

## Active Sites for Isotopic Exchange of Oxygen between Proton-exchanged ZSM-5 Zeolites and Water

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Mass and infrared spectroscopy on the title reaction have indicated the presence of three kinds of framework oxygen ( $O^1$ ,  $O^2$  and  $O^3$ , corresponding to easily, moderately, and hardly exchanging oxygens respectively), of which  $O^1$  and  $O^2$  are bridging oxide ions bound to Al and exchangeable with water by the contribution of neighbouring proton, and  $O^3$  is a bridging oxide ion between two Si atoms.

Zeolites can readily exchange their lattice oxide ion with the oxygen of  $H_2O$ ,  $CO_2$ , and  $O_2$ , while keeping their highly crystalline frameworks.<sup>1-3</sup> Water molecules have an important role in the formation of aluminosilicate anions, which lead to the nucleation and crystallisation of zeolites.<sup>4,5</sup> In addition, zeolites can catalyse various reactions of hydrocarbons with oxygen-containing molecules.<sup>6-8</sup> It is important to clarify how the oxygen of the water molecules reacts with or is incorporated into the zeolite framework.<sup>9</sup> Here, oxygen exchange between water molecules and ZSM-5 zeolite has been investigated as a function of the Al content and the active sites for the exchange and the reaction mechanism is also elucidated.

Parent ZSM-5 (denoted as MFI) zeolites were supplied by Tosoh Corporation. Each proton-exchanged zeolite was abbreviated as MFI-23. The  $SiO_2/Al_2O_3$  ratios obtained by atomic absorption spectroscopy well agreed with those obtained by  $^{29}Si$  MAS NMR, showing that there is no extra framework aluminium ion on these zeolites.

The exchange was traced in a closed circulation system by a mass spectrometer. The circulation system was heated to suppress the adsorption of water on the glass wall. The sample was evacuated at 873 K for 30 min, exposed to  $O_2$  (40 kPa), evacuated again for 30 min, and then cooled to the reaction temperature. No dealumination occurred during the  $^{18}O$  exchange reaction. The IR spectra were measured at room temp. using a FTS-7 spectrometer (Bio-rad). It was assumed that the number of acidic OH groups was equal to that of the Al atoms in the zeolites. The number of the bridging oxide ions of Si-O-Al including acidic OH and Si-O-Si were calculated by  $4 \times$  (number of Al atoms) and [(total amount of the framework oxygen) -  $4 \times$  (number of Al atoms)], respectively (Table 1).

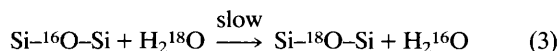
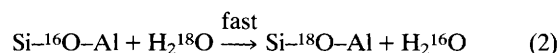
The  $^{18}O$  content in the gaseous water on the MFI zeolites at 573 K is shown as a function of the reaction time (Fig. 1). Initially the  $^{18}O$  content in steam steeply decreased, then gradually decreased, and finally reached an approximately constant value. The initial dramatic decrease in  $^{18}O$  content shows the existence of the easily exchangeable oxygen. The almost constant values at 300-420 min suggest that a portion of lattice oxygen hardly takes part in the exchange at 573 K.

The decrease in the  $^{18}O$  content is represented by eqn. (1) by Takaishi and Endoh<sup>2a</sup> and Yashima *et al.*<sup>2b</sup>

$$n_g dy_g/dt = -n_g y_g \sum k_i n_i (1 - y_i) + n_g (1 - y_g) \sum k_i n_i y_i \quad (1)$$

where the subscript g denotes the gaseous water, there are  $j$  kinds of framework oxygen,  $n$  is the number of oxygen atoms in each oxygen phase,  $k$  is the exchange rate constant, and  $y$  is the fraction of  $^{18}O$ .  $n_1 + n_2 + \dots + n_j$  correspond to the total oxide ion in zeolite framework.  $n_i$  and  $k_i$  are estimated by fitting the experimental data and the line of eqn. (1) calculated by Runge-Kutta method. As shown by the solid line in Fig. 1, the change in the  $^{18}O$  content fits well with the assumption that there are three kinds of framework oxygen,  $O^1$ ,  $O^2$ , and  $O^3$ . The experimental data could not be reproduced by using one or two kinds of framework oxygen. Therefore, MFI zeolites have at least three kinds of framework oxygen exchangeable with water molecules. The values of  $n_1$ - $n_3$  and  $k_1$ - $k_3$  obtained by eqn. (1) were hereafter used and listed in Table 1.

$n_i$  and  $k_i$  ( $i = 1-3$ ) of MFI-23 varied little at 573 K with the partial pressure of water vapour 0.8-1.9 kPa, showing that the rate-limiting step is not the diffusion of water vapour into the zeolite micropores. The values of  $k_1$ ,  $k_2$ , and  $k_3$  were in the range 5500-7000, 200-240, and 0.6-1.1, respectively. Clearly the respective values of  $k_i$  ( $i = 1-3$ ) were almost constant, or independent of the silica/alumina ratios. In contrast,  $n_1$ ,  $n_2$ , and  $n_3$  changed with the change in ratios:  $n_1$  and  $n_2$  decreased with increasing silica-alumina ratios while  $n_3$  increased.  $n_1 + n_2$  and  $n_3$  are approximately in agreement with the numbers of bridging framework oxygens of Si-O-Al and Si-O-Si, respectively (Table 1). Therefore, it is suggested that the exchange between Si- $^{16}O$ -Al and  $H_2^{18}O$  [eqn. (2)] is fast and the exchange between Si- $^{16}O$ -Si and  $H_2^{18}O$  [eqn. (3)] is slow at 573 K.



IR spectra of MFI-23 showed bands at 3735, 3612, 1219, and 1092  $cm^{-1}$  in  $\nu(OH)$  and  $\nu[Si-O-T(T = Si, Al)]$  regions when it was kept in contact with  $H_2^{16}O$  (1.7 kPa) at 573 K for 3 h followed by evacuation at the same temperature for 0.5 h. In comparison with literature values<sup>10,11</sup> each band can be assigned as follows; 3735  $cm^{-1}$ ,  $\nu(\text{silanol})$ ; 3612  $cm^{-1}$ ,  $\nu(\text{acidic OH})$ ; 1219 and 1092  $cm^{-1}$ ,  $\nu(Si-O-T)$ . The spectra varied when MFI-23 was kept in contact with  $H_2^{18}O$  (1.7 kPa) at 573

Table 1 Calculated values of  $n_1$ - $n_3$  and  $k_1$ - $k_3$ <sup>a</sup>

Zeolite	Number of Al and framework oxygen /mmol g <sup>-1</sup>			$n$ /mmol g <sup>-1</sup>			$k$ /min <sup>-1</sup> mol <sup>-1</sup>		
	Al	Si-O-Al	Si-O-Si	$n_1$	$n_2$	$n_3$	$k_1$	$k_2$	$k_3$
MFI-23	1.32	5.3	28.0	3.00	3.33	27.0	7000	200	1.1
MFI-40	0.78	3.1	30.2	1.13	1.33	30.8	5500	240	0.9
MFI-50	0.64	2.6	30.7	1.00	1.10	31.2	5500	240	0.6

<sup>a</sup> Reaction temperature, 573 K.

K for 3 h. The 3735, 1219, and 1092  $\text{cm}^{-1}$  bands little shifted, showing that the isotopic exchange of oxygen between water and SiOH or Si-O-T is slow. On the other hand, the band at 3612 shifted to 3606  $\text{cm}^{-1}$ , demonstrating that the exchange is fast.

The  $^{18}\text{O}$  content in each band was evaluated from the deconvolution of the IR band and the change with time (Fig. 2).<sup>†</sup> The  $^{18}\text{O}$  content in the acidic OH sharply increased and almost equaled that of the water vapour while those of silanol and Si-O-T increased little. The  $^{18}\text{O}$  contents decreased in the order of acidic OH  $\gg$  Si-O-T > silanol.

When the exchange was carried out on MFI-23 in a large excess of  $\text{H}_2^{18}\text{O}$  at 573 K, the  $^{18}\text{O}$  contents in the gaseous water and bands of acidic OH and Si-O-T after 5 h were 93, 92 (1.2  $\text{mmol g}^{-1}$ ), and 9.6% (3.1  $\text{mmol g}^{-1}$ ), respectively. Therefore, the total amount of  $^{18}\text{O}$  in MFI-23 was 4.3  $\text{mmol g}^{-1}$  and ca. four times greater than that of Al atoms in MFI-23 (1.3  $\text{mmol g}^{-1}$ ). The amount of  $^{16}\text{O}$  (inactive for the exchange, 29  $\text{mmol g}^{-1}$ ) was approximately in agreement with that of  $n_3$  (27  $\text{mmol g}^{-1}$ ).

It was concluded that  $\text{O}^1$  and  $\text{O}^2$  are bridging framework oxygen bound to Al, that the oxygen exchange of  $\text{O}^1$  and  $\text{O}^2$  with water is promoted by the neighbouring proton, and that  $\text{O}^3$  is a bridging framework oxygen between two Si atoms.

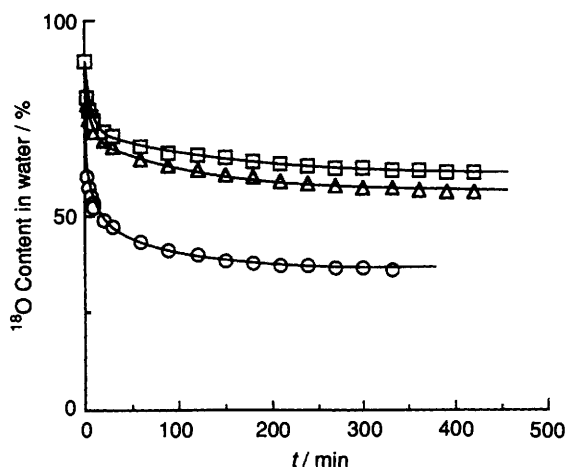


Fig. 1 Change of  $^{18}\text{O}$  contents in gaseous water at 573 K as a function of reaction time. Sample weight, 20 mg;  $\text{pH}_2\text{O}$ , ca. 1.9 kPa.  $\square$ , MFI-50;  $\Delta$ , MFI-40;  $\circ$ , MFI-23; —, calculated line.

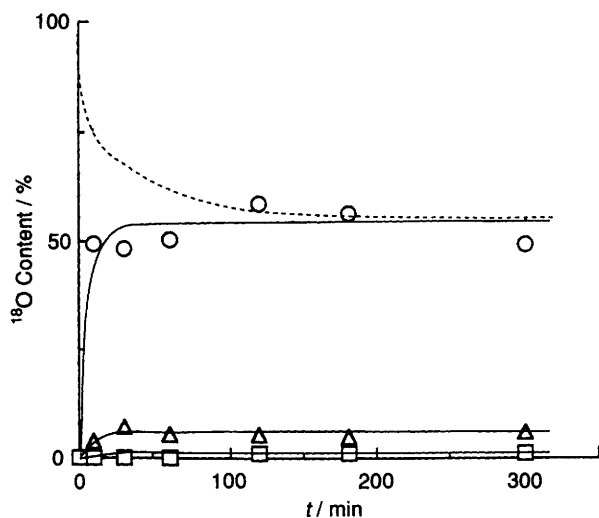
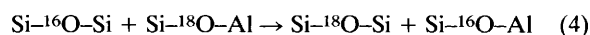


Fig. 2 Change of  $^{18}\text{O}$  contents in IR bands at 573 K as a function of reaction time.  $\circ$ ,  $\Delta$ ,  $\square$ , and --- correspond to  $^{18}\text{O}$  contents in the IR bands of  $\nu(\text{acidic OH})$ ,  $\nu(\text{Si-O-T})$ ,  $\nu(\text{SiOH})$ , and gaseous water, respectively. Sample, MFI-23.

This was further supported by the fact that the exchange hardly occurs with the parent zeolite Na-MFI.

The same reaction mechanism was also concluded for mordenite and L-type zeolites. The difference between  $n_1$  and  $n_2$  may result from protruded and shielded Si-O-Al oxide ions, respectively.

When MFI-23, which was kept in contact with  $\text{H}_2^{18}\text{O}$  at 573 K for 2 h and then evacuated at the same temperature for 0.5 h, was heated to 873 K with evacuation, the IR spectrum varied: The acidic OH bands at 3607  $\text{cm}^{-1}$  shifted to the higher frequency of 3609  $\text{cm}^{-1}$ , while the 3735  $\text{cm}^{-1}$  band shifted little and the band for  $\nu(\text{Si-O-T})$  red-shifted. The band intensities of OH changed little by the evacuation up to 873 K, showing that the dehydration from the OH species to yield an oxide ion and  $\text{H}_2\text{O}$  did not occur. Quantitative analysis of the IR spectra confirmed that the amount of  $^{18}\text{O}$  increase in the bridging framework oxygens, 0.32  $\text{mmol g}^{-1}$ , approximately agreed with the decrement in acidic OH bands 0.35  $\text{mmol g}^{-1}$ . Therefore, the oxygen exchange of  $\text{O}^1$  and  $\text{O}^2$  with  $\text{O}^3$  proceeds at higher temperature as shown in eqn. (4). This was further confirmed by the fact that  $n_1$ - $n_3$  of MFI-23 slightly changed between 423 and 673 K and greatly changed at and above 773 K.



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#### Footnote

<sup>†</sup> The  $^{18}\text{O}$  contents in the bands are estimated from the spectra. Here, for convenience the  $\nu(\text{acidic OH})$  and  $\nu(\text{Si-O-T})$  regions of MFI zeolites were separated into 3670, 3612, and 3562  $\text{cm}^{-1}$  bands and 1219, 1173, and 1092  $\text{cm}^{-1}$  bands, respectively. This does not affect the later discussion since the  $^{18}\text{O}$  content of acidic OH was calculated by the sum.

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