

FT-IR Study of H_2^{16}O and H_2^{18}O adsorption on H-ferrierite

Byongjin Lee ^a, Junko N. Kondo ^a, Kazunari Domen ^{a,*}, Fumitaka Wakabayashi ^b

^a *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226, Japan*

^b *Department of Science and Engineering, National Science Museum, 3-23-1 Hyakunin-cho, Shinjuku-ku, Tokyo 169, Japan*

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Abstract

The adsorption structure of water on H-ferrierite at room temperature was investigated with Fourier transform infrared spectroscopy using H_2^{16}O and H_2^{18}O . From the isotope shifts, three bands from 3000 to 1500 cm^{-1} were conclusively assigned to the so-called A, B, C triplet of the hydrogen-bonded complex of water and the Brønsted acid hydroxyl groups on zeolites. The shifts of other bands also confirmed that the structure of adsorbed water molecules on H-ferrierite is the hydrogen-bonded one. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ferrierite; FT-IR; Water adsorption; Hydrogen-bonded model; Protonated model; Isotope labeling

1. Introduction

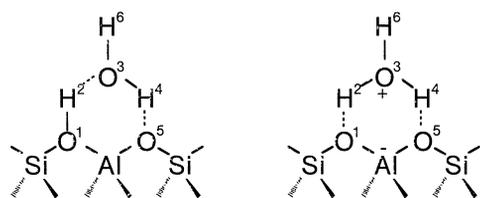
Structures of adsorbed water molecules on zeolites have been extensively studied, and two models have been proposed; the hydrogen-bonded [1] and the protonated models [2] (Scheme 1). The IR spectra of H_2O on H-form zeolites could be explained by both models [1,2]. We experimentally demonstrated using H_2^{18}O that the hydrogen-bonded model was appropriate for water adsorption on H-ZSM-5 [3]. Although H_2^{18}O adsorption in H-ZSM-5 was successfully explained by the hydrogen-bonded model, recent theoretical study of methanol in ferrierite suggests possibility of the favorable protonated structure of water in the zeolites having smaller channel structures [4].

H-ZSM-5 has a three-dimensional channel structure which consists of straight ($5.3 \text{ \AA} \times 5.6 \text{ \AA}$) and sinusoidal channels ($5.1 \text{ \AA} \times 5.5 \text{ \AA}$) [5]. On the other hand, ferrierite has a two-dimensional channel system, where the sizes of the channels are smaller than H-ZSM-5; 10-ring ($5.4 \text{ \AA} \times 4.2 \text{ \AA}$) and 8-ring ($4.8 \text{ \AA} \times 3.5 \text{ \AA}$). The smaller channel structure and the local composition of ferrierite might cause different electrostatic field from H-ZSM-5 [6], which may possibly protonate adsorbed water molecules. In this study we used IR method for the clarification of the structure of adsorbed water molecules on Brønsted acid sites of H-ferrierite.

2. Experimental

Self-supporting disks of H-ferrierite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 17.0$) provided by Toso were made for

* Corresponding author.



(a) hydrogen-bonded model (b) protonated model

Scheme 1. Two proposed model structures of water adsorption on H-form zeolites. (a) Hydrogen-bonded model; (b) Protonated model.

the sake of in-situ IR investigation. A sample disk was placed in a quartz-made IR cell and pretreated at 773 K as previously reported [3]. H_2^{16}O and H_2^{18}O were introduced at room temperature and circulated for 30 s, then evacuated for more than 5 min before IR measurements. IR spectra were recorded on a JASCO FT/IR-7000 spectrometer using an MCT detector with a spectral resolution of 4 cm^{-1} and by averaging 64 scans.

3. Discussion

Adsorption of H_2^{18}O reveals the interaction between the OH group on zeolites and water molecules very clearly. For instance, a subtracted IR spectrum of adsorbed H_2^{16}O molecules on H-ZSM-5 showed the OH stretching bands at 3704 and 3552 cm^{-1} which were assigned to $\nu(\text{O}^3\text{H}^6)$ and $\nu(\text{O}^3\text{H}^4)$ modes, respectively (Fig. 1), in both adsorption models (Scheme 1). The broad bands at 2877 and 2463 cm^{-1} were originated from the A, B, C triplet in the H-bonded model [1] (C band could not be observed in the case of H-ZSM-5) or from $\nu_a(\text{H}^2\text{O}^3\text{H}^4)$ and $\nu_s(\text{H}^2\text{O}^3\text{H}^4)$ modes in the protonated model [2], respectively. In the case of the IR investigation by isotope labeling to D_2O , it is difficult to distinguish the OH groups of zeolite and OD of water molecules due to a rapid isotope exchange reaction. However, H_2^{18}O adsorption is very useful since the shift

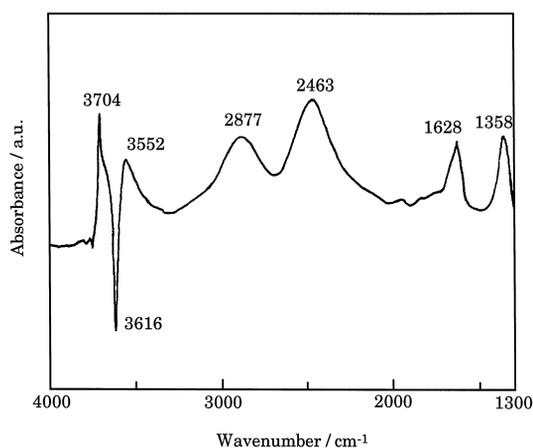


Fig. 1. Subtracted IR spectrum of H_2O adsorption (0.5 Torr) on H-ZSM-5 at 303 K.

of IR band of O^3 in Scheme 1 would be easily distinguishable.

Fig. 2b and c show FT-IR spectra of H_2^{16}O and H_2^{18}O adsorption on H-ferrierite at 303 K. Fig. 2a is a background spectrum of H-ferrierite before water adsorption. The bands at 3750 and 3604 cm^{-1} in Fig. 2a are originated from the terminal and bridging OH groups on H-ferrierite. Terminal OH band showed no difference between H_2^{18}O and H_2^{16}O adsorption. The

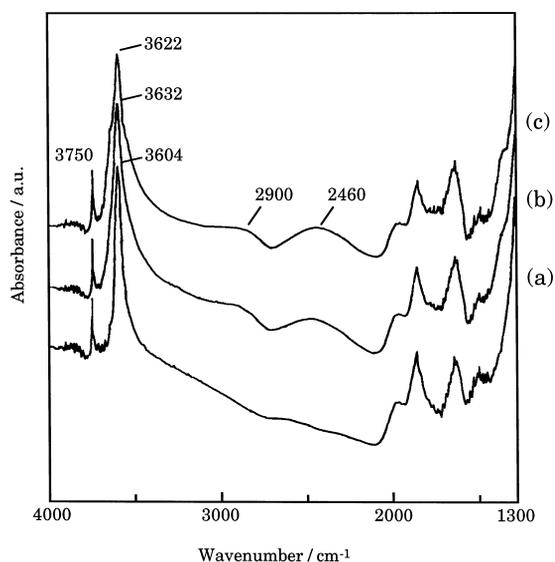


Fig. 2. FT-IR spectra of H-ferrierite (a), and (a) with 0.1 Torr of H_2^{16}O (b) and H_2^{18}O (c) at 303 K.

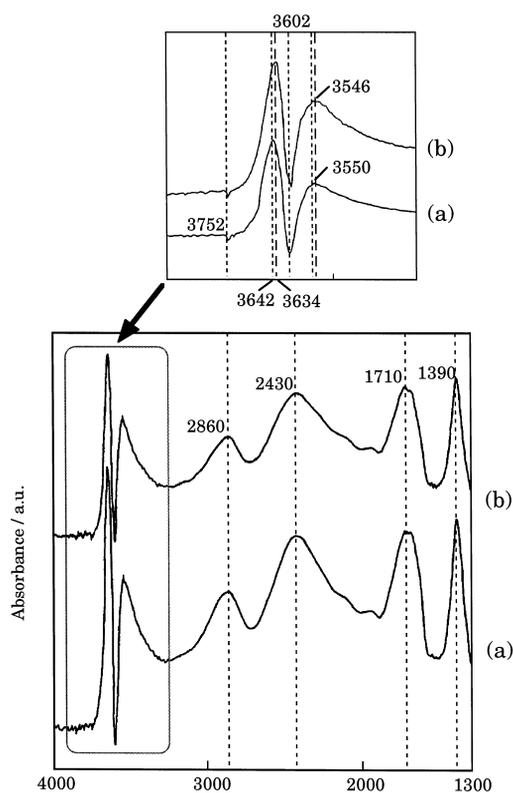


Fig. 3. Subtracted spectra of H_2^{16}O (a) and H_2^{18}O (b) adsorption on H-ferrierite.

bridging OH band, known as the Brønsted acidic sites, shifted to the higher frequency by the water adsorption, which is due to the interaction of water molecules (Fig. 2b and c). The band shifted from 3632 to 3622 cm^{-1} by changing

the adsorbate from H_2^{16}O to H_2^{18}O . The absorption bands from 3300 to 2000 cm^{-1} region were too weak to judge the shifts by H_2^{16}O and H_2^{18}O adsorption, since only small amounts of water were introduced for a short contact time. Three bands from 2000 to 1300 cm^{-1} have been originated by the framework of zeolite (Si–O combinations and overtone) [7].

More significant features of IR spectra of water adsorption were demonstrated in the subtracted spectra. Fig. 3a and b show subtracted spectra of H-ferrierite in evacuation (Fig. 2a) from those with adsorbed H_2^{16}O (Fig. 2b) and H_2^{18}O (Fig. 2c). All of the observed bands were regarded as in the same analogy to the result of H-ZSM-5 (Fig. 1), and the observed frequencies are summarized in Table 1. Negative bands at 3602 cm^{-1} is due to the decrease of bridging OH groups by indication with water molecules. The bands at 2860, 2430, and 1710 cm^{-1} did not shift from H_2^{16}O to H_2^{18}O adsorption, which confirms the assignment of the bands to the so-called A, B, C triplet. Therefore, these bands were not explained by the $\nu_a(\text{H}^2\text{O}^3\text{H}^4)$, $\nu_s(\text{H}^2\text{O}^3\text{H}^4)$, and $\delta_a(\text{H}^2\text{O}^3\text{H}^6)$ modes in the protonated model, and adsorbed water on Brønsted acid sites of H-ferrierite is concluded to be hydrogen-bonding.

In the case of H_2^{18}O adsorption on H-ZSM-5, the C band at around 1700 cm^{-1} was not appeared but 1629- cm^{-1} band was observed,

Table 1
Comparison of IR bands from the H_2^{18}O and H_2^{16}O adsorption on H-ferrierite and H-ZSM-5 at 303 K

H-ferrierite			H-ZSM-5 ^a			Origin	Assignment
Observed bands (cm^{-1})		Frequency ratio	Observed bands (cm^{-1})		Frequency ratio		
H_2^{16}O	H_2^{18}O	$\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$	H_2^{16}O	H_2^{18}O	$\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$		
3642	3602	0.9890	3698	3686	0.9968	water	$\nu(\text{O}^3\text{H}^6)$
3550	3546	0.9988	3582	3573	0.9975	water	$\nu(\text{O}^3\text{H}^4)$
2860	2860	1.000	2877	2877	1.000	zeolite	A ^b
2430	2430	1.000	2463	2463	1.000	zeolite	B ^b
1710	1710	1.000				zeolite	C ^b
			1629	1624	0.9969	water	$\delta(\text{HOH})$
1390	1390	1.000	1353	1353	1.000	zeolite	$\delta(\text{O}^1\text{H}^2)$

^aRef. [3].

^bRef. [1].

which shifted by the H_2^{18}O adsorption (Fig. 1). Hence, we considered the band was not the C band of the A, B, C triplet but related to the HOH bending, $\delta(\text{HOH})$, mode of the physisorbed species in the microcavities[3]. A, B, C triplet has been generally considered as the Fermi resonance [8], and relative intensities of A, B, C bands change gradually from $I_A \cong I_B \gg I_C$ to $I_A < I_B \cong I_C$ with the enhancement in hydrogen bond [9]. In the case of ferrierite, C band at 1710 cm^{-1} was clearly observed in contrast to the case of H-ZSM-5. Hence, it becomes clear that the interaction of the water molecules with acidic OH groups is stronger on H-ferrierite than H-ZSM-5; the C band of the adsorbed water is obviously observed on H-ferrierite. This result is in good agreement with the result of the molecular dynamics study which indicates the strong interaction of water molecules in the channel of ferrierite [10]. The 1390 cm^{-1} band has been attributed to the in-plane OH bending $\delta(\text{OH})$ band of the perturbed zeolitic OH groups [11].

Enlarged spectra in OH stretching region in the inset of Fig. 3 clearly show the shift of 3642- and 3550-cm^{-1} bands (a) to 3634- and 3546-cm^{-1} (b) by replacing H_2^{16}O to H_2^{18}O , respectively. Frequency ratio of $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ was 0.9988, which agrees with the isotope shift.

Invariability of the bands at 2860, 2430 and 1710 cm^{-1} for both H_2^{18}O and H_2^{16}O strongly supports the hydrogen bonded model is reasonable. Shift of $\nu(\text{O}^3\text{H}^6)$ from 3642 to 3634 cm^{-1} and unchanged $\delta(\text{O}^1\text{H}^2)$ band at 1390

cm^{-1} also support the hydrogen bonded model. Therefore, it is concluded that even for H-ferrierite with smaller channel structure than H-ZSM-5, hydrogen bonded model was appropriate for the water adsorption.

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