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Catalytic Activity of the Hydroxyl Group Produced by NO_2 Adsorption on Ca-Exchanged Zeolites

YUJI WADA, KIYOSHI OTSUKA, AND AKIRA MORIKAWA

Department of Chemical Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

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The enhancement of acid catalysis by the adsorption of nitrogen dioxide has been studied on the calcium ion-exchanged X-type zeolites of various degrees of the exchange. The enhancement is ascribed to the formation of the acidic hydroxyl group by the adsorption of nitrogen dioxide. As the ion-exchange degree increases, the formation of the hydroxyl group shows an optimum at 50 ~ 60%, but the catalytic activity for the isomerization of butenes continuously increases with steep acceleration at the exchange degree of 40 ~ 50%. The activity of an acidic hydroxyl group is strongly dependent on the number of calcium ion in the supercage of the zeolite. The formation of nitrate ion and nitrato complex observed by ir spectroscopy on the zeolite has been discussed in relation to the hydroxyl group formation.

INTRODUCTION

The acid properties of zeolites are improved by the addition of inorganic gases such as carbon dioxide (*1–3*), sulfur dioxide (*4–6*), hydrogen sulfide (*7, 8*), nitrogen dioxide (*6, 9–11*), and others (*12, 13*). The authors have reported the results obtained from the kinetic and spectroscopic studies on the catalytic activity-enhancement of calcium-exchanged X-type zeolites by preadsorbed nitrogen dioxide for the isomerization of butenes (*10, 11*). The enhancement has been ascribed to the increase in the number of acidic hydroxyl groups due to the preadsorption of nitrogen dioxide (*10, 11*).

Both the activity and the amount of the acidic hydroxyl group in various zeolites are dependent on the type of exchangeable cations in the zeolitic silica–alumina framework (*14, 15*). Hirschler has proposed that the polarizing action by the electric field of the cation tends to free (makes acidic) a proton of a hydroxyl group attached to an adjacent silicon or aluminum atom (*16*). Ward has reported the change in the activity of the acidic hydroxyl group on H–Y zeolite by the back-exchange with calcium or magnesium ion, attributed to the polarizing effects of the back-exchanged cation (*17*). Taking into account such effects of the exchangeable cation on the properties of the acidic hydroxyl group, the activity of the hydroxyl group formed by the adsorption of nitrogen dioxide must be also affected by the degree of the exchange of sodium ion by calcium ion, since the polarizing power of calcium ion is greater than that of sodium ion.

The authors have found a remarkable increase in the catalytic activity of the hydroxyl group formed by the NO_2 preadsorption for butene isomerization with an increase of the degree of the exchange (*10*). In the present paper, the catalytic activity for the butene isomerization and the amount of the acidic hydroxyl group of the calcium-exchanged X-type zeolites increased by the preadsorption of nitrogen dioxide will be compared for the different temperatures of degassing the zeolites. In addition, the adsorbed species of nitrogen dioxides will be explored through ir spectroscopic investigation of the various zeolites after the adsorption of nitrogen dioxide. These experiments must reveal factors controlling the catalytic activity of a hy-

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droxyl group on the zeolites with various degrees of the ion exchange.

EXPERIMENTAL

Zeolites. Sodium X-type zeolite, NaX, was prepared by soaking Linde Molecular Sieve 13X in a 1.0 *N* aqueous solution of sodium chloride at room temperature. The zeolite exchanged by calcium ion at the exchange degree of 35, 44, 59, or 78% was prepared by the usual ion exchange method with 0.1 or 1.0 *N* aqueous solution of calcium dichloride at room temperature. The Ca-exchanged X-type zeolite with an exchange degree of 100% was prepared at 70°C. The zeolites used in this work are denoted by CaNaX(x), where x expresses the degree of the exchange by calcium cation in percentage. The degree of the exchange was determined by the equation $n(\mathrm{Al})$-$n(\mathrm{Na})/n(\mathrm{Al})$, where $n(\mathrm{Al})$ and $n(\mathrm{Na})$ are the numbers of Al and Na atom in the zeolites, determined by atomic absorption spectrometry and flame photometry, respectively.

Materials. Nitrogen dioxide was prepared by the reaction of chemically pure nitric oxide (Takachiho Chemical Co. Ltd.) with oxygen gas and purified by distillation *in vacuo* untill its colorless solid was obtained at liquid nitrogen temperature. *cis*-2-Butene purchased from Phillips Petroleum Co. was used after bulb to bulb distillation *in vacuo*.

Apparatus. The reaction system used was a closed, gas-circulating apparatus with a volume of 329 ml. A small portion of reacting gas was sampled and analyzed by gas chromatography.

Procedures. The experimental procedure of butene isomerization was described in detail elsewhere (*10, 11*). The zeolites were usually calcined in oxygen gas at 400°C (unless otherwise mentioned) and degassed at the same temperature for 2 hr. Nitrogen dioxide with an appropriate pressure was kept in contact with the zeolites for 5 min and evacuated for 10 min at 100°C. The amount of adsorbed NO_2 was calculated by subtracting the amount evacuated from that introduced. The rate of formation of a product at a reaction time of 5 min was tentatively adopted as the activity of the catalysts.

Infrared measurement. A drum-shaped, quartz-walled cell was used for the ir study of the zeolites. A wafer of the zeolite 20 mm in diameter and weighing about 10 mg was placed in the cell and degassed at 200°C for 1 hr. Subsequently, the temperature of the sample was raised to 400 or 500°C and further degassed for 1 hr. All the spectra were recorded at 100°C. The adsorption of nitrogen dioxide onto the wafer was performed by the same method as described in the procedure sections.

RESULTS

Table 1 shows the relations between the activities of both double-bond-migrating and geometrical isomerization of *cis*-2-butene at 100°C and the amount of adsorbed NO_2 for the CaNaX zeolites of various exchange degree. The preliminary results obtained for the zeolites degassed at 500°C are given to Table 1 (*10*). The rates of isomerization were gradually decreased as the reactions proceeded. Therefore, the initial rate determined as mentioned in the experimental procedure section was regarded as the catalytic activity. The rates of isomerizations were dependent on the pressure of *cis*-2-butene, fitted to a Langmuir–Hinshelwood type of rate equation, $r = kKP/(1 + KP)$, where r is the rate, P the pressure of the butene, and k and K are constants. All the experiments were carried out at a pressure of *cis*-2-butene of 117 Torr which was large enough to say $1 \ll KP$ in the above rate equation for all the catalysts tested here. In the absence of adsorbed NO_2, CaNaX zeolites with an exchange degree of less than 78% were not very active in isomerizations, while CaNaX(100) was appreciably active. An enhanced activities for the isomerizations are here defined as differences of the rates in the presence and absence of adsorbed NO_2.

TABLE 1

Catalytic Activities of CaNaX Adsorbing NO_2

Zeolites	Degassed at 400°C			Degassed at 500°C		
	NO_2[a]	Activity[b]		NO_2[a]	Activity[b]	
		c → 1	c → t		c → 1	c → t
NaX	0	0.00	0.00	0	0.00	0.00
	3.98	0.07	0.00	5.86	0.07	0.04
	8.01	0.18	0.03	13.9	0.30	0.31
CaNaX(35)	0	0.00	0.00	2.81	0.14	0.11
	4.03	0.21	0.08	6.88	0.37	0.29
	8.71	0.52	0.10	7.69	0.73	0.30
CaNaX(44)	0	0.00	0.00	8.22	1.72	0.90
	4.15	0.51	0.18	—	—	—
	8.29	1.27	0.71	—	—	—
CaNaX(59)	0	0.28	0.06	2.97	0.97	0.46
	4.62	1.27	0.51	4.79	2.10	1.11
	9.15	3.98	1.89	8.09	3.20	2.23
CaNaX(78)	0	0.03	0.11	0	0.02	0.02
	4.26	4.10	5.02	2.74	2.93	1.93
	7.44	6.44	9.50	5.50	5.33	5.82
CaNaX(100)	0	7.72	11.5	0	3.55	4.86
	2.68	12.1	18.9	2.82	9.20	10.7
	7.97	21.7	23.5	6.89	15.4	16.6

[a] Amount of adsorbed NO_2 in 10^{-4} mol g^{-1} unit.

[b] Initial rate (see text) in 10^{-7} mol sec^{-1} g^{-1} unit. c → 1 and c → t denote the double-bond migration and geometrical isomerization, respectively.

The enhanced activities were proportional to the amount of adsorbed NO_2 for every zeolite. Therefore, the specific enhancement, i.e., moles of butene formed per mole of NO_2 adsorbed, mol sec^{-1} $mol_{NO_2}^{-1}$, is adopted as a measure of the enhancing action of NO_2 on isomerization. Figure 1 shows the relation between the specific enhancement and the degree of the ion exchange. The curve in Fig. 1 indicates that the specific enhancement for the double-bond migration increases steeply above an exchange of around 40%. The same behavior was observed for the geometrical isomerization as shown in Fig. 1.

When nitrogen dioxide was adsorbed on CaNaX(78), the intensity of the ir adsorption band at 3645 cm^{-1} due to the acidic hydroxyl group was increased (*11*). The enhancement of butene isomerization by the adsorption of NO_2 has been ascribed to the acid catalysis by this hydroxyl newly formed group (*11*). The formation of the

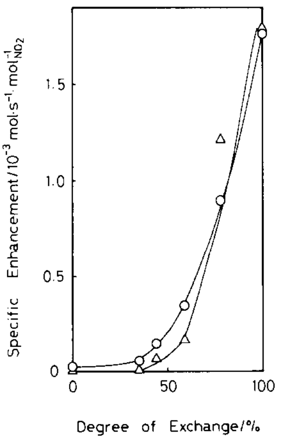


FIG. 1. Enhancement of the isomerization of *cis*-2-butene by a unit amount of NO_2 adsorption. (○) The double-bond migration; (△) the *cis–trans* isomerization.

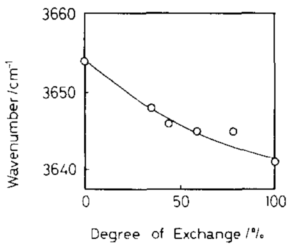


FIG. 2. Shift of the wavenumber of OH band formed by NO_2 adsorption for the degree of ion exchange of the zeolites degassed at 400°C.

hydroxyl group by the adsorption of NO_2 was also observed by ir spectrometry for all the zeolites used in this work. Though the hydroxyl bands were observable even in the absence of NO_2, they are negligibly small. The wavenumbers of the band maxima of the hydroxyl group formed by the adsorption of NO_2 were not exactly identical among the zeolites of various degrees of ion exchange and fell within the range of wavenumber, 3641 ~ 3654 cm^{-1}. Figure 2 shows the relation between the wavenumber of the band maximum and the degree of the exchange of the zeolite. The wavenumber was decreased monotonically as the degree of exchange was increased. Since little variation in the value of the half width of the band was observed, it is considered that the extinction coefficient of the hydroxyl group is unchanged. Therefore, the absorption intensity of the band can be considered as the measure of the amount of the hydroxyl group present in the zeolites. The increase in the absorption intensity of the hydroxyl band around 3650 cm^{-1} after the adsorption of NO_2 is plotted in Fig. 3 against the amount of the adsorbed NO_2 for various CaNaX zeolites. The absorption intensity increased linearly as the amount of the adsorbed NO_2 on various CaNaX zeolites increased. This figure indicates that the hydroxyl group is newly formed on CaNaX in proportion to the amount of the adsorbed NO_2 for all the zeolites.

The slopes of the straight lines in Fig. 3, corresponding to the amount of the hydroxyl group formed by the adsorption of a unit amount of NO_2 per gram of catalyst, addressed here by the specific increase of the hydroxyl group, were plotted against the degree of the calcium ion exchange as shown in Fig. 4. The value of the specific increase reached a maximum at the exchange degree of around 60% and decreased above this value. This value determined for CaNaX(100) is rather less than that for CaNaX(0), i.e., NaX. A similar trend was obtained for the zeolites degassed at 500°C, as displayed by triangles in Fig. 4. When NO_2 was adsorbed on CaNaX(78), the several ir absorption bands appeared in the region of wavenumber 1250 ~ 1550 cm^{-1} and were increased with increasing amounts of the adsorbed NO_2 (Fig. 5). Though the bands are very broad, the four peaks of wavenumbers, ~1530, ~1450, ~1380, and ~1280 cm^{-1}, are distinguishable. When NO_2 was adsorbed on NaX zeolite, the observed spectrum was different from that of CaNaX(78). The two bands at ~1400 and ~1280 cm^{-1} were observed. When the amount of adsorbed NO_2 was increased, the intensity of the band at ~1400 cm^{-1} was increased, while that at ~1280 cm^{-1} was decreased.

DISCUSSION

This paper mainly deals with the results and discussion on the double-bond migra-

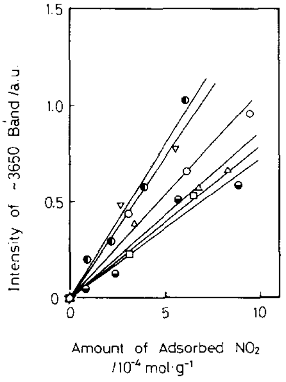


FIG. 3. Influence in the absorption intensity of the ~3650 cm^{-1} band by the adsorption of NO_2. (□) NaX, (△) CaNaX(35), (▽) CaNaX(44), (◐) CaNaX(59), (○) CaNaX(78), (◒) CaNaX(100).

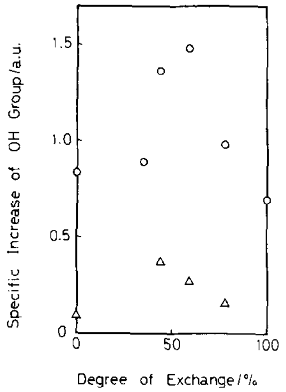


FIG. 4. Specific increase in OH by a unit amount of NO_2 against the degree of the exchange. Degassed at (○) 400°C, (△) 500°C.

tion from *cis*-2-butene to 1-butene, since the *cis–trans* isomerization appears to involve a mechanism different from acid catalysis (*11*). In fact, nitrogen dioxide adsorbed on porous Vycor glass catalyzes only the *cis–trans* isomerization of 2-butene through a nitro-butyl radical intermediate (*18*). However, the kinetic feature of the *cis–trans* isomerization investigated in the present work was very similar to the double-bond-migrating isomerization.

In H–X and –Y zeolites, prepared by the thermal decomposition of their NH_4^+-exchanged form, six different types of hydroxyl groups have been identified by means of ir spectroscopy (*14*). Among these hydroxyl groups, it is accepted that the hydroxyl group giving the ir absorption band at 3650 cm^{-1} concerns O_1 type oxygen in the zeolite framework and causes acid catalysis (*19*). The absorption bands around 3650 cm^{-1} were increased by the adsorption of NO_2 without any band shift by changing its adsorption amount. The small variation in the wavenumber of the band maximum was observed for different degrees ion exchange as shown in Fig. 5. However, the half width of the absorption band remained unchanged. Therefore, it is concluded that the same type of hydroxyl group attached to O_1 oxygen was additionally formed on the individual zeolites by the adsorption of nitrogen dioxide.

Though the observed ir absorption spectra shown in Fig. 5 were poorly resolved,

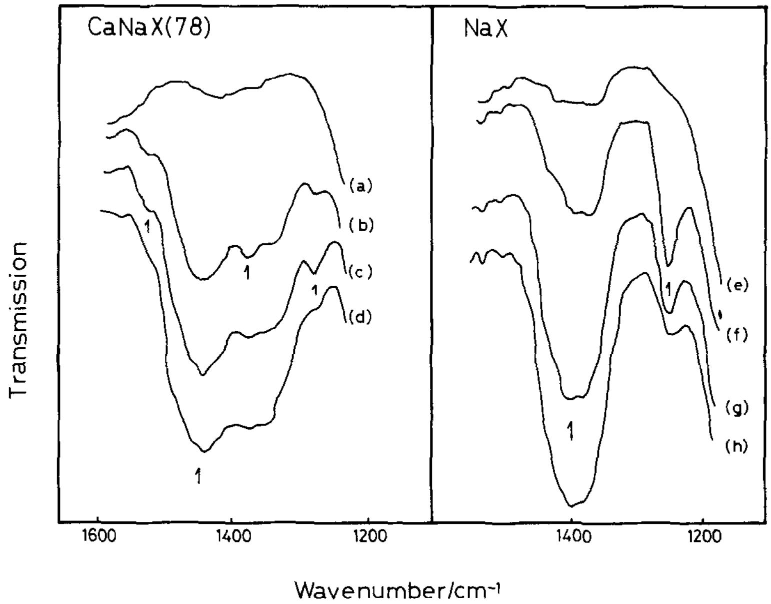
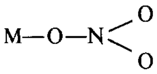
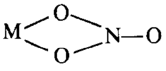
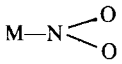


FIG. 5. Infrared spectra of the region of adsorbed NO_2 on CaNaX(78) and NaX. (a) After pretreatment, (b) the amount of NO_2, 5.65×10^{-4} mol g^{-1}, (c) 10.4×10^{-4}, (d) 15.1×10^{-4}, (e) after pretreatment, (f) 1.72×10^{-4}, (g) 4.02×10^{-4}, (h) 6.15×10^{-4}.

TABLE 2

Plausible Species of Nitrogen Oxides Adsorbed on CaNaX and NaX

Structure[a]		(Wavenumber/cm^{-1})[b]	Wavenumber/cm^{-1}	
			CaNaX	NaX
Nitrate ion	NO_3^-	(1380)	1380	1400
		(1530 ~ 1480 1290 ~ 1250)		
Nitrato complex		(1565 ~ 1500 1300 ~ 1260)	1530 1280	
Nitrite ion	NO_2^-	(1260)	1280	1280
Nitrito complex		(1440 ~ 1335)	1380 1450	1400
	$M-O-N=O$	(1470 ~ 1450)		

[a] M indicates metal.
[b] Assignment shown in Ref. (*20*).

the adsorbed species of nitrogen dioxide (*20*) possibly corresponding to the observed bands are summarized in Table 2. The absorption band at 1380 ~ 1400 cm^{-1} can be attributed to nitrate ion. The bands at 1530 and 1280 cm^{-1} are attributed to a nitrato complex. Alternatively, the latter is possibly assigned to nitrite ion. However, these bands are not proportionally increased as the amount of adsorbed nitrogen dioxide is increased, though the bands at 1380 ~ 1400 cm^{-1} increase in parallel with the growth of the ~3650 cm^{-1} hydroxyl band. Therefore, when NO_2 is adsorbed on CaNaX, nitrate ion may be mainly produced, as well as the acidic hydroxyl group. Thus, reactions (1) and/or (2) must proceed on CaNaX by the adsorption of nitrogen dioxide:

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

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

where proton H^+ has to be bound to O_1 oxygen of the zeolite framework. Electron e may be trapped to the zeolite framework. NO_3 bound to calcium ion must be in the form of a nitrate ion or nitrato complex. OH bound to calcium ion in the left-hand side of Eq. (1) is the basic hydroxyl group formed by the dissociation of water coordinating to calcium ion (*21*), $Ca^{2+}(H_2O) \rightarrow Ca^+(OH) + H^+$, during preheating of the zeolites. The new hydroxyl group was produced not only on Ca-exchanged zeolites but also NaX zeolite (Fig. 4). Therefore, the following equation of the formation of the hydroxyl group must be accounted for in addition to Eqs. (1) and (2).

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

The absorption band region of nitrito complexes overlaps that of the nitrate ion. However, the formation of the complexes by the adsorption of nitrogen dioxide on the zeolites may be free from the promotion of their acidity. Reactions (1), (2), and (3) were irreversible, since the absorption bands of the hydroxyl group, or adsorbed nitrogen oxide species, could not be removed by prolonged degassing even at 200°C.

It is well known that the hydroxyl group attaching to O_I-type oxygen does not exist on NaX zeolite (*21, 22*), since the electrostatic field of the sodium ion is not strong enough to dissociate water molecules coordinating to it. When the positive charge of the sodium ion is compensated with nitrate ion through Eq. (3), the hydroxyl group attaching to O_I oxygen is consequently produced even on NaX zeolite.

When the zeolite is degassed at a higher temperature, the production of the acidic hydroxyl group should be reduced. In fact, the increment of the ir absorption intensity of the acidic hydroxyl band for the same amount of the adsorbed NO_2 was much lower for the zeolites degassed at 500°C as shown in Fig. 4.

The increase in the intensity of ~3650 cm^{-1} ir band is interpreted by reactions (1), (2), and (3) for all zeolites. The enhancement of the catalytic activity is ascribed to the increase in these hydroxyl groups.

Among the zeolites of the various ion exchange degree, however, no correspondence exists between the increase in the number of the acidic hydroxyl group and the enhancement of the catalytic activity induced by the adsorbed nitrogen dioxide of a unit amount (Figs. 1 and 4), suggesting that the activity of the hydroxyl group depends upon the ion exchange degree of the zeolite. The enhancement by a unit amount of NO_2 (Fig. 1) divided by the relative amount of the hydroxyl group formed by a unit amount of NO_2 (Fig. 4) for all zeolites corresponds to the catalytic activity of a unit amount of hydroxyl group, as shown in Fig. 6. The catalytic activity of the ~3650 cm^{-1} hydroxyl groups formed on NaX by the adsorption of NO_2 was very low and those for the calcium ion-exchange zeolites steeply increased at the exchange degree of around 40 ~ 50% and reached a maximum at the 100% exchange. The results shown in Fig. 6 lead us to the conclusion that the activity of the hydroxyl group formed by the NO_2 adsorption is enlarged by the calcium cations. The activation energies for the double-bond migration of *cis*-2-butene on the zeolites of various degrees of ion exchange, degassed at 500°C, have been reported to be 23.6, 22.9, 20.6, and 15.5 kcal mol^{-1} for zeolites of the exchange degree of 35, 44, 59, and 78%, respectively (*10*). This decrease reflects the greater stabilization of the reaction intermediate of the isomerizations, i.e., a secondary butyl carbenium ion, by the more active Brønsted acid site produced on the zeolites.

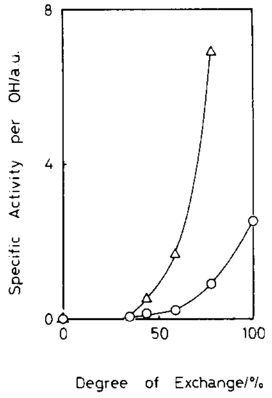


FIG. 6. Specific activity of a unit amount of OH for the degree of the exchange. Degassed at (○) 400°C, (△) 500°C.

Barthomeuf (*23*) and Bielański and Datka (*24*) have reported that the ir absorption band of the hydroxyl group on zeolites shifts to a lower frequency when its acid strength increases. As shown in Fig. 2, the larger band shift was observed for the hydroxyl group formed by a certain amount of NO_2 adsorbed on the higher level of ion-exchange for the zeolite. The increase in the acid strength of the hydroxyl group can be interpreted by the theory proposed by Hirschler (*16*) and Richardson (*25*). The exchange of sodium ion with calcium ion, which has a stronger polarization ability than the sodium ion, results in an increase of the acid strength of the hydroxyl group in the zeolites. For each ion exchanged zeolite, on the other hand, no ir band shift was observed when the amount of adsorbed NO_2 was increased. This experimental result suggests that the adsorption of NO_2 causes the formation of Brønsted acid sites of a homogeneous acid strength for a given degree of the calcium ion exchange.

The critical value of the exchange degree of 40 ~ 50%, at which the activity of the hydroxyl group formed begins to increase, corresponds to the exchange degree at which calcium ions begin to occupy the cation site in the supercage (*26*). The calcium ion in the small cage has little effect on the hydroxyl group attached to O_1 oxygen, while that in the supercage can activate it strongly enough to isomerize butenes.

The acidic hydroxyl group produced on the zeolites degassed at 500°C is catalytically more active as seen from the results shown in Fig. 6. It is considered that degassing at the higher temperature recalls the full charge of calcium ion by the removal of the hydrated water, giving it a stronger polarizing effect on the acidic hydroxyl group produced by the NO_2 adsorption. These discussions are supported by the fact that the ir band of the hydroxyl group of the zeolites degassed at 500°C shifted to lower frequency, compared to those degassed at 400°C.

The change of the amount of the hydroxyl group formed by the adsorption of NO_2 shown in Fig. 4 may be explained as follows. Calcium ion in the supercage coordinates more water or hydroxyl group than the sodium ion by its strong power of polarization. Therefore, the amount of the hydroxyl group formed by the NO_2 adsorption increases from a exchange degree of around 40% at which the calcium ion appears in the supercage and must continue to increase with the degree of the exchange. The decrease of the formation of the hydroxyl group above 60% may result from the increase of the calcium in the form of $Ca^+{-}O{-}Ca^+$, which is produced by degassing the zeolites (*27*). The number of this form may be larger for the higher degree of the ion exchange, and, consequently, the number of the hydrated water molecules or the basic hydroxyl groups is decreased.

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