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Enhancement of Catalytic Activity of Calcium X-Type Zeolite by Preadsorption of Nitrogen Dioxide

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The ability of preadsorbed nitrogen dioxide to induce the isomerization of butenes on calcium-ion-exchanged X-type zeolite catalyst has been studied by kinetics and ir absorption spectroscopy. The induced catalytic activity for the reaction increases linearly with increasing amounts of adsorbed nitrogen dioxide. The formation of zeolitic, acidic hydroxyl groups on the adsorption of nitrogen dioxide is proportional to the amount of adsorbed nitrogen dioxide as has been demonstrated with ir absorption spectra of the catalyst. The induced catalytic activity is ascribed to catalysis by this newly formed, acidic hydroxyl group.

INTRODUCTION

It has been reported that inorganic gases, such as CO_2, HCl, HBr, HCN, SO_2, NO_2, etc. (*1–22*), show an enhancement of catalytic activity and selectivity. Recently, Mirodatos *et al.* (*4, 5*) postulated a mechanism for the carbon dioxide enhancement of the zeolite catalysts used in the isomerization or cracking of hydrocarbons. Their mechanism describes the carbon dioxide as reacting with basic OH groups on zeolites to form new acidic OH groups (*4, 5*).

Otsuka *et al.* (*20*) have found that sulfur dioxide preadsorbed on metal oxides, zeolites, or silica is highly selective for inducing the *cis–trans* isomerization of 2-butenes around their double bond, accompanying it with rather small enhancement of double bond migration. They propose a mechanism calling for a reaction of the olefins with sulfur dioxide to form a polysulfone radical intermediate. The 2-butyl radical moiety of the intermediate can now rotate about its central carbon–carbon bond followed by olefins' detachment to produce the geometrical isomers of 2-butene. On the other hand, the enhanced migration of 2-butene double bonds by sulfur dioxide preadsorbed on cation-exchanged zeolites has been explained by a similar mechansim as postulated in the case of carbon dioxide (*20*).

Ishinaga *et al.* have briefly reported that preadsorption of SO_2, NO_2, or Cl_2 on cation-exchanged zeolites leads to a considerable enhancement of their catalytic activities in the dehydration of 2-propanol compared with the enhancement caused by the adsorbates containing hydrogen in their structures, such as HCl, H_2S, and H_2O, and that the adsorption of the non-hydrogen-containing inorganic gases increases the number of the acidic OH groups in the zeolites, as was confirmed by ir spectroscopy (*23*).

For butene isomerization the enhancement of catalytic activity by nitrogen dioxide has been investigated for various catalysts (*21, 22*). Nitrogen dioxide preadsorbed on porous Vycor glass induces only *cis–trans* isomerization of 2-butenes, which has been attributed to the formation of a nitrobutyl radical intermediate (*21*). On the other hand, when nitrogen dioxide is preadsorbed onto a cation-exchanged zeolite, marked increases in the catalytic activities for both types of isomerization, double-bond migration and *cis–trans* isomerization, are observed.

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We here report the results of both kinetic studies on the isomerization of 2-butene catalyzed by a calcium-ion-exchanged X-type zeolite on which nitrogen dioxide is adsorbed, and ir spectroscopic investigations of the zeolite to elucidate the mechanism for the enhancement of the catalytic activity resulting from the preadsorption of nitrogen dioxide onto the zeolite.

EXPERIMENTAL

Materials. The calcium-exchanged X-type zeolite used was prepared from Linde molecular sieve 13X by the usual ion-exchange method with a 1 *N* aqueous solution of calcium dichloride at room temperature. The zeolite was stored over a saturated ammonium chloride aqueous solution. The catalyst thus prepared lost 27% in weight by degassing at 500°C *in vacuo*. The weight of the catalyst in this text is referred to in its dried form. The BET surface area of the dried zeolite as determined by nitrogen gas adsorption was 750 $m^2 g^{-1}$. The degree of exchange was 78% calculated on the basis of the material balance of aluminum and residual sodium atoms which were determined by atomic absorption spectrometry.

Nitrogen dioxide was prepared by the same method as described previously (*21*). *cis*-2-Butene purchased from Phillips Petroleum Company was purified by repeated bulb to bulb distillation *in vacuo*.

Apparatus. A conventional, closed, gas-circulating apparatus with a volume of 329 ml was used for the reaction.

A drum-shaped, quartz-walled cell provided with NaCl or CaF_2 windows was used for measuring the ir absorption spectra of a wafer of the catalyst which was supported by a holder at the center of the cell. A heating wire was wound around the outside of the cylinder and a thermocouple probe was through a thin tube attached to the cylinder inwards as close as possible to the holder. Both ends of the cylinder were water-cooled to prevent heating the grease used to solder the windows in place.

The ir absorption spectra were measured with a Shimadzu IR-430 infrared spectrometer.

Procedures. After calcining at 500°C in dry oxygen for 1 hr, the catalyst was degassed for 2 hr at the same temperature and then cooled to the reaction temperature in a stream of helium gas. Nitrogen dioxide with an appropriate pressure was kept in contact with the catalyst for 5 min and evacuated for 10 min. The amount of adsorbed nitrogen dioxide was determined by subtracting the amount evacuated from that introduced. Since nitrogen dioxide in the gas phase is in equilibrium with its dimer, N_2O_4, the amount of nitrogen dioxide in this text is expressed as moles of monomer NO_2 adsorbed on a gram of catalyst. The reaction was started by introducing and circulating a reactant gas, *cis*-2-butene or 1-butene. A small amount of the gas in the reaction system was periodically sampled and analyzed by gas chromatography. All kinetic data were obtained when the conversion of a reactant gas was less than 3%.

A wafer of the catalyst 20 mm in diameter and weighing about 10 mg was pressed at 3.8 tons cm^{-2}, placed in the ir cell holder, heated up to 200°C in a dry oxygen gas within 20 min, kept for an additional 10 min, and degassed at the same temperature for 1 hr. Subsequently, the temperature of the sample was raised to 400°C, degassed for 1 hr, and cooled to 100°C. The deuterated sample of the catalyst was obtained by an additional heating in D_2O vapor (15 Torr) at 200°C for 1 hr, prior to the degassing at 400°C. All ir absorption spectra were recorded at 100°C.

RESULTS

Kinetics of butene isomerization. Figure 1 shows the time course for the production of 1-butene and *trans*-2-butene from *cis*-2-butene with a catalyst of calcium-exchanged X-type zeolite, CaX. The catalyst without adsorbed nitrogen dioxide had little isomerization activity at 100°C as is shown by curve (a). When nitrogen dioxide was adsorbed on the catalyst, a considerable

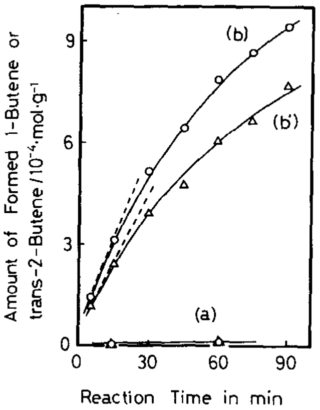

FIG. 1. The yields of 1-butene and *trans*-2-butene from the isomerization of *cis*-2-butene. The reaction was carried out at 100°C with a *cis*-2-butene pressure of 83 Torr. (a) In the absence of NO$_2$; (b) and (b′) in the presence of adsorbed NO$_2$, 2.7×10^{-4} mol g^{-1}. (○) 1-Butene, (△) *trans*-2-butene.

increase in the isomerization activity was observed as is shown by curves (b) and (b′). The rates of product formation were calculated from the slopes of the curves at a reaction time of 5 min. See the dashed lines in Fig. 1.

The formation rates of both 1-butene and *trans*-2-butene depend upon the amount of adsorbed NO$_2$ as depicted in Fig. 2. Although the rate of 1-butene formation is proportional to the amount of adsorbed NO$_2$, the rate of *trans*-2-butene formation seems not to be exactly proportional to the amount of adsorbed NO$_2$ at low levels of NO$_2$. However, over most of the range of adsorbed NO$_2$ tested in these experiments, the rate of *trans*-2-butene formation is linearly dependent on the amount of adsorbed NO$_2$. It was found that when 1-butene was used as a reactant, the rates of *cis*- and *trans*-2-butene formation were proportional to the amount of adsorbed NO$_2$ and the ratio of the formation rate for the *cis* and *trans* isomers of 2-butene was constant, 1.2, and independent of the amount of adsorbed NO$_2$, as depicted in Fig. 3.

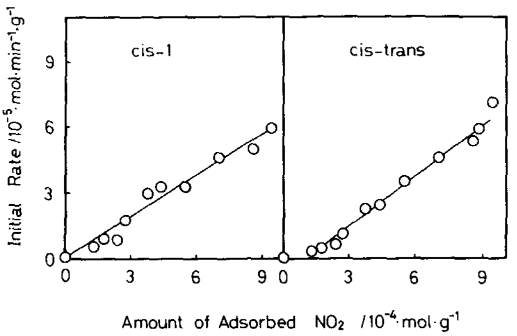

FIG. 2. The dependence of the initial rates of 1-butene and *trans*-2-butene formation on the amount of adsorbed NO$_2$. The reaction was carried out at 100°C with a *cis*-2-butene pressure of 83 Torr.

Figure 4 shows a plot of the rates at 100°C for 1-butene and *trans*-2-butene formation as a function of the initial pressure of *cis*-2-butene. The values P/R, i.e., the pressure of the reactant, P, divided by the rate of formation, R, were linearly related to P. Therefore, the following relationship holds for both isomerization reactions:

$$R = \frac{kKP}{1 + KP} \qquad (1)$$

where k and K are constants. A similar rate equation has been obtained for the conver-

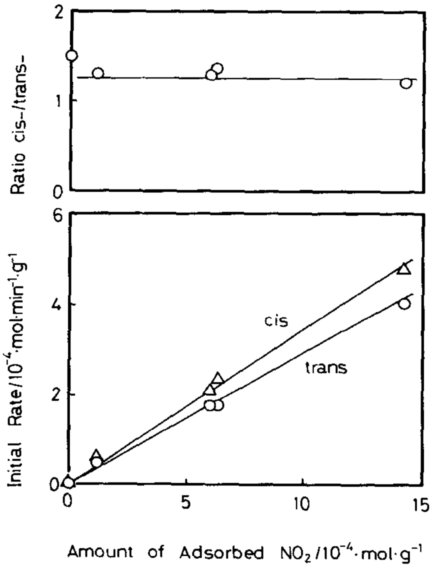

FIG. 3. The dependence of the initial rates of *cis*- and *trans*-2-butene formation and the ratio of these rates on the amount of adsorbed NO$_2$. The reaction was carried out at 100°C with a 1-butene pressure of 115 Torr.

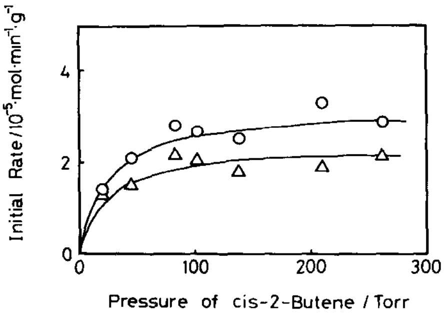

FIG. 4. The dependence of the initial rates of 1-butene and *trans*-2-butene formation on the pressure of *cis*-2-butene. The reaction was carried out at 100°C with a constant amount of adsorbed NO_2, 5.5×10^{-4} mol g^{-1}. (○) 1-Butene, (△) *trans*-2-butene.

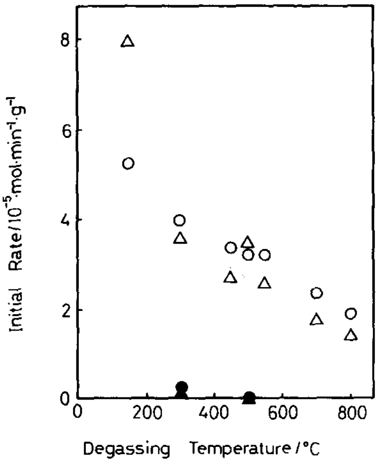

FIG. 5. Influence of the catalyst degassing temperature on the initial rates of 1-butene and *trans*-2-butene formation. The reaction was carried out at 100°C with 5.5×10^{-4} mol g^{-1} adsorbed NO_2 and a *cis*-2-butene pressure of 83 Torr. (●) 1-Butene, (▲) *trans*-2-butene in the absence of adsorbed NO_2; (○) 1-butene, (△) *trans*-2-butene in the presence of the adsorbed NO_2.

sion of *cis*-2-butene on NaY zeolites slightly exchanged by calcium (*24*). The values of k and K for the best fit to the observed rate data are listed in Table 1 together with those obtained for other reaction temperatures, 80 and 120°C. The values were determined for the two types of isomerization, from *cis*-2-butene to both 1-butene and *trans*-2-butene, and are denoted by *c*-1 and *c–t*, respectively. The two solid curves in Fig. 4 are calculated using Eq. (1) and the constants shown in Table 1. The Arrhenius plots of k values in Table 1 give the same activation energy of 15.5 kcal mol^{-1} for both 1-butene and *trans*-2-butene formation.

For a constant amount of adsorbed NO_2, 5×10^{-4} mol g^{-1}, a lower catalytic activity is observed the higher the degassing temperature of the catalyst. (See Fig. 5.)

The activity induced by the adsorbed NO_2 is poisoned when ammonia is adsorbed on the catalyst after the adsorption of NO_2. This decrease of activity with increasing ammonia is shown in Fig. 6. All activity disappeared when the amount of adsorbed ammonia became more than 70% of the amount of adsorbed NO_2.

Infrared spectra of the catalyst. The ir absorption spectra observed for catalysts treated under various conditions are shown in Fig. 7. After the catalyst was degassed at 400°C, spectrum (a) was observed in the region corresponding to the stretching vi-

TABLE 1

Kinetic Parameters for *cis*-2-Butene Isomerization

	k_{c-1}	k_{c-t}	K_{c-1}	K_{c-t}
80°C	0.90	0.71	2.8	1.7
100°C	3.0	2.2	0.63	0.67
120°C	7.1	5.3	0.49	1.9

Note. k: 10^{-5} mol min^{-1} g^{-1}; K: 10^{-1} Torr.

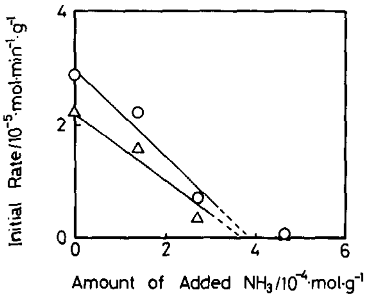

FIG. 6. Influence of added ammonia on the initial rates of 1-butene and *trans*-2-butene formation. The reaction was carried out at 100°C with 5×10^{-4} mol g^{-1} NO_2 and a *cis*-2-butene pressure of 83 Torr. (○) 1-Butene, (△) *trans*-2-butene.

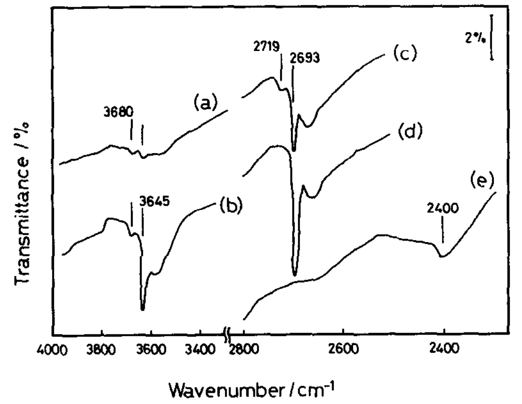

FIG. 7. Infrared, spectra of CaX zeolite after (a) the pretreatment and (b) the adsorption of NO_2, 17.7×10^{-4} mol g^{-1}, and after (c) the D_2O treatment, (d) adsorption of NO_2, 19.2×10^{-4} mol g^{-1}, and (e) the NH_3 addition.

bration of the OH group. Two absorption bands were observed at 3680 and 3645 cm^{-1}. The latter band is assigned to the stretching vibration of an acidic hydroxyl group in the zeolite. The ir absorption at 3680 cm^{-1} has been ascribed by Mirodatos *et al.* (*4*, *5*) to the stretching vibration of a basic hydroxyl group bound to metal ions like $Me^+(OH)$. After nitrogen dioxide was adsorbed onto the catalysts, a great increase in the absorption intensity of the acidic hydroxyl band was observed. The catalyst treated with D_2O gave spectrum (c). The absorption bands of 2693 and 2719 cm^{-1} correspond to the acidic and the basic deuteroxyl group, respectively. Spectra (c) and (d) clearly show that adsorption of NO_2 on the deuterated zeolite enlarges the intensity of the acidic deuteroxyl band, while the basic one decreases. On adding NH_3 to the deuterated zeolite which already had adsorbed NO_2, the deuteroxyl group newly formed by the NO_2 adsorption disappeared and a 2400-cm^{-1} band arose, assigned to N–D stretching vibration, as shown by spectrum (e) in Fig. 7.

The increment to the absorption intensity for the 3645-cm^{-1} acidic band is proportional to the amount of adsorbed NO_2 as shown in Fig. 8. The higher the temperature was for the preliminary degassing of the zeolite, the smaller the observed increment. The slopes of the straight lines for the individual pretreatment temperature in Fig. 8 (which, provided the absorbance is proportional to the number of the hydroxyl groups in the zeolite, correspond to the number of the acidic OH groups produced by the adsorption of a unit amount of NO_2) decreased with increasing degassing temperature.

DISCUSSION

All kinetic features for both the *cis–trans* isomerization and the double bond migration of butenes are identical except for the result shown in Fig. 2, i.e., the induced catalytic activity for the *cis–trans* geometrical isomerization seems not exactly proportional to the amount of adsorbed nitrogen dioxide and the increment of the activity is less sensitive to small amounts of NO_2, while at larger values of NO_2 the increment for *cis–trans* isomerization is somewhat higher than that for the case of double bond migration. This behavior may be explained in either of two ways as follows. (i) Two isomerization mechanisms are involved. The activity for one of them is proportional to the amount of adsorbed NO_2 while the other is operative only for the *cis–trans* isomerization if the adsorbed amount of NO_2 is greater than a threshold value. (ii) A

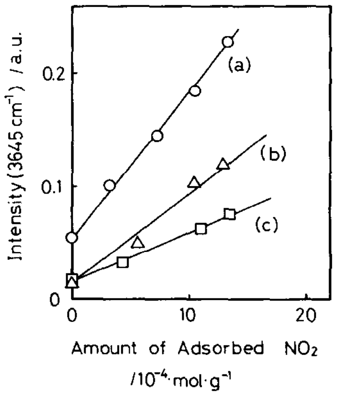

FIG. 8. The plot of the absorbance of 3645-cm^{-1} band against the amount of adsorbed NO_2. The zeolite was degassed at (a) 300°C, (b) 400°C, and (c) 500°C.

unique mechanism of isomerization is present, but the selectivities from *cis*-2-butene to 1-butene and to *trans*-2-butene are dependent on the amount of adsorbed NO_2. With the present experimental data there is not enough information available to clarify the detailed mechanism for the geometrical isomerization. Both the kinetic equation, Eq. (1), and the value of the activation energy of 15.5 kcal mol^{-1} for the geometrical isomerization are similar to those for double bond migration. Therefore, the mechanism of the geometrical isomerization is assumed to be not drastically different from that of the double bond migration. Considering, however, that NO_2 adsorbed on porous Vycor glass selectively catalyzes the *cis–trans* isomerization of butene by NO_2 radical catalysis (*21*), we cannot discard the first explanation for *cis–trans* isomerizations on zeolite. Further discussions will be concerned mainly with the results obtained for the double bond migration reactions of butenes.

It is clear from the results shown in Figs. 5, 6, and 8 that the generation of acidic hydroxyl groups on the zeolite is essential for the enhancement of the isomerization reactions and the enhanced catalytic activity probably originates in the interaction of butene molecules with the acid sites of the zeolite. Therefore, it is stressed that a secondary butyl carbenium ion intermediate is likely involved in the reactions observed in the present work. This is further supported by the fact that both the *cis–trans* geometrical isomerization and the *cis*-1 double-bond-migrating isomerization occur simultaneously, which is in contrast to the case when only *cis–trans* isomerization occurs via the radical mechanism resulting from nitrogen dioxide-adsorbed, porous Vycor glass (*21*).

It is generally pointed out that the ratio of rates for the formation of *cis*- and *trans*-2-butene from 1-butene is close to unity when the reactant is isomerized to 2-butenes on acid catalysts, e.g., zeolites (*25*), silica-alumina (*26*), or others (*27*), through a secondary carbenium ion intermediate. In the present work, a product ratio of 1.2 was observed independent of the amount of absorbed NO_2 (Fig. 3).

When the adsorption of *cis*-2-butene to the acid sites thus formed is assumed to be in equilibrium with its pressure and the rate-determining step for the reaction is present in a subsequent process, i.e., the conversion of adsorbed butene to the surface intermediate to form 1-butene, the Langmuir–Hinshelwood type of rate equation, Eq. (1), is easily deduced. One of the constants, K_{c-1} in Table 1, corresponds to the equilibrium constant for *cis*-2-butene adsorption onto the surface, and the other constant, k_{c-1}, to the rate constant for the conversion. The activation energy of 15.5 kcal mol^{-1} for the *c*-1 conversion process is reasonable in comparison to the literature values for the isomerizations of butenes on other acid catalysts (*25, 26, 28*). If the same intermediates are involved in both types of isomerizations, the K values for the double bond migration and *cis–trans* isomerization should be very similar. However, since the kinetic data obtained here have an appreciable error as can be inferred from Fig. 4, giving K values with about 100% error ranges, it seems unsuitable to discuss the similarity of K_{c-1} and K_{c-t} at present. Different values of K would be anticipated if there were two secondary carbenium ion intermediates with different stabilities corresponding to the individual isomerizations, *c*-1 and *c–t*.

Adsorbed nitrogen dioxide has two probable modes of operating to enhance catalytic activity: (i) increasing the activity of the acid sites already present on the zeolite and (ii) increasing the number of acid sites active for butene isomerization. Since there is such good correspondence between catalytic activity (Fig. 2) and the NO_2-induced increase in the 3645-cm^{-1} ir absorption band for the zeolite's acidic hydroxyl group (Fig. 8), the latter explanation clearly is adequate.

For an X-type zeolite in which the cation is exchanged by alkaline earth metal ions, the formation of acidic hydroxyl groups by calcination is expressed by the following equations (*29–32*):

$$Ca^{2+}(H_2O)_n \rightarrow (H_2O)_{n-1} + Ca^{+}(OH) + H^{+} \quad (2)$$

$$Ca^{+}(OH) + Ca^{2+} \rightarrow Ca^{+}\text{–}O\text{–}Ca^{+} + H^{+}, \quad (3)$$

where the alkaline earth metal ion is represented by calcium ion and n is the number of waters of hydration. A weak-intensity absorption band for the basic deuteroxyl group is observed in the ir spectrum (c) in Fig. 7, suggesting that the fraction of $Ca^{+}(OH)$ species is small for the zeolite after the present pretreatments. The conversion of basic hydroxyl groups to acid hydroxyl groups by nitrogen dioxide is suggested to occur as follows:

$$Ca^{+}(OH) + NO_2 \rightarrow Ca^{+}NO_3 + H^{+} + e, \quad (4)$$

where H^{+} is actually observed as $H^{+}\text{–}O^{-}Z$ in the ir spectrum. The electron on the right side of the above equation may be trapped in the zeolite lattice, probably at a Lewis acid site. This is similar to the reactions proposed by Mirodatos *et al.* (*4*) for the CO_2 enhancement of catalytic activity or by Otsuka *et al.* (*20*) for SO_2. Provided the acidic and basic hydroxyl groups have similar extinction coefficients, the uncompensated increase in the acidic hydroxyl group is not explained (see Fig. 7), unless another process for the formation of hydroxyl groups by NO_2 adsorption is considered. NO_2 may react with water bound tightly to the Ca^{2+} cations to produce the hydroxyl group in the following reactions, as proposed for the cases of CO_2 adsorption (*33, 34*) and SO_2 adsorption (*20b*):

$$Ca^{2+}(H_2O) + NO_2 \rightarrow Ca^{+}NO_3 + 2H^{+} + e. \quad (5)$$

The possible production of nitric acid by the reaction of nitrogen dioxide with free water on the catalyst can be ignored in this situation for the following reasons. First, the presence of free water is not expected for a catalyst degassed at a temperature higher than 400°C. Second, only a trace of gas uncondensable at a liquid-nitrogen temperature was observed, suggesting it is safe to neglect the reaction of NO_2 with water to form nitric acid and nitric oxide, $H_2O + 3NO_2 = 2HNO_3 + NO$. Thus, the induced activity of CaX zeolite following the adsorption of NO_2 can be attributed to the formation of a new acidic hydroxyl group by Eq. (4) and/or Eq. (5).

If all of the NO_2 molecules adsorbed on the catalyst contribute to the formation of acidic hydroxyls by the reactions of Eqs. (4) and (5), a constant enhancement of activity is expected from a constant amount of adsorbed NO_2. However, the presence of another type of adsorption is suggested by the results shown in Fig. 8, which demonstrate that a unit amount of adsorbed NO_2 produces smaller amounts of acidic hydroxyls for higher degassing temperatures. This also corresponds well with the results obtained for the catalytic effect from a constant amount of adsorbed NO_2, as shown in Fig. 5. The data are interpreted to mean that for higher degassing temperatures an increasing fraction of the adsorbed NO_2 is ineffective for the production of active acidic sites. If ammonia is selectively adsorbed to the active acidic sites, the number of the sites can be estimated from the result of Fig. 4 to be 3×10^{13} molecules cm^{-2} when the amount of adsorbed NO_2 is 4.2×10^{13} molecules cm^{-2}. Therefore, if the acidic site is formed only via Eq. (4), 70% of the adsorbed NO_2 molecules contribute to the formation of acid sites, and if only via Eq. (5), 35% contribute. The dehydrated forms of calcium cations, Ca^{2+} or $Ca^{+}\text{–}O\text{–}Ca^{+}$, formed by Eq. (3) may provide sites for the ineffective adsorption of nitrogen dioxide molecules.

If one considers the zeolites degassed at various temperatures, rather appreciable hydroxyl absorption bands are observed at

3645 cm^{-1} even in the absence of nitrogen dioxide as is represented by the intercepts in Fig. 8. However, these groups are not active for the isomerization of butene at the reaction temperatures. In contrast the hydroxyl groups newly formed by the adsorption of NO_2 are particularly active. This may be explained by the method proposed by Mirodatos *et al.* (*5*), who suggest that the catalytic ability of hydroxyl groups formed by the polarizing effect of cations, e.g., by Eq. (2), is inhibited by the basicity of the basic hydroxyl group and that the inhibited hydroxyl groups are released by removing the basic hydroxyl group, e.g., by Eq. (4), which simultaneously generates a new acidic hydroxyl group. An alternative explanation is that the different catalytic activity for the acidic hydroxyl groups may be attributed directly to their different acid strength. The acidity of the acidic hydroxyl group has been related to wavenumber shifts in the ir absorption maximum at around 3640 cm^{-1} (*35, 36*). In this work, however, no such noticeable shift has been observed for the hydroxyl band between the presence and absence of adsorbed nitrogen dioxide. As far as the acidic hydroxyl groups are concerned, the catalytic isomerization of 2-butene must be more sensitive to the difference in the acidity of these active sites than the shift of their ir spectral band is.

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