The Exchange Reaction of Deuterium with the Hydroxyl Groups of Zeolite Catalysts

Toshinobu Imanaka, Yasuaki Okamoto, Kazunori Takahata, and Shiichiro Teranishi
Osaka University, Department of Chemical Engineering, Faculty of Engineering Science, Toyonaka, Osaka

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In order to estimate the reactivity of each hydroxyl group, the exchange reaction of deuterium with the hydroxyl groups on the surfaces of the HX, HY, and CaHX zeolites and aerosil was investigated kinetically by an infrared method. The hydroxyl groups appearing at 3660 cm^{-1} on the HX and HY zeolites were more readily exchanged with deuterium than were the other hydroxyl groups on the two zeolites. However, in the case of the CaHX, the order of activities of each hydroxyl group changed with the pressure of deuterium. The rate equation for the reaction is expressed by a Langmuir-type equation. This fact indicates the homogeneity of each hydroxyl group on zeolite. It was found that adsorbed water and carbon dioxide catalyzed the exchange reaction. Furthermore, a compensation effect between the apparent activation energies and the frequency factors occurs in this reaction.

The existence of hydroxyl groups on the surface of zeolite has been shown by infrared spectroscopy.[1-3] The reactivity of a particular hydroxyl group has been estimated from the strength of the interaction with adsorbed olefins,[4,5] bases,[6] and cumene for the HY catalyst.[7] These results show that the hydroxyl group observed at 3650—3640 cm^{-1} is more active than that in the 3550—3540 cm^{-1} region. In this paper, the exchange reaction of deuterium with the hydroxyl groups on the surfaces of zeolites was studied kinetically in order to estimate the reactivity of each hydroxyl group by means of an infrared method. The infrared method has been shown by Carter *et al.*[8] to be useful for investigating the reactivity of a particular hydroxyl group on the surface, as distinct from measuring the overall rate of the exchange of deuterium with a surface hydroxyl group. However, in the kinetic treatment of a reaction, the apparent rate constant, and the adsorption equilibrium constant, and the reactivity of the hydroxyl group must be discussed in terms of the true rate constant.

By the infrared method, Pimentel *et al.*[9] and Eishens and Pliskin[10] have reported the exchange reactions of surface hydroxyl groups on silica gel, and Fry and his co-workers[11] have treated them in some detail. As for alumina, Peri and Hannan[12] have investigated them qualitatively, and Carter *et al.* have studied the reaction kinetically.

The effects of adsorbed water on the reactions catalyzed by zeolites have been reported by many investigators.[13] In the exchange reaction of deuterium with the hydroxyl groups on the zeolite catalyst, similar effects are also found. We found that adsorbed carbon dioxide accelerates its reaction rate. Furthermore, a compensation effect is observed in this reaction; the occurrence of this effect is discussed.

Experimental

Materials. The 13X, 10X, and NaY zeolites were of a commercial grade. The HX, CaHX, and HY zeolites were prepared from their sodium or calcium forms by conventional cation exchange procedures using analytical-grade NH_4Cl. The degree of ion exchange was determined by flame-photometric analysis. In both HX and HY zeolites, 75% of the calcium ions were exchanged. The silica/alumina ratios are 1.4, 1.2, and 2.5 for HX, CaHX, and HY respectively, according to chemical analysis. The aerosil was of a commercial grade. The deuterium used for the exchange reactions had a stated purity of 99.5%.

Procedure. Disks, transparent to infrared radiation, were prepared by pressing the zeolites between polished stainless steel plates to about 10 ton/cm^2. The thickness varied between 7 and 10 mg/cm^2. The platelets were then placed in an IR cell and slid from the salt windows to the center of the IR cell, where they could be heated. The cell can be used in conjunction with a conventional high-vacuum system, and the sample can be treated with gases at any desired temperature. Spectra were taken at room temperature using a Hitachi grating spectrometer. Potassium bromide windows were used on the cell.

The experiments reported in this paper were performed as follows. The disks of HX, HY, CaHX, and aerosil were heated at 300, 400, 350, and 500°C respectively for 14—16 hr under a vacuum of 10^{-5} mmHg in the IR cell. After evacuation, the sample was cooled to room temperature under a vacuum, and the infrared spectrum was recorded. Then, the sample was heated to a reaction temperature and deuterium was introduced. After the desired time had elapsed, sample was cooled to room temperature and the spectrum was again recorded. This procedure was then repeated.

The reaction temperatures were 260—300°C, 280—300°C, 300—330°C, and 400—450°C for HX, HY, CaHX, and

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aerosil respectively.

In order to investigate the effect of adsorbed water on the exchange reaction, a small amount of water was added to the system as follows. A trace of adsorbed water was added to the sample by evacuation under a vacuum of 10^{-3} mmHg for 6 hr. Then, the exchange reaction was carried out by adding pure deuterium. In order to add more water to the sample, the reaction was carried out by introducing deuterium containing a small amount of water after the samples had been treated under such conditions.

Mixtures of carbon dioxide and deuterium gas were also placed in contact with the sample in order to study the effects of adsorbed carbon dioxide on the reaction.

Results and Discussion

Typical infrared spectra obtained at room temperature for the sample studied, before and after exposure to deuterium for varying periods of time, are shown in Figs. 1a and 1b. For example, in the original spectrum of the HX zeolite, before exposure to deuterium three different bands due to surface hydroxyl groups were observed. These bands appeared at wave numbers of 3745, 3660, and 3560 cm^{-1}. After exposure to deuterium, additional bands due to OD groups were observed at 2752, 2697, and 2635 cm^{-1}. The wave numbers of the OH groups due to exchange reactions are summarized in Table 1.

Table 1. Wave numbers of OH and OD groups

Sample	Wave number of OH group cm^{-1}	Wave number of additional OD group, cm^{-1}
HX	3745	2752
	3660	2697
	3560	2635
HY	3660	2690
	3548	2622
CaHX	3660	2693
	3595	2659
	3566	2633
aerosil	3755	2760

The reactivity of each hydroxyl group is qualitatively as follows. In the case of the HX zeolite, the OH group occurring at 3660 cm^{-1} is exchanged more readily with deuterium than are the other OH groups under the present experimental conditions. The lowest-frequency OH group (3560 cm^{-1}) has a subsequent activity, while the highest one (3745 cm^{-1}) is most inactive. Although the difference in activities between them is not very great, the OH group observed at 3660 cm^{-1} is 1.5—2 times more active than that at 3745 cm^{-1}. In the case of the HY zeolite, the OH group occurring at 3660 cm^{-1} is a little more active than that at 3548 cm^{-1}. These facts correspond to those estimated from the strength of the interaction with olefins, bases, and aromatics.[12] However, the behavior of the surface hydroxyl groups on the CaHX zeolite is more complecated than in the case with the HX and HY zeolites. When the pressure of deuterium is lower than about 15 cmHg, the OH group observed at 3566 cm^{-1} has the highest activity, that at 3660 cm^{-1} has the next highest one, and that at 3595 cm^{-1} has the lowest one. When the pressure is higher than about 20 cmHg, however, the OH group occurring at 3595 cm^{-1} is more active than those at 3660 and 3566 cm^{-1} which have nearly the same reactivity. The surface OH group on aerosil (3755 cm^{-1}) is much more difficult to exchange than those of the zeolites used. This paper is mainly concerned with the OH groups occurring at 3660 cm^{-1} on HX, HY, and CaHX, and that occurring at 3755 cm^{-1} on aerosil.

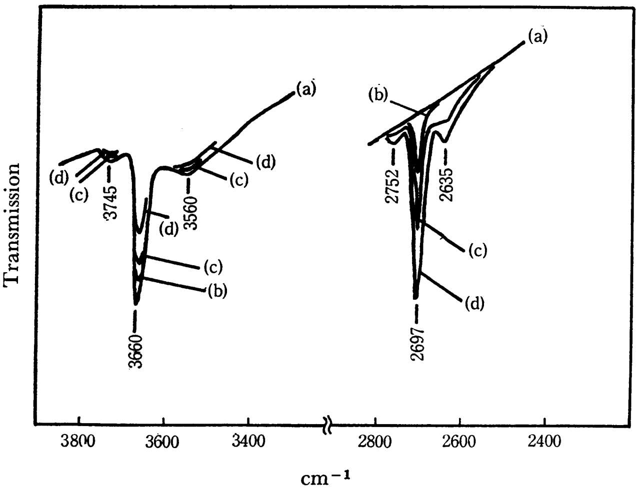

Fig. 1a. Typical infrared spectra of HX as a function of time of treatment with D_2 (13.95 cmHg) at 180°C: (a), 0; (b), 1; (c), 3; (d), 7 hr.

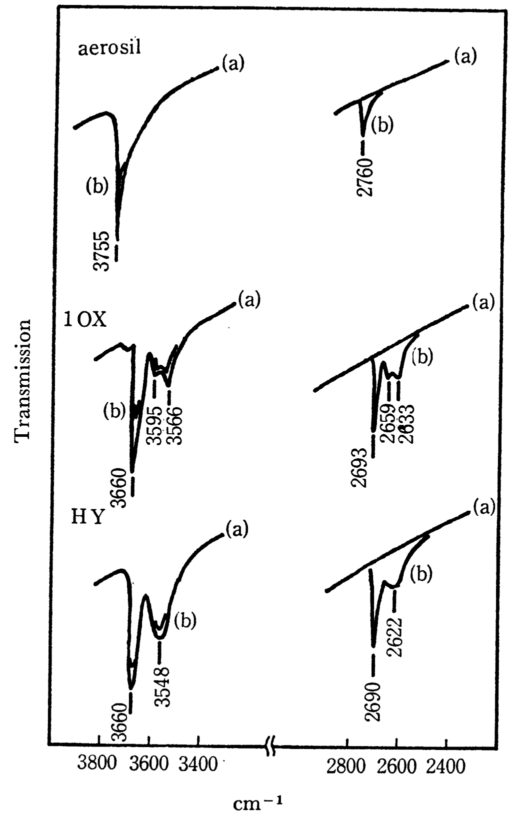

Fig. 1b. Typical infrared spectra of OH and OD groups on HY, CaHX, and aerosil: (a), before exposure to D_2; (b), after exposure to D_2.

If deuterium is adsorbed on the zeolite surface in a Langmuir-type reaction, and the exchange reaction occurs between adsorbed deuterium and hydroxyl groups, the rate equation can be expressed as follows;

$$-\mathrm{d(OH)}/\mathrm{d}t = k\theta\mathrm{(OH)} \tag{1}$$

$$\theta = KP/(1+KP) \tag{2}$$

Therefore,

$$-\mathrm{d(OH)}/\mathrm{d}t = kKP/(1+KP)\mathrm{(OH)} \tag{3}$$

where (OH) is the concentration of surface hydroxyl groups; θ, the coverage of deuterium; k, the rate constant; K, the adsorption equilibrium constant of deuterium; and P, the pressure of deuterium. However, in our experiments, when sliding the samples from the salt windows to the center of the IR cell, the absolute concentration of the hydroxyl group, that is, (OH) in Eq. (3), could not be measured reproducibly. Therefore, Eq. (3) must be transformed into the following equations

$$-\mathrm{d}\ln\mathrm{(OH)}/\mathrm{(OH)}_0/\mathrm{d}t = kKP/(1+KP) \tag{4}$$

$$\mathrm{(OH)}_0 = \mathrm{(OH)} + \mathrm{(OD)} \tag{5}$$

where (OD) is the concentration of OD groups and where $\mathrm{(OH)}_0$ is the sum of the concentrations of OH and OD groups, that is, the concentration of OH groups before exposure to deuterium. Only $\mathrm{(OH)}/\mathrm{(OH)}_0$ can be measured in our experiments. Recently it has been reported that the extinction coefficients of OH and OD groups are equal; therefore, the concentrations of OH and OD groups can be represented by their optical densities. Figures 2 and 3 show that the rate equation of the exchange reaction can be expressed by Eq. (4) or (3). That is, each hydroxyl group is considered to be homogeneous. However, for η-alumina, Carter and his co-workers[8] have reported a rate expression which indicates a surface heterogeneity in the alumina. This difference seems to be ascribable to the purity of η-alumina and/or to the crystallinity of zeolite.

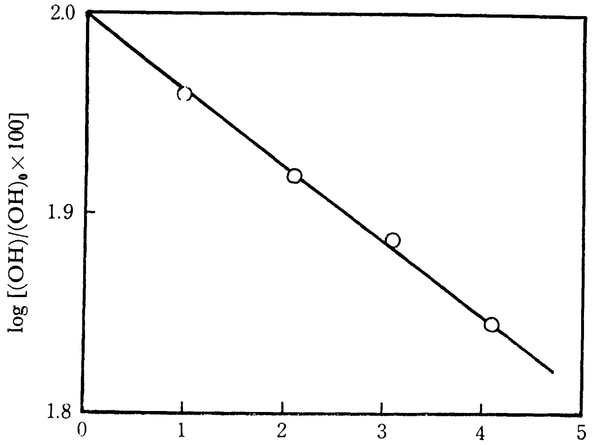

Fig. 2. Exchange of D_2 with the hydroxyl group (HX 3660): reaction pressure; 6.47 cmHg, reaction temperature; 300°C.

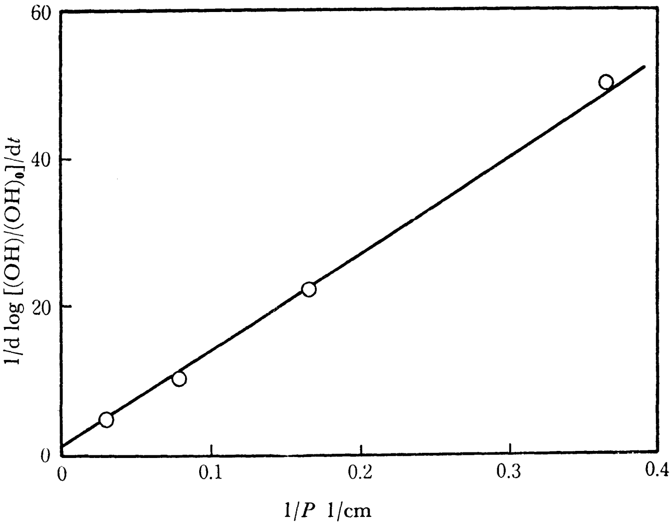

Fig. 3. Langmuir plot of exchange reaction of HX 3660: reaction temperature; 300°C, pressure; cmHg.

From Eq. (4), the rate constant, k, and the adsorption equilibrium constant, K, can be calculated. When the reaction pressure is low, the apparent rate constant, k, can be represented by kK according to Eq. (6):

$$\begin{aligned} -\mathrm{d(OH)}/\mathrm{d}t &= kKP/(1+KP)\mathrm{(OH)} \\ &= kKP\mathrm{(OH)} \quad (\text{when } KP \ll 1) \\ &\equiv k'P\mathrm{(OH)} \end{aligned} \tag{6}$$

Here, the values of the apparent activation energy, E_a, the frequency factor, A, the activation entropy, ΔS_a, the heat of adsorption, ΔH_a, and the entropy of adsorption, ΔS_a, are calculated from the temperature dependencies of k, k', and K. These values are summarized in Table 2.

The apparent activation energies for the exchange reaction of deuterium with hydroxyl groups have been reported by many investigators. The only value of E_a for a particular OH group, that is, the OH group occurring at 3785 cm^{-1} on η-alumina,[7] is 7—12 kcal/mol. Hall and his co-workers[14,15] have evaluated E_a by measuring the overall rate of exchange for

TABLE 2. KINETICAL CONSTANTS OF EXCHANGE REACTION

OH group	E_a (kcal/mol)	ln A	ΔH_a (kcal/mol)	ΔS_a (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
HK 3660	7.7	2.5	−10	−28	18	−32
HY 3660	41	32	−4.9	−16	46	−5
CaHX 3660	18	9.0	−0.1	−8.2	18	−49
Aerosil 3775	5.3	−2.2	0	−6.7	5.3	−69

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silica gels (22—23 kcal/mol), γ-alumina (6 kcal/mol) and silica-alumina (8—10 kcal/mol). For the HY zeolite, the value of E_a has been shown to be 20—30 kcal/mol by Imai.[16] The E_a values in Table 2 can not be compared directly with their values, but they seem to be appropriate.

The adsorption heats of the deuterium of the HX and HY zeolites are very large in comparison with those on Na-13(2.06 kcal/mol) and Ca-13(2.49 kcal/mol).[17] They may be explained in terms of the interaction between the electrostatic field of the sodium ion and deuterium. Furthermore, the values of ΔH_a are calculated from the temperature dependence of K in Eq. (4); therefore, they are the values for active deuterium only. Since the values of Na-13Y and Ca-13Y, have, however, been obtained by measuring adsorption isotherms, they are average values of active and non-active deuterium. In the case of the CaHX zeolite, the calcium ions retained in it are considered to exist on the S_I site only. Therefore, the exchange reaction with the hydroxyl group observed at 3660 cm^{-1} may not be influenced by calcium ions. This is confirmed by the following facts. The OH group occurring at 3660 cm^{-1} on a CaHX zeolite consisting of about 65% of calcium ions is exchanged more readily than that on a CaHX zeolite consisting of 42% calcium ions. Moreover, it has been reported[18] that the activity of the isomerization of *n*-hexane on calcium containing type-Y zeolite catalysts greatly increases when more than 40% of the sodium ions are replaced by calcium ions these facts agree with the effect of calcium ions on the exchange reaction. In the case of aerosil, the heat of adsorption is compatible with that measured on silica.[19]

The adsorption entropies of deuterium on HX and HY are very large. If a deuterium molecule adsorbs on the surface and migrates with two freedoms of translation, the value of the adsorption entropy must be about −9 e.u. Therefore, it is considered that deuterium molecule adsorbed on the HX and HY zeolites migrates in the only defined region, interacting with the cations.

In the case of the CaHX zeolite, however, the adsorption entropy is a degree of free migration. Hence, the deuterium molecule on the CaHX zeolite, which reacts with the surface hydroxyl group of 3660 cm^{-1}, is considered to migrate over a wide region without interacting with the calcium ions in the S_I sites.

It is found that the small of water adsorbed on the zeolites catalyzes the exchange reaction of deuterium with the surface hydroxyl groups. The rate equation is expressed by Eq. (1) when the amount of adsorbed water is small. The k, k', and K values for the HX zeolite in the presence of adsorbed water are shown in Table 3. In the case of Condition A, the sample was evacuated at 300°C for 6 hr under a vacuum of 10^{-3} mmHg before exposure to pure deuterium. In the case of Condition B, after the sample has been treated under the same conditions as in A, it was placed in contact with the deuterium which contains a small amount of water. The apparent rate constant, k', increases monotonously as the amount of adsorbed water is increased; that is, the exchange rate increases with an increase in the amount of adsorbed water. However, the rate constant, k, has a maximum value. This fact can be explained as follows. The exchange reaction of hydroxyl groups with D_2 is very fast in comparison with that with deuterium. When the amount of adsorbed water is very small, the reaction is accelerated by the exchange reaction between the proton of the water molecule and the deuteron of the deuterium molecule. When the water content is increased, however, water molecules shield the electrostatic field of the cations and, consequently, deactivate the deuterium molecule. The two opposite roles of adsorbed water give the rate constant a maximum value. The increase in K may be explained in terms of the interaction between deuterium and water. The catalytic effect of adsorbed water is more complex than is initially apparent.

TABLE 3. EFFECT OF ADSORBED WATER ON EXCHANGE REACTION

	No adsorbed water	A	B
k' (1/hr)	1.42×10^{-2}	1.75×10^{-2}	0.113
k (1/hr)	1.50	2.18	0.730
K (1/cmHg)	9.45×10^{-3}	8.03×10^{-3}	0.155

It is found that carbon dioxide also influences the exchange reaction. A typical reaction is shown in

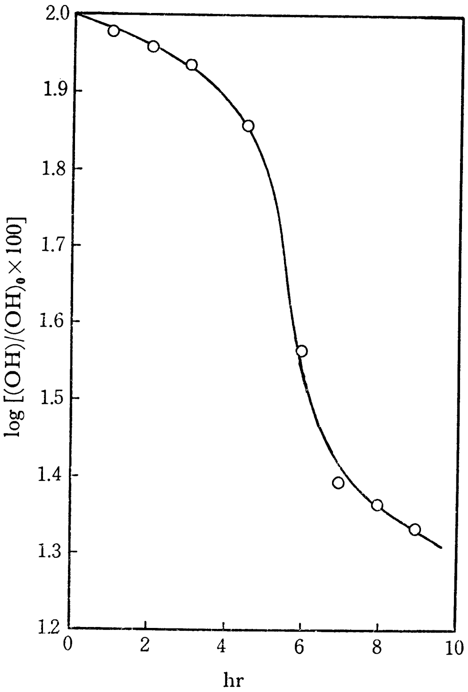

Fig. 4. Effect of carbon dioxide on exchange reaction of HX 3660: reaction temperature; 280°C, pressure of CO_2; 1.34 cmHg, pressure of D_2; 2.08 cmHg.

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Fig. 4. The rate equation cannot be expressed by Eq. (1) or (2) in this case. The reaction rate gradually becomes fast and then slows down with the progress of the exchange reaction. The decrease in the rate is not due to a opposite reaction, because a large excess of deuterium is present during exchange reactions. The effect of carbon dioxide may be interpreted in terms of the interaction between deuterium and carbon dioxide, and in terms of the competitive adsorption of two gases.

A compensation effect is found in this reaction. Figure 5 shows the relation between E_a and $\ln A$. The linear relations between ΔS_a and ΔH_a, and also between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ hold. Generally, k is considered to be variable in a series of reactions. Therefore, the compensation effect may result from compensatory relations of both k and K. When the apparent rate constant is expressed by kK, a normal compensation effect occurs; when it is expressed by k/K, an anti-compensation effect can occur under specific conditions.

With regard to the detailed mechanism of the exchange, the information presently available is not sufficient to establish it with any certainty. It is conceivable, however, that a proton of the hydroxyl group interacts with an adsorbed deuterium molecule, forms a triatomic intermediate, and removes a HD molecule, with the consequent formation a OD group.

Conclusions

The hydroxyl groups occurring at 3660 cm^{-1} on HX and HY zeolites were more readily exchanged with deuterium than were the other hydroxyl groups on the two zeolites. However, in the case of CaHX, the order of activities of each hydroxy group was changed with the pressure of deuterium; this fact is considered to be ascribable to the effect of calcium ions.

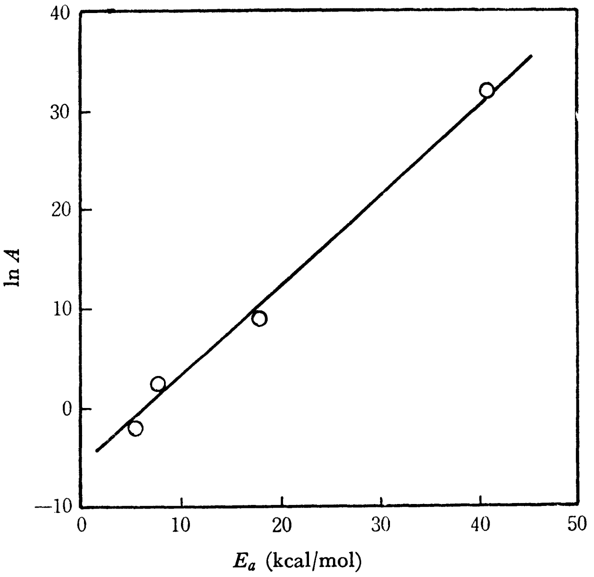

Fig. 5. Compensation effect.

The rate equation for the reaction is expressed by a Langmuir-type equation. This fact indicates the homogeneity of each hydroxyl group on zeolites, contraty to the case with η-alumina. The adsorbed water and carbon dioxide catalyzed the exchange reaction. The adsorbed water accelerates the reaction by the exchange reaction between the proton of the water molecule and the deuteron of the deuterium molecule, but it also shields the electrostatic field, with a consequent deactivation of adsorbed deuterium.

It was found that the compensation effect holds for k, k', and K in this exchange reaction. In general, this effect may result from the existence of the compensatory relation between the entropy and the enthalpy.