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Changes of Activity and Selectivity of MgNaX Zeolites for Butene Isomerization Enhanced by Nitrogen Dioxide Adsorption

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Enhancement of butene isomerization on Mg-exchanged X-type zeolites by the adsorption of nitrogen dioxide was investigated by means of kinetics and ir spectroscopy. The catalytic activity of the zeolites for the double-bond migration of butenes was increased when the amount of adsorbed NO_2 was enlarged. The selectivity of the *cis–trans* isomerization of 2-butenes exceeded their double-bond migration when the amount of adsorbed NO_2 was increased. These phenomena have been explained in terms of intensification of the acid strength of an acidic hydroxyl group on the zeolites by adsorbed NO_2. The formation of nitrato complexes, identified by the observation of ir spectra of the zeolites, was related to the intensification.

INTRODUCTION

It has been reported that the enhancement of the activity of acid catalysis by Ca-exchanged X-type zeolites after the adsorption of NO_2 is attributed to the formation of the acidic hydroxyl group whose catalytic activity is intensified by calcium cations in the zeolites (*1*, *2*). This intensification is explained by the polarization of the hydroxyl group in the strong electrostatic field of the calcium cations. Such an effect by the calcium cations is interpreted by a general rule that when a reaction system, here composed of a butene molecule and an acidic hydroxyl group, is exposed to a perturbation of another species, the calcium cations, then the rate of a reaction must therefore reflect the properties of the perturbing species. Thus, not only an enhancement of the zeolite catalytic activity but also a change in the selectivity of the zeolite should be observed by the promotion of the NO_2 adsorption. As reported in the previous paper (*1*), the activity enhancement on CaNaX zeolites by NO_2 adsorption was simply attributed to the formation of a new, acidic hydroxyl group, and the small change in the selectivities of butene isomers in their isomerizations was almost independent of the amount of the adsorbed NO_2.

Preliminary experiments with magnesium cation-exchanged X-type zeolites showed that the selectivities of *cis–trans* and double-bond migrating isomerizations varied with the amount of adsorbed NO_2, suggesting that the effect of the adsorbed nitrogen dioxide on acidic properties of the zeolites changes with its quantity. This paper deals with not only the formation of an acidic hydroxyl group by NO_2 adsorption but also the identification of the adsorbed species of nitrogen dioxide, which is supposed to strengthen the acid properties of the magnesium ion-exchanged X-type zeolites.

EXPERIMENTAL

Materials

Magnesium cation-exchanged X-type zeolites, MgNaX, were prepared by a conventional ion-exchange method in an aqueous solution of magnesium dichloride at room temperature or 70°C. The degree of the exchange of sodium cation by magnesium is denoted by the number in the parentheses added to MgNaX. Four kinds of the zeolite, MgNaX(39), MgNaX(50),

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MgNaX(70), and MgNaX(78), were prepared.

Nitrogen dioxide was produced by the reaction of nitric oxide (Takachiho Chemical Co. Ltd.) with oxygen gas. Moisture in the reacting gases was carefully removed.

cis-2-Butene was purchased from Phillips Petroleum Company, and 1-butene and *trans*-2-butene were from Takachiho Chemical Company Ltd. They were purified by bulb to bulb distillation *in vacuo*.

Apparatus

A closed-gas-circulating system with a volume of 329 ml was used for the experiments of butene isomerization. A drum-shaped cell made of quartz was used for measurements of infrared spectra of the zeolites. A Shimazu IR-430 infrared spectrometer was used. The details of the instruments have been described elsewhere (*1*).

Procedures

The zeolite was degassed for 2 hr at a controlled temperature before use in experiments. The zeolite was brought into contact with NO_2 at 100°C for 5 min and was degassed for 10 min at the same temperature. The amount of adsorbed NO_2 was calculated by subtracting the amount of NO_2 collected during the degassing from that introduced. The isomerization reaction were carried out at 100°C. The composition of the reacting gas was determined by gas chromatography.

Thin, self-supporting wafers of the zeolites to be tested, which were prepared by a press, were used as specimens in the infrared measurements. The wafer settled in the ir cell was degassed at 200°C for 1 hr and successively degassed at 400°C for 1 hr. The method of the adsorption of NO_2 was the same as used in the reaction experiment. All the spectra were measured at 100°C.

RESULTS

All of MgNaX zeolites prepared in this work were inactive for butene isomerization at 100°C. When a certain amount of NO_2 was preadsorbed on them, appreciable catalytic activities for the reaction were observed. The catalytic activity is defined by the rate of the reaction, which is determined from the slope of the kinetic curve of change in a butene isomer concentration at the reaction time of 5 min. Figure 1 shows the relation between the catalytic activity of MgNaX(70) for the isomerization of 1-butene and the amount of preadsorbed NO_2. When a calcium cation-exchanged zeolite was used for the reaction, the activity increased in proportion to the amount of NO_2 (*1*). In the present case, however, the differential of the activity (with respect to the amount of adsorbed NO_2) became correspondingly greater with increase in the amount of adsorbed NO_2 as shown in Fig. 1. The ratio of the activity for *cis*-2-butene formation to that for *trans*-2-butene changes when the amount of adsorbed NO_2 is increased, but is not far from unity, sug-

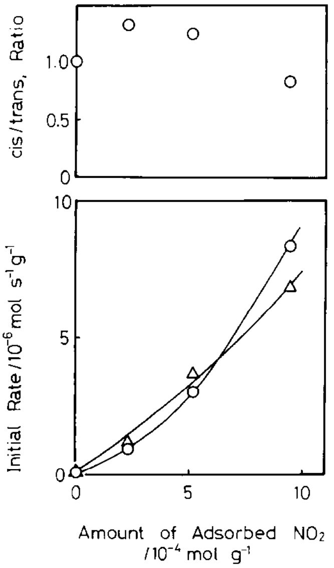

FIG. 1. Dependence of the initial rates of *cis*- and *trans*-2-butene formation and of the ratio of these rates on the amount of adsorbed NO_2 for MgNaX(70) degassed at 500°C. The reaction was carried out at 100°C with the initial 1-butene pressure of 115 Torr. (△) *cis*-2-butene, (○) *trans*-2-butene.

gesting that the isomerization proceeds through a secondary butyl carbenium ion. Figure 2 shows the enhancement of the catalytic activity of the isomerization of *cis*-2-butene by the adsorption of NO_2. A large acceleration for the increase of the activity for *cis* to *trans* isomerization is displayed in Fig. 2. On the other hand, no remarkable acceleration is observed for the double-bond migration, i.e., *cis*-1 isomerization. The ratio of the activity for the *cis–trans* isomerization to that for the double-bond migration increases from 0.5 to 4 with an increase in the amount of adsorbed NO_2.

The enhancement by the adsorption of NO_2 was varied by changing the temperature of the preliminary degassing of the zeolites. The activity for the isomerization of *cis*-2-butene was plotted against the amount of adsorbed NO_2 for two different temperatures of the degassing as shown in Fig. 3. The large enhancement was obtained for the low temperature of the degassing. Particularly, an extraordinary rise in the selectivity of *cis–trans* isomerization was observed for the lower temperature of the degassing.

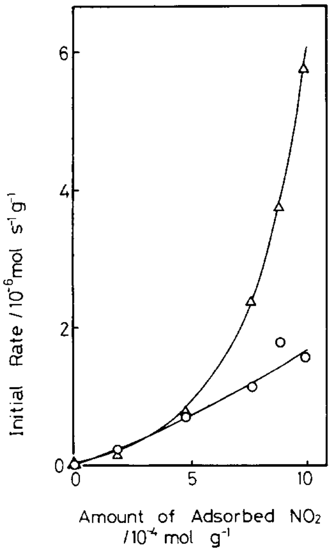

FIG. 2. Dependence of the initial rates of 1-butene and *trans*-2-butene formation from *cis*-2-butene on the amount of adsorbed NO_2 for MgNaX(70) degassed at 500°C. The reaction was carried out at 100°C with the initial *cis*-2-butene pressure of 83 Torr. (○) 1-butene, (△) *trans*-2-butene.

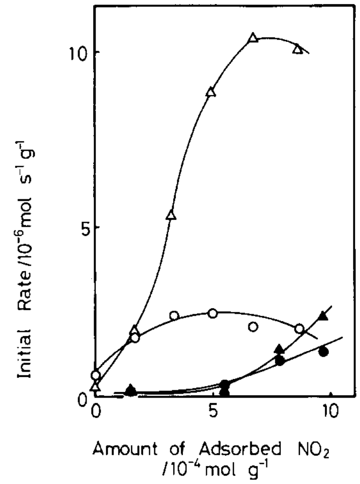

FIG. 3. Influence of the catalyst degassing temperature on the enhanced isomerization of *cis*-2-butene for MgNaX(70). The reaction was carried out at 100°C with the initial *cis*-2-butene pressure of 115 Torr. (●) 1-butene, (▲) *trans*-2-butene for degassing temperature of 750°C, (○) 1-butene, (△) *trans*-2-butene for 260°C.

The selectivity of the isomerization, when enhanced by the adsorption of NO_2, depended strongly on the degree of ion exchange. Figure 4 shows the change in the ratio of the activity of *cis–trans* isomerization to that of double-bond migration with

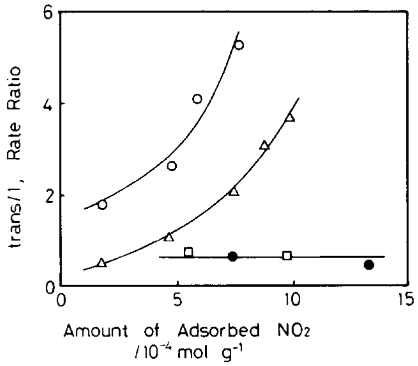

FIG. 4. Change in the *trans*/1-butene ratio in the *cis*-2-butene isomerization on various MgNaX with increase in the amount of adsorbed NO_2. (□) MgNaX(39), (●) MgNaX(50), (△) MgNaX(70), (○) MgNaX(78).

increasing the amount of adsorbed NO_2 for the zeolites of the various ion-exchange degrees. The selectivity was increased for MgNaX(70) and MgNaX(78) while unchanged for MgNaX(39) and MgNaX(50).

MgNaX zeolite degassed at 400°C gave an ir absorption band around 3650 cm^{-1}, attributed to the acidic hydroxyl group (*3, 4*). The absorption intensities of MgNaX(70) and MgNaX(78) grew by the adsorption of NO_2 as shown in Fig. 5. A similar tendency was observed for MgNaX(39) and MgNaX(50). As discussed in the previous paper (*2*), the intensity can be regarded as a measure of the number of the acidic hydroxyl group on the surface of the zeolites. Therefore, the results shown in Fig. 5 indicate that the number of the acidic hydroxyl group on the zeolites increases with increase of the amount of adsorbed NO_2. However, the efficiency of NO_2 to increase the intensity of the band declined at its larger amount on the surface. No more increase in the intensity was observed over the amount of NO_2 at 5×10^{-4} mole g^{-1}.

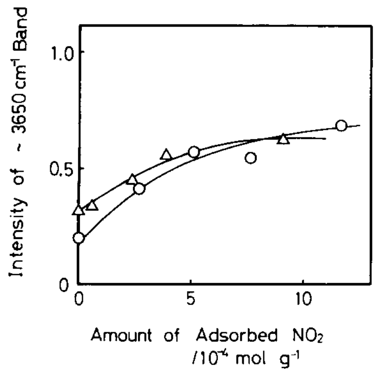

FIG. 5. Increase in the acidic hydroxyl group by the adsorption of NO_2 for MgNaX(70), (○), and for MgNaX(78), (△).

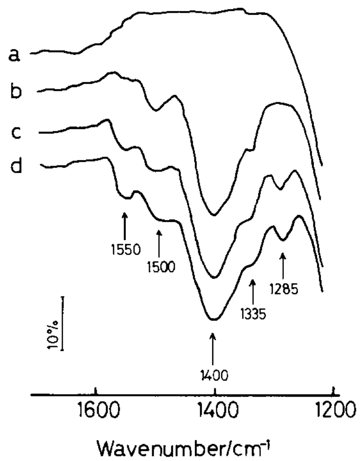

FIG. 6-1. The ir spectra of MgNaX(70) in the absence and the presence of adsorbed NO_2. a: After pretreatment; b: after the adsorption of NO_2. 6.02×10^{-4} mole g^{-1}, c: 8.78×10^{-4} mole g^{-1}, d: 10.6×10^{-4} mole g^{-1}.

Figures 6-1 and 6-2 represent the ir spectra observed in the wavenumber region corresponding to the vibrations of adsorbed NO_2 species on the zeolites of MgNaX(70) and MgNaX(78). Five absorption bands, ~1550, ~1500, ~1400, ~1335, and ~1285 cm^{-1}, were observed. The sample of MgNaX(70) shows the ~1400 cm^{-1} band stronger than MgNaX(78). For the latter sample, the bands of ~1500 and ~1335 cm^{-1} were especially strong and appeared clearly even at the low level of NO_2 adsorption. The bands of ~1285 and ~1550 cm^{-1} increased acceleratively with increasing amount of adsorbed NO_2 for both zeolites. On the other hand, the increments of the bands of ~1400, ~1500, and ~1335 cm^{-1}

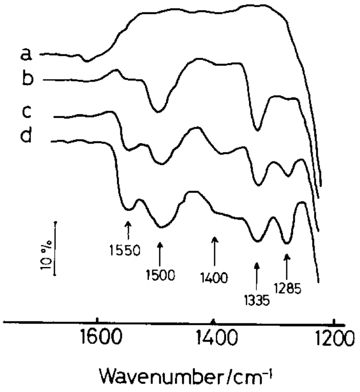

FIG. 6-2. The ir spectra of MgNaX(78) in the absence and the presence of adsorbed NO_2. a: After pretreatment; b: after the adsorption of NO_2, 2.97×10^{-4} mole g^{-1}, c: 4.24×10^{-4} mole g^{-1}, d: 5.17×10^{-4} mole g^{-1}.

were observable only at the rather small amount of adsorbed NO_2.

DISCUSSION

The ir absorption bands of the adsorbed NO_2 species, shown in Figs. 6-1 and 6-2, are assigned as follows (*2*). The band of ~1400 cm^{-1} is assigned to nitrate ion. The bands of ~1500 and ~1335 cm^{-1} can be identified with one type of nitrato complex, and those of ~1550 and ~1285 cm^{-1} with another type, which are, hereafter, denoted by nitrato(I) and nitrato(II), respectively. The rise in intensity of these bands was compared with the increase (stepwise) of adsorbed NO_2. From the comparison it is suggested that the nitrato(II) complex is formed mainly when there is a large amount of adsorbed NO_2, whereas nitrato(I) requires less adsorbed NO_2 (to be formed) and its band grows parallel to the acidic hydroxyl group band. Therefore, reactions for the formation of the hydroxyl group identical to those proposed for CaNaX in the previous papers (*1, 2*) can be assumed for MgNaX:

$$Mg^+(OH) + NO_2 \rightarrow Mg^+NO_3 + H^+ + e \quad (1)$$

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

$$Na^+(H_2O) + NO_2 \rightarrow NaNO_3 + 2H^+ + e \quad (3)$$

NO_3 indicates nitrate ion or nitrato(I). Since the band intensities for nitrato(II) rose after the formation of the hydroxyl group was almost leveled off (see Fig. 5), the complex(II) must have no direct relation to the reactions described above. It is evident that the enhancement of the catalytic activity results from the acid catalysis by the acidic hydroxyl group formed through the above reactions.

Although the number of the acidic hydroxyl group formed on MgNaX(70) seems to have leveled off at large amounts of adsorbed NO_2, as shown in Fig. 5, the catalytic activities displayed in Figs. 1 and 2 are acceleratively increased. Similar behavior was observed for MgNaX(78). The increases of the activities—what cause can be attributed to them? Neither apparent broadening of the band of the acidic hydroxyl group nor formation of additional new bands of hydroxyl groups were found on the ir spectrum of the zeolites. Therefore, it is concluded that no additional, acidic hydroxyl group is formed at large amounts of adsorbed NO_2. However, it can be plausibly supposed that the adsorbed nitric oxide species act to enlarge the acid strength of the acidic hydroxyl group which has been formed at small amounts of adsorbed NO_2. Misono *et al.* have suggested that the selectivities of butene isomers in butene isomerization depend upon the acid strength of acid sites on metal sulfate catalysts (*5, 6*), and the *cis–trans* isomerization predominates over double-bond migration on stronger acid sites. If their hypothesis is applied to the present catalyst system, the selective enhancement in the activities of *cis–trans* isomerization at large amounts of adsorbed NO_2 (Figs. 1, 2, and 4), which occurs despite the constancy in the number of the acidic hydroxyl group (Fig. 5), may be attributed to the intensification of their acid strength. Lombardo *et al.* have reported that, as the acidity of NaY zeolite is increased by substituting a small amount of Ca^{2+} for $2Na^+$, *cis–trans* isomerization of the 2-butenes is enhanced, relative to double-bond migration (*7*). Goldwasser *et al.* discuss the relation between the *cis/trans* ratio of the products in 1-butene isomerization and the interaction of intermediate, 2-butyl carbenium ion, with the catalyst surface as follows (*8*). When the carbenium ion is free on a surface of high acidity, the barrier between the intermediate and the product 2-butene molecules are about equal. This may not be true, however, if the intermediate is something less than a free ion and is affected by special interactions with the surface which change its energetic factors. In this case, the *cis/trans* ratio can deviate to a value larger than unity. Reference to the result shown in Fig. 1 indicates that variation of the *cis*/*trans* ratio from 1.5 to a value lower than 1 may support the enlargement of the acid strength of acidic hydroxyl groups by the adsorbed nitric oxide species at rather large amount of adsorbed NO_2.

The supposition that the acid strength of acidic hydroxyl groups is intensified by the adsorbed nitric oxide species is also rationalized by the following experimental results. When ammonia gas was adsorbed on MgNaX(70) at 100°C, the ir band of 3650 cm^{-1} disappeared. This is attributed to the ammonium ion formation by the reaction between ammonia and the acidic hydroxyl group, already discussed in the previous paper (*1*). No change in the ir absorption bands of the adsorbed species of NO_2 was observed even after the adsorption of ammonia, suggesting no reaction between them. The ir bands of the acidic hydroxyl group did not appear when the zeolite was degassed at 100°C for 1 hr; however, they reappeared partially by subsequent degassing at temperatures 200 and 250°C for 1 hr. Percentage reappearance of the ir bands by degassing is summarized in Table 1. The decreases of the adsorbed nitrogen dioxide species and the acidic hydroxyl group by degassing, measured by ir analysis in the absence of ammonia, are qualitatively indicated in the same table. The decrease of the NO_2 species was predominant only at degassing temperatures above 300°C. Therefore, no desorption of NO_2 can be expected at temperatures lower than 250°C. As can be seen in Table 1, a small reappearance of the hydroxyl group was observed for a large amount of the adsorbed NO_2 when the degassing temperature was 200°C. Subsequent degassing at 250°C was also found to maintain the trend in reappearance. It is reasonable that the stability of ammonium ion increases with increasing acid strength of the hydroxyl group. Therefore, when the recovery of the hydroxyl group stays at a low level despite a high degassing temperature, it is realized that the acid strength of the original hydroxyl group is high, compared to the case when the recovery reaches an appreciable value. It is thus concluded that when a larger amount of nitrogen dioxide was adsorbed, the hydroxyl group of the higher acid strength was produced, i.e., the adsorbed NO_2 intensified the acid strength of the hydroxyl group at the high level of NO_2 adsorption (Fig. 5).

It was found that the intensification in the acid strength by the adsorption of NO_2 was always accompanied with the formation of nitrato(II) complex. More nitrato(II) complex was formed on MgNaX(78) than on

TABLE 1

Change of Surface Species by Degassing at Various Temperatures

	Amount of adsorbed NO_2 (10^{-4} mole g^{-1})	Temperature of degassing (°C)			
		100	150	200	250
Decrease of adsorbed NO_2 species[a]		(−)	(−)		(±)
Decrease of acidic hydroxyl group[a]		(−)	(−)		(±)
Recovery (%) of acidic hydroxyl group by degassing after ammonia adsorption	(0)	0		87	95
	(1.84)	0		16	81
	(4.20)	0		15	82
	(6.70)	0		11	39
	(9.63)	0		1	

[a] Notation: (−), none; (±), very little.

MgNaX(70). Regarding the ratio of the catalytic activity of *cis–trans* isomerization to double-bond migration as the relative measure of the acid strength (*5*, *6*), the change in the selectivity shown in Fig. 4 indicates that the intensification in acid strength is larger for MgNaX(78) than MgNaX(70). The lack of change in the selectivity for MgNaX(39) and MgNaX(50) indicates the absence of the intensification, corresponding to the fact that no nitrato(II) was observed on them. In addition, the large increase in the selectivity is coincident with the appearance of the band of nitrato(II), as seen from Figs. 1, 2, and 6. Therefore, it is plausible that the nitrato(II) complex intensifies the acid strength of the newly formed hydroxyl group.

An increase of acid strength of solid acid by chemical species on its surface has been reported by some investigators (*9–12*). Chapman *et al.* have reported that the cracking of cumene on porous glass was enhanced by treatment with ammonia fluoride; this was explained by the electron withdrawal to the fluoride ion causing an increase of the acid strength of neighboring hydroxyl group (*9*). Hattori *et al.* have also reported that silica–alumina and silica–titania are converted to solid super acid by the adsorption of SbF_5, which is attributed to electron withdrawal from the surface of silica–alumina or silica–titania to SbF_5 (*12*). The nitrato complex may strengthen the acid property of the neighboring hydroxyl group through attracting electrons of the hydroxyl group in a manner similar to that described above.

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