Infrared study of H/D isotope exchange reaction of alkanes and Brønsted acidic hydroxyl groups on FER zeolite

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H/D isotope exchange between n-alkanes and the acidic OD groups in ferrierite was observed by infrared spectroscopy. The real activation energies were estimated by adding the heats of adsorption to the apparent activation energies, resulting in almost the same value for all n-alkanes. The transition state for the reaction is discussed.

Keywords: IR, isotope exchange, Brønsted acid, hydroxyl groups, zeolites

1. Introduction

Infrared (IR) spectroscopy is one of powerful methods to investigate the properties of zeolites [1]. The observation of probe molecules adsorbed on hydroxyl groups in zeolite pores is a representative method for the characterization of zeolites. N_2, CO and other small molecules with weak basicity have been used as probes, which can detect strong acid sites even in small pores [2–10]. We have further applied the IR method to the examination of the behaviors of olefins with Brønsted acidic OH groups on H-form zeolites such as initial interaction, stable adsorption and reactions, which were observed below room temperature [11–13]. More practical investigations are, however, on the behavior of zeolites at high temperature because the substantial catalytic reactions of zeolites occur above 673 K [14].

Isomerization of hydrocarbons is a representative reaction over zeolites at high temperatures. Adsorption of alkanes in the pores of zeolites has been examined by the measurements of heat of adsorption and quantum chemical calculations [15–20]. Although ZSM-5 with MFI structure and Y zeolite with FAU structure have been well investigated, zeolites with small pores are still limited [15]. Ferrierite (FER) has been found to show higher selectivity for isomerization of n- to isobutene than ZSM-5 due to its specific pore size (10-membered ring 5.4×4.2 Å, and 8-membered ring 4.8×3.5 Å) [21–23]. It is thus regarded as an interesting issue to study the behavior of hydrocarbons interacting in the small pores of FER.

We recently reported that the quantitative analysis by FT-IR of the high-temperature behavior of Brønsted acidic OH groups became improved [24]. Taking an advantage of the method, we report in this paper on the H/D isotope exchange reaction of the acidic OD groups on FER with alkanes.

2. Experimental

For the sake of *in situ* IR investigations, FER zeolite (Tosoh Corp., $SiO_2/Al_2O_3 = 17.0$) was pressed into a self-supporting disk, then placed in a quartz-made cell connected to a conventional closed circulation system. All sample disks were pretreated at 773 K with exposure to 100 Torr of O_2 gas for 1 h, and then evacuated at the same temperature for 1 h. For detecting the isotope exchange reaction with alkanes, acidic OH groups on FER were deuterated at 673–748 K (higher temperature than the exchange reaction) with 100 Torr of D_2 (purity >99.95%) for 1 h. IR spectra of FER before and after D_2 treatment are shown in figure 1. Almost all the acidic OH groups were exchanged to OD, while about half of the neutral silanol still remained. 100 Torr of methane (Tokyo Gas Chem.

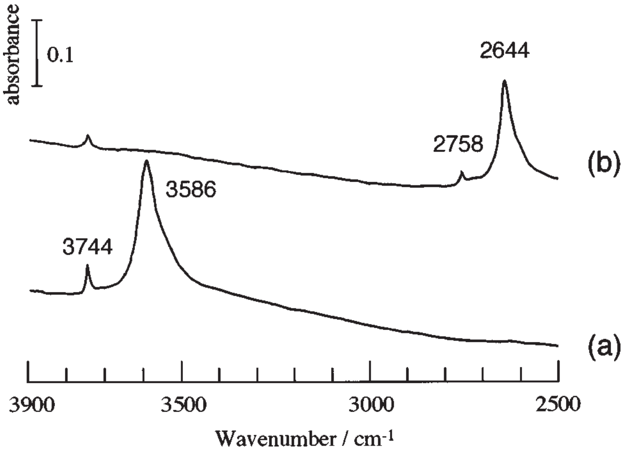

Figure 1. IR spectra of (a) H- and (b) D-FER.

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Corp., purity 99.5%), ethane (Takachiho Chem. Corp., purity 99.5%), propane (Sumitomo Kasei Corp., purity 99.5%) and hexane (Aldrich, purity >99%) were introduced at 598–748 K, and the decrease and increase of the acidic OD and OH bands were observed for 30 min.

IR spectra were measured using a JASCO FT/IR-7000 spectrometer with an MCT detector. All spectra were collected with 4 cm^{-1} of resolution and 64 average scans. An IR spectrum of a vacant cell under vacuum measured at room temperature was used as a background spectrum.

3. Results

After introduction of alkanes, the decrease and increase of the acidic OD and OH bands were observed. Time courses of the isotope exchange reaction were measured by integrating the intensity of the acidic OD and OH groups on FER, and an example in case of ethane is shown in figure 2. Although several kinds of OH groups were reported to exist on FER [25], there was too much uncertainty to deconvolute a broad band (figure 1) into several bands for quantitative interpretation of separate OD/OH groups. Therefore, total intensities of the band at 2644 (OD) and 3586 (OH) cm^{-1} were integrated. As shown in figure 2, a good coincidence between the decrease of OD groups and the increase of OH groups was obtained at each temperature. The ratio of the molar absorption coefficient ($\varepsilon_{OH}/\varepsilon_{OD}$) was estimated from the ratio of the intensities of decreased OD band and increased OH band as 1.50. The quantitative analysis shown below was performed using the OD band due to its better signal to noise ratio.

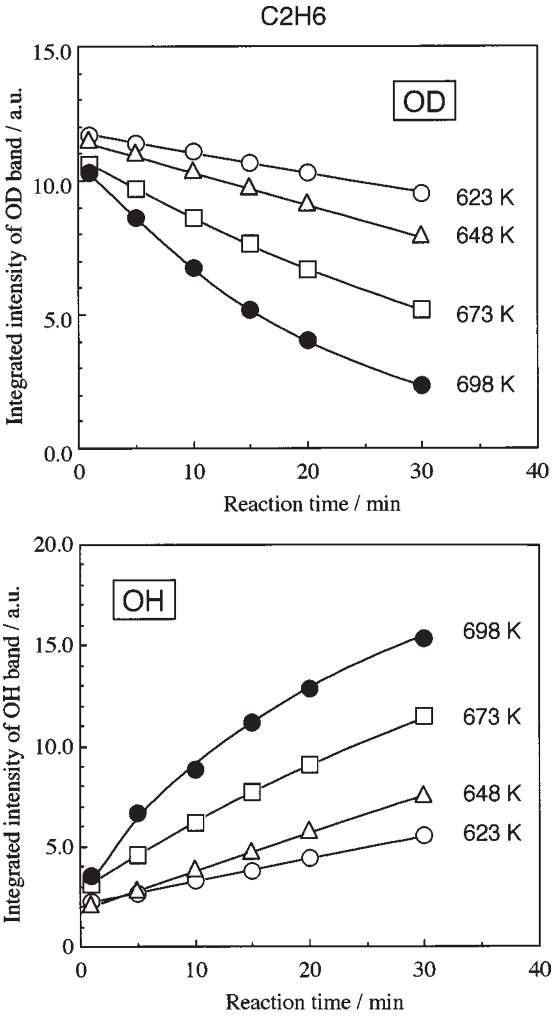


Figure 2. Time courses of the decrease and increase of the acidic OD and OH bands on D-FER during the isotope exchange reaction with C_2H_6 at various temperatures.

The dependence of the rate of the isotope exchange reaction (r) on the concentration of the acidic OD groups ([OD]) was found to be unity, which was demonstrated by linear dependence of the logarithm of the integrated intensity of OD groups on the time course (figure 3) at all temperatures. This is in good agreement with the isotope exchange reaction of acidic OD groups on deuterated ZSM-5 with n-butane [26], and indicates that the reaction proceeded homogeneously in spite of the existence of several OH species on FER [25].

The rate constant at each temperature was estimated from the integrated intensity at time t, $[OD]_t$, and the integrated intensity before introduction of alkane, $[OD]_0$, through the equation

$$\frac{[OD]_t}{[OD]_0} = \exp(-kt), \tag{1}$$

where k represents the rate constant. The apparent activation energies of the isotope exchange reaction of the acidic OD groups with alkanes were obtained by Arrhenius plots, as shown in figure 4. The obtained apparent activation energies are summarized in table 1 together with the heats of adsorption and estimated real activation energies. The values in table 1 are also plotted in figure 5. Heats of adsorption of n-alkanes (C_3–C_6) on FER (open triangles in figure 5) were measured by calorimetry and the values increase in proportion to the increase of the carbon number by 10 $kJ\,mol^{-1}$ per carbon (the straight line in figure 5) [18].

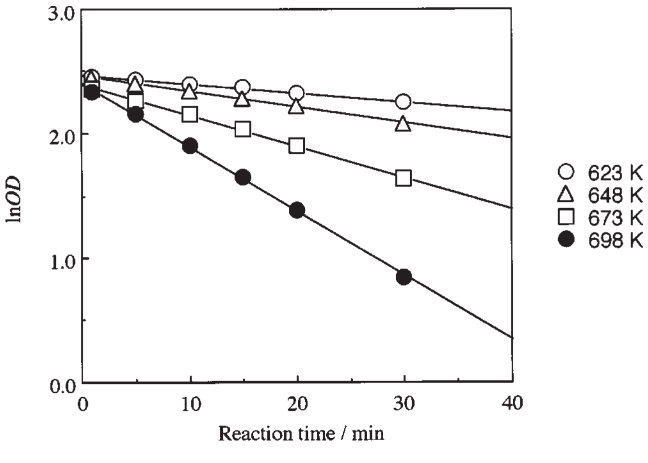


Figure 3. The linear dependence of the rates of the isotope exchange reaction between the acidic OD groups and C_2H_6 on the OD fraction.

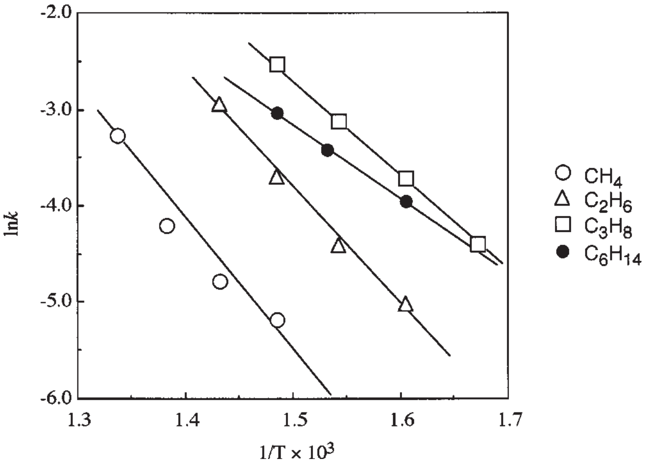


Figure 4. Arrhenius plots for the isotope exchange reaction between alkanes and the acidic OD groups.

Table 1
Apparent activation energy for isotope exchange reaction of OD groups on FER and alkanes.

Alkane	Apparent activation energy[a] (kJ mol^{-1})	Heat of adsorption[b] (kJ mol^{-1})	Estimated real activation energy[c] (kJ mol^{-1})
CH_4	107 ± 16	29	136
C_2H_6	101 ± 6	39	140
C_3H_8	81 ± 8	49	130
C_6H_{14}	64 ± 5	79	143

[a] This study.
[b] Estimated from [8].
[c] Obtained by sum of apparent activation energy and heat of adsorption.

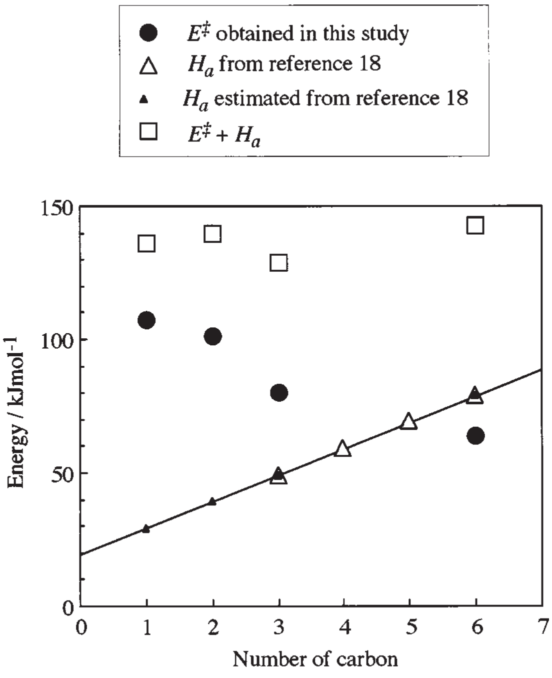


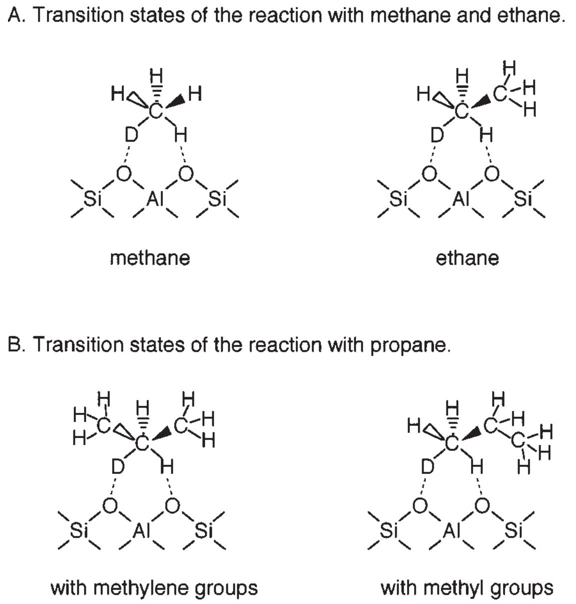
Figure 5. Obtained apparent activation energies (●), heats of adsorption (△ and ▲) and estimated activation energies for the rate-determining step (□).

Therefore, extrapolated values for CH_4 and C_2H_6 (filled triangles) were used for estimation of the energy differences between the adsorbed and the transition states. The energy differences were estimated as sums of apparent activation energies and heats of adsorption (open squares). As seen in figure 5, the activation energies for the rate-determining step of the H/D isotope exchange reaction of the acidic OD groups with CH_4, C_2H_6, C_3H_8 and C_6H_{14} appeared almost the same, in the range of 130–143 kJ mol^{-1}.

4. Discussion

The mechanism of H/D isotope exchange reaction of the acidic OH (OD) groups with D- (H-) alkanes has been discussed together with those of hydride transfer, dehydrogenation and cracking, based on the results of quantum chemical calculations [27–31]. The concerted mechanism was first proposed for isotope exchange reaction of CD_4 and acidic OH groups, where each H and D atom in pentacoordinated transition state interacted with two O atoms in the lattice [27,28]. Then, the evaluation of the nature and geometry of transition states of reactions of alkanes with the acidic OH groups was extended to C_2H_6, which could compare isotope exchange, dehydrogenation and cracking [29,30]. Kazansky et al. concluded that the isotope exchange of ethane was also a concerted reaction, and that the charge of the alkyl fragment was rather negative [29] or covalent [30,31], in contrast to those of dehydration and cracking with positively charged hydrocarbon transition states. They also pointed out an interesting proposal that the isotope exchange was not an acid-catalyzed reaction but represented as a concerted mechanism which was intermediate between acid and base catalysis [29].

The almost the same energy barriers for H/D isotope exchange reaction of CH_4 and C_2H_6 with the acidic OD groups in the present study may be explained by the results of quantum chemical calculations [30], which concluded that the effect of a carbonium ion stabilization due to the attachment of one additional carbon atom was not really important for this reaction. In other words, the predicted transition state for H/D isotope exchange reaction, covalent and carbonium ion geometry, is experimentally supported in this study (scheme 1(A)). In the case of C_3H_8 and C_6H_{14}, two opportunities are open for the isotope exchange reaction, on primary and secondary carbons (scheme 1(B)). The reaction on the secondary carbon would be favored, if the transition states were carbenium ions. A large energy difference between the primary and the secondary carbons was reported experimentally [32] and theoretically [31]. In such a case, the activation energy for C_3H_8 and C_6H_{14} should be much smaller than those of methane and ethane. However, they also appeared almost the same as CH_4 and C_2H_6. This fact further supports the proposed structure and nature of the transition state for H/D isotope exchange reaction of alkanes with the acidic hydroxy groups [27–31]. In summary, the mechanism of H/D isotope exchange reaction of


A. Transition states of the reaction with methane and ethane.

B. Transition states of the reaction with propane.

Scheme 1. Proposed transition states for the H/D isotope exchange reaction of the acidic OD groups with alkanes.

light alkanes with the acidic OD groups was proposed to be concerted and the hydrocarbon fragments in transition states were supposed to be covalent, by good agreement of the prediction from quantum chemical calculations and the experimental results obtained in this study, where the activation energies for the rate-determining step for all the n-alkanes resulted in almost the same value.

5. Conclusions

H/D isotope exchange reaction between n-alkane (CH_4, C_2H_6, C_3H_8 and C_6H_{14}) and the acidic hydroxy groups on D-FER was studied by IR spectroscopy. The real activation energy for isotope exchange reaction was estimated by adding the heat of adsorption of each alkane, and all of them appeared almost the same value (130–143 $\mathrm{kJ\,mol^{-1}}$). By comparison with the recent results of the quantum calculations, the isotope exchange reaction was considered to proceed via a concerted mechanism through the covalent transition state with penta-coordinated geometry, where the effect of the difference of the alkyl groups in chain length and that between primary and secondary are small.

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