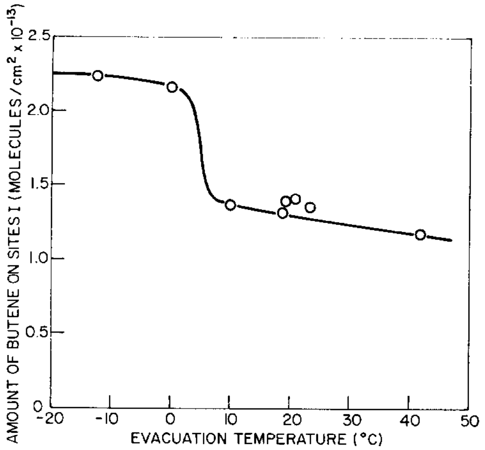

FIG. 7. Effect of evacuation temperature on the amount of butene retained on sites I. Time for evacuation was 30 min at −13 and 10°C, and 15 min for other points.

Comparing Figs. 4 and 5, one easily notices that, when the activity of alumina becomes lower with increasing amount of ammonia adsorbed at 250°C, the size of peak I of butene also becomes smaller. An interesting fact is that the activity is less affected by ammonia adsorbed at room temperature (Fig. 4), and that peak I is also less affected (curve e in Fig. 5). The amount of ammonia for curve e is comparable to that for curve d. In another experiment in which a smaller amount of ammonia (2.2×10^{13}) was adsorbed at room temperature, the ammonia peak in TPD started at about 350°C so that the peak II, if any, could be clearly seen. Nevertheless, peak II was completely eliminated, while the catalyst still kept 75% of the original activity. The results indicate that sites I on alumina are responsible for isomerization, but not sites II. The isomerization sites are discussed below in more detail.

3. Pressure Effect

Figure 6 shows an adsorption isotherm of butene at 23°C and the effect of pressure on the rate of 1-butene isomerization. 1-Butene was used as the adsorbate for the isotherm, but it became, of course, a mixture of *n*-butenes during the measurements. After the isotherm was measured, the catalyst was evacuated for 1 hr at −13°C and TPD was carried out. The TPD gave peaks I and II, the sum of which was 2.5×10^{13} molecules/cm², as indicated in Fig. 6. The amount of butene desorbed in the peak II was estimated as 3×10^{12} molecules/cm² from the area distribution of the peaks in TPD. The size of the peak II was also the same as that of curve a in Fig. 5 which was obtained by evacuating at 19°C before TPD, so that the amount of butene on sites II did not vary between −13 and 19°C. When butene was adsorbed at higher temperature, however, peak II became larger and finally saturated at 200°C. The saturated amount of butene on sites II was found to be 1.3×10^{13} molecules/cm².

The increase in adsorption temperature did not change the size of peak I. When the catalyst was evacuated at various temperatures after adsorption, however, subsequent TPD showed interesting results, as shown in Fig. 7. The figure indicates that the amount retained on sites I becomes almost constant when the temperature of evacuation is 0°C or lower, but it decreases abruptly in a narrow range between 0 and 10°C. Apparently the activation energy of desorption changes sharply at about 60% of the saturated amount on sites I which was determined as 2.2×10^{13} molecules/cm² from Fig. 7. What is clear from the above discussion is that the adsorbed amount on sites I and II is constant (2.5×10^{13}) at room temperature independent of pressure, and the adsorption above this amount in the isotherm in Fig. 6 is much weaker, most likely physical adsorption.

The net rate of 1-butene isomerization, *r*, which was plotted in Fig. 6 was calcu-

TABLE 1

Results of Reaction with 2-C_4D_7

Expt		Total amount (molecules)	Distribution (%)						
			d_8	d_7	d_6	d_5–d_2	d_1	d_0	$+\Delta d_7$
1 = Reactant	2-Butene	2.69×10^{19}	92.8	7.2	—	—	—	—	
Product (23°C, 30 min)	1- and 2-Butene	2.69×10^{19}	91.0	9.0	—	—	—	—	4.9×10^{17}
									Total d_1
2 = Preadsorption	2-Butene	4.1×10^{18a}	92.8	7.2	—	—	—	—	
Reactant	1-Butene	1.89×10^{20}	—	—	—	—	—	100.0	
Product (19°C, 6 min)[b]	1-Butene	1.43×10^{20}	—	—	—	—	1.0	99.0	1.4×10^{18}
	2-Butene	4.60×10^{19}	7.9	2.3	—	—	2.3	87.5	1.1×10^{18}
				1-Butene-d_1/2-butene-d_1					1.3
									Total d_1
3 = Reactant	1-Butene	9.48×10^{19}	—	—	—	—	—	100.0	
	2-Butene	9.04×10^{19}	92.8	7.2	—	—	—	—	
Product (19°C, 8 min)[b]	1-Butene	5.80×10^{19}	—	—	—	—	15.6	84.4	9.0×10^{18}
	2-Butene	1.27×10^{20}	54.0	14.4	1.8	—	5.6	24.2	7.1×10^{18}
				1-Butene-d_1/2-butene-d_1					1.3

[a] On sites I. Total preadsorption was 5.7×10^{18} molecules.

[b] Conversion of 1-butene was 22.4% in Expt 2 and 39.8% in Expt 3.

lated from the equation,

$$r = kN(1 - x_e), \qquad (2)$$

where k is the first order rate constant defined by Eq. (1), N the total number of butene molecules in the system, and x_e is the fraction of 1-butene at equilibrium. The results in Fig. 6 shows that the net rate is independent of the reactant pressure, and consequently independent of physical adsorption. Therefore, the surface concentration of intermediate should be constant over a wide range of pressure supporting the view that sites I are responsible for the isomerization.

4. *Reaction with 2-Butene-d_8*

Some experiments were carried out with 2-butene-d_8, the results of which were listed in Table 1. Experiment 1 was made in the static adsorption system with smaller volume, while the rest of experiments were carried out in the recirculation reaction system. In the latter case, the reaction was stopped by isolating the reactor and the gas phase material was separated into 1- and 2-butenes by a larger capacity gas chromatograph. Each separated butene was analyzed by a mass spectrometer at a low ionizing voltage to give only parent peaks. A test experiment confirmed that no exchange occurred between butene and the column packing and butene molecules themselves. The results are discussed in the following section.

III. ACTIVE SITES FOR ISOMERIZATION

No definite mechanism can be concluded from the present results alone. Nevertheless, some mechanistic consideration is given in connection with the active sites. A total of 4.9×10^{17} hydrogen atoms was exchanged with butene in Expt. 1 in Table 1. This corresponds to 1.0×10^{12} atoms/cm^2 and it is much smaller than sites I (2.2×10^{13}/cm^2). These exchanged protons would not be directly related with isomerization, while they could be a part of sites II. When a small amount of 2-butene-d_8 was adsorbed on deuterated alumina, a deuteroxyl band at 2788 cm^{-1} was considerably reduced while other OD bands remained unchanged. No absorption ascribable to butene or butyl radical was detected probably because the surface concentration was too small. On a spectrum of alumina (broken line in Fig. 2) the deuteroxyl groups at 2788 cm^{-1} were estimated as about 15% of the total deuteroxyl groups from areas under the bands and by assuming the same extinction coefficient for all deuteroxyl groups. The total number of hydroxyl groups was found to be 8×10^{13}/cm^2 from the exchange with deuterium gas at 600°C so that the population of the deuteroxyl groups giving 2788 cm^{-1} band was estimated as about 1.2×10^{13}/cm^2. This is close to the density of sites II (1.3×10^{13}/cm^2), and the adsorption of ammonia not only eliminates this highest frequency hydroxyl band (Fig. 2) but also eliminates peak II of butene as already described. It is likely that sites II are isolated aluminum ions associated with adjacent hydroxyl groups. We also found that ethylene chemisorbed on sites II exchanged hydrogen with protons on the surface (*20*).

In Expt 2 in Table 1, the total number of d_8- and d_7-butenes found in the gas phase product was 4.7×10^{18} molecules which agreed rather well with 2-butene-d_8 preadsorbed on sites I (4.1×10^{18} in total or 8.5×10^{12}/cm^2). Also, more than 95% of the preadsorbed butene-d_8 came out in the gas phase as d_8 without exchange. Therefore, the change in the activation energy of desorption observed in Fig. 7 seems to be due to an induced heterogeneity (repulsive force between molecules) at least partly. Butene molecules adsorbed on sites I can thus communicate with the gaseous molecules perhaps to a greater extent than assessed by Rosynek and Hightower (*15*).

The results of reaction with a 1:1 mixture of 1-butene-d_0 and 2-butene-d_8 show that only single exchange of hydrogen occurred for both reactants even at 40% conversion (Expt 3 in Table 1). A small amount of d_6 is believed to have come from d_7 in the reactant. Different mechanisms or reaction paths for the isomerization and the intermolecular exchange of hydrogen between olefin molecules have been postulated mainly because of similar or greater degree of exchange found in the unisomerized molecules to that in the isomerized molecules (*5*, *7*). In the present results too, the total amount of 1-butene-d_1 found in the product was slightly larger than that of 2-butene-d_1, as shown in Table 1. However, this does not necessarily prove two independent mechanisms for the reactions. Ozaki and Kimura (*3*) postulated a proton donor–acceptor mechanism that a protonic carbonium ion is formed by acquiring a proton either from Bronsted acid centers or from a carbonium ion ($C_4H_8^+$) formed by the chemisorption of olefin on Lewis acid centers. It seems then possible that the protonic carbonium ion releases a proton resulting in the exchange of hydrogen without isomerization, or, alternatively, resulting in the isomerization with exchange depending on the proton to be released. In other words, both reactions have the same intermediate, and the intermolecular exchange reaction without isomerization takes place when the backward reaction from the intermediate to the reactant occurs. The ratio of 1-butene-d_1: 2-butene-d_1 was constant (1.3) for Expts 2 and 3 in Table 1 in spite of a large difference in conversion (22:40%). This fact supports the above view that the isomerization and exchange take place through the same path. If this is true, the experimental method could become critical. When the diffusion control becomes serious, the isomerization may approach equilibrium in the vicinity of the surface while the exchange still keeps going, thus misleading the interpretation of results. In the case of exchange between D_2 and olefin, however, it would proceed on different sites from those responsible for isomerization as evidenced by the selective poisoning by CO_2 (*14, 15*).

The deuterium distribution of Expt 3 in Table 1 shows that the 2-butene-d_0 formed was about four times larger than 2-butene-d_1, while a simple statistics with the 1:1 mixture of d_0 and d_8 reactants gave equal amounts of both products, if the isomerization proceeds by the above mechanism. Although a definite explanation is impossible at this stage, the difference in the reactivity of 1-butene and 2-butene chemisorbed on Lewis centers might be partly responsible. Indeed, the first order rate constant for the isomerization of 1-butene and *cis*-2-butene was different by a factor of 2, as seen in Fig. 4, and the net rate of *cis*-butene isomerization calculated from Eq. (2) was about one third of that of 1-butene. Moreover, an isotope effect has been observed in butene isomerization (*5, 8, 9*).

The present results about the active sites for isomerization can be explained also by the mechanism of Ozaki and Kimura (*3*) with chemisorbed olefin on Lewis acid centers as proton donor. Lewis acid centers would be exposed aluminum ions on the alumina surface, as most investigators agree, and at the same time those sites are the sites I previously found on alumina by the temperature-programmed desorption of olefins (*19, 24*). Butene chemisorbed on these Al ions acts as a proton donor and serves as an active site for isomerization. Since butene strongly chemisorbs on these sites (but not as strongly as it does on sites II), the rate of isomerization is pressure independent as observed in Fig. 6. Ammonia also chemisorbs on these Al ions at 250°C or higher forming NH_2 species as already discussed, and blocks the isomerization. The amount of butene remaining on sites I after evacuation at 19°C was calculated roughly by measuring with a planimeter the area of peak I on the curves in Fig. 5 and others, and plotted with the activity of the catalyst in Fig. 8. The figure shows that the activity is roughly proportional to the amount of butene on sites I supporting the above mechanism.

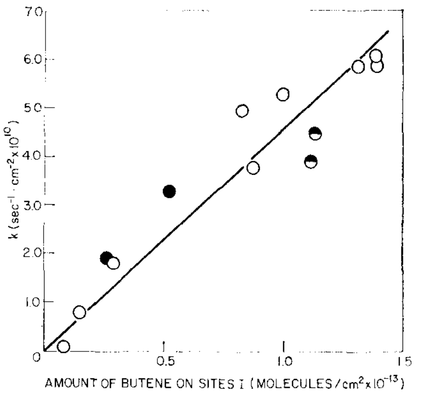

FIG. 8. Activity for isomerization versus the amount of butene on sites I. Symbols are the same as in Fig. 4.

Also, these Lewis acid centers would probably be a pair or triplet of exposed aluminum ions. Strong acidity had been predicted on those sites by Peri (*27*). When two olefin molecules chemisorb on the sites to transfer a proton, the binding force to the sites would become weaker, thus on pumping at relatively low temperatures, about half of the sites could be evacuated as shown in Fig. 7. Also, if one ion of the pair is covered by ammonia, both will lose the activity for isomerization. This may explain a part of the difference between the amount of ammonia required to block isomerization (3.3×10^{13} molecules/cm^2) and the saturated amount of stronger chemisorption of ammonia (1.1×10^{14}), although a greater part of the difference would be due to isolated Al ions which chemisorb ammonia strongly but are not active for isomerization.

Thus the minimum amount of ammonia required to kill the isomerization activity of sites I is estimated as about 1.4×10^{13} molecules/cm^2 from Fig. 7 as the amount of butene strongly retained on sites I. Ammonia chemisorbed at 250°C also covers sites II (Fig. 5) whose population is 1.3×10^{13}/cm^2. Therefore, at least a total of 2.7×10^{13} molecules/cm^2 of ammonia will be required to eliminate the activity of the catalyst, and this value is reasonably close to 3.3×10^{13} molecules/cm^2 found in Fig. 4 as the upper limit of active sites. Moreover, since the isomerization activity of alumina is proportional to butene on sites I (Fig. 8), it is unlikely that other sites than sites I are involved directly in the isomerization of olefin.

Ammonia weakly chemisorbed did not block the isomerization effectively (Fig. 4). It did, however, reduce the rate constant, k, faster than it covered the sites of weaker chemisorption. For example, the rate of isomerization became about 60% when ammonia covered 20% of the sites. The fact rather supports the view that the sites for the weaker chemisorption of ammonia (oxide ions) are not directly responsible for the isomerization. The slight effect of poisoning by weakly chemisorbed ammonia might have resulted from a small amount of stronger chemisorption formed even at room temperature. Alternatively, the chemisorption of butene on sites I may also require an oxide ion adjacent to Al ion as suggested by Rosynek and Strey (*17*). An extrapolation of the poisoning effect of ammonia adsorbed at room temperature gave about 50% of the surface coverage required to kill the total activity, and the site density of stronger chemisorption of ammonia was also about 50% of that of the weaker chemisorption, as described earlier.

It is not clear yet why the chemisorption of butene on sites II on the present alumina has a greater activation energy requiring higher temperature to saturate the sites in a reasonable time, while sites II on γ-alumina were readily saturated by olefins even at room temperature (*19*, *24*). Lucchesi *et al.* (*28*) found by infrared spectroscopy, however, a great difference in the rate of ethylene chemisorption between two alumina samples, crystallographically similar but prepared by different processes.

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