

## TEMPERATURE-PROGRAMMED DESORPTION STUDY OF MOLECULAR OXYGEN ADSORBED ON MFI-TYPE ZEOLITES

Myung Hun Kim, Sun Jin Kim, Suk Bong Hong<sup>†</sup>, Gon Seo\* and Young Sun Uh<sup>†</sup>

Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

\*Department of Chemical Technology, Chonnam National University, Kwangju 500-757, Korea

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**Abstract** – The adsorption of molecular oxygen at room temperature on the proton form of MFI zeolites with different Si/Al ratios has been investigated by temperature-programmed desorption (TPD). The internal Si-OH defects (silanol groups) in these zeolites are found to serve as O<sub>2</sub> adsorption sites. The apparent activation energies (17.5-21.8 kcal·mol<sup>-1</sup>) of desorption determined from O<sub>2</sub> TPD measurements reveal that the extent of interactions between the Si-OH defects and the adsorbed O<sub>2</sub> molecules becomes weaker with decreasing Al content in the zeolite.

Key words : MFI Zeolites, Internal Silanol Groups, O<sub>2</sub> Adsorption, TPD

### INTRODUCTION

Understanding the nature of hydroxyl groups in zeolites is the starting point for a comprehensive investigation of the relationships between the acidity and catalytic activity of this important class of microporous materials [Corma, 1995; Venuto, 1994]. Therefore, the characterization of these hydroxyl groups has been one of the main concerns in zeolite science and technology [Farneth and Gorte, 1995; Engelhard and Michel, 1987]. Most of the hydroxyl groups observed in zeolites are directly connected to their structural elements and variously influenced by the metal cations balancing the framework negative charges. In addition, some of them are held as part of extraframework metal cation complexes or Al species ejected from the zeolite structure.

Typically, three different types of structural hydroxyl groups can exist in zeolites: (i) bridging hydroxyl groups which act as Brønsted acid sites are protons associated with negatively charged framework oxygens linked into adjacent Al and Si atoms, i.e., Si-OH-Al bridges, (ii) internal Si-OH defects generated by hydrolysis of Si-O-Si linkages, missing framework Al or Si atoms, stacking faults, disorder, etc., and (iii) terminal Si-OH groups that are always present at the external surface of the zeolite crystals. Among these types of hydroxyl groups, internal Si-OH defects as well as bridging hydroxyl Brønsted acid sites are known to influence many important properties of zeolites, such as their ion exchange and adsorption properties [Chester et al., 1985; Moser et al., 1989; Hong et al., 1996]. While there are extensive references on the physico-chemical properties of bridging hydroxyl Brønsted acid sites in zeolites, much fewer investigations to date involving internal Si-OH defects have been reported [Woolery et al., 1986; Dessau et al., 1987].

The purpose of this work is to elucidate the nature and

extent of interactions between the internal Si-OH defects and the adsorbate molecules in zeolites. Here we report the results obtained from temperature-programmed desorption (TPD) measurements of nonpolar O<sub>2</sub> molecules adsorbed on MFI zeolites with Si/Al ratio ranging from 14 to ∞.

### EXPERIMENTAL

Six MFI zeolite samples with different Si/Al ratios were used in this study. The proton form of two MFI zeolites with Si/Al ratios of 14 and 27 was obtained from ALSI-PENTA Zeolithe GmbH. The other four MFI zeolites with Si/Al ratio ranging from 50 to ∞ were synthesized using NaOH and tetrapropylammonium (TPA) bromide according to the procedures described elsewhere [Jacobs and Martens, 1987]. The Al content in the final product was varied by adjusting the amount of Al source added in the synthesis mixture. The pure-silica MFI sample (total Si/Al ratio > 18,000) was also prepared in the presence of NH<sub>4</sub>F and TPABr [Chezeau et al., 1989]. As-synthesized samples were calcined in flowing O<sub>2</sub> at 823 K for 12 h, refluxed twice in 1.0 M NH<sub>4</sub>NO<sub>3</sub> solutions for 6 h, and then calcined in air at 773 K for 12 h to ensure that the samples were in their complete proton form.

All MFI zeolites prepared here were phase pure and show high crystallinities as seen by X-ray powder diffraction using a Rigaku D/Max-IIA diffractometer (Cu K<sub>α</sub> radiation). Chemical analysis for Si and Al in these samples was performed by a Jarrell-Ash Polyscan 61E inductively coupled plasma (ICP) spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. The N<sub>2</sub> BET surface area measurements were performed on a Micromeritics ASAP 2000 analyzer. The crystal morphology and size were determined by a Hitachi Model X-650 scanning electron microscope.

Temperature-programmed desorption (TPD) of O<sub>2</sub> was recorded on a Micromeritics TPD/TPR 2900 analyzer. A given amount of the samples was first activated in flowing He at 773 K for 2 h. Then, pure O<sub>2</sub> (20 cm<sup>3</sup>·min<sup>-1</sup>) was passed over

<sup>†</sup>To whom all correspondence should be addressed.

E-mail : sbhong@kistmail.kist.re.kr or uhyoung@kistmail.kist.re.kr

the sample at room temperature for 0.5 h. The thermogravimetric analyses (TGA) determined by a Du Pont 950 thermogravimetric analyzer reveal that the water content of MFI zeolites used here is in the range of 3-12 wt%, depending on their framework Si/Al ratios. Thus, the amount of the samples placed into the TPD cell was varied from 0.31 to 0.34 g in order to ensure that all samples after activation had the exactly the same weight, i.e., 0.30 g. The treated samples were subsequently purged with He at 373 K for 2 h to remove the physisorbed O<sub>2</sub>. Finally, the TPD curves were obtained in flowing He (30 cm<sup>3</sup>·min<sup>-1</sup>) from 373 to 873 K with heating rates ranging from 5 to 30 K. In all TPD experiments the desorbed gas was identified as O<sub>2</sub> alone by a Balzers MSC 200 mass spectrometer.

## RESULTS AND DISCUSSION

Fig. 1 shows the TPD curves of O<sub>2</sub> adsorbed at room temperature on the proton form of six MFI zeolites with different Si/Al ratios, which were recorded at a heating rate of 20 K·min<sup>-1</sup>. All MFI samples used in obtaining the TPD curves in Fig. 1 were prepared by the conventional method which includes the addition of OH<sup>-</sup> ions as mineralizing agents in the synthesis mixture. Fig. 1a was obtained from the MFI(I) sample with a Si/Al ratio of 14. No detectable desorption peaks are observed. As seen in parts b-f of Fig. 1, however, one desorption peak begins to appear in the temperature region of 530-640 K with increasing Si/Al ratio in the zeolite. This clearly shows that one particular type of O<sub>2</sub> adsorption sites is developed when the Al content in MFI zeolites is gradually lowered.

Typically, the amount of basic adsorbates desorbing above some characteristic temperature in the TPD measurement is taken as the acid-site concentration, and the temperature at peak maximum (T<sub>M</sub>) of desorption peaks has been used to determine heats of desorption that are medietely related to the acid strength distribution. The amounts of desorbed O<sub>2</sub> for the proton form of MFI zeolites with Si/Al ratios higher than 14 were evaluated from their TPD peak areas and are listed in Table 1. These data reveal that the amount of desorbed O<sub>2</sub> molecules becomes larger with decreasing Al con-

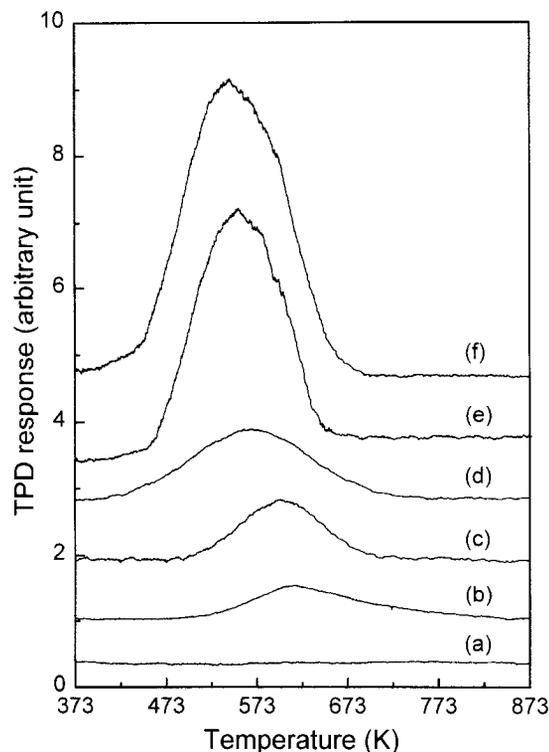


Fig. 1. O<sub>2</sub> TPD curves from the proton form of MFI zeolites with different Si/Al ratios: (a) MFI(I), (b) MFI(II), (c) MFI(III), (d) MFI(IV), (e) MFI(V), and (f) MFI(VI) samples. The heating rate is 20 K·min<sup>-1</sup>.

tent in the MFI zeolite. Therefore, it is most likely that the desorption peaks in Fig. 1 are not due to O<sub>2</sub> adsorbed on bridging hydroxyl Brønsted acid sites generated by the presence of Al atoms in their framework, because the potential number of Brønsted acid sites in zeolites becomes smaller with decreasing the framework Al content. This can be further supported by the fact that the smaller Al content the zeolite has, the lower T<sub>M</sub> value of desorption peak it shows. The acid strength of bridging hydroxyls normally increases when there is a decrease in the number of Al atoms in next nearest neighbor positions of the Al atom which supports the Brønst-

Table 1. TPD results of O<sub>2</sub> adsorbed at room temperature on the proton form of MFI zeolites with different Si/Al ratios

Sample	Si/Al ratio	BET surface area <sup>a</sup> (m <sup>2</sup> ·g <sup>-1</sup> )	T <sub>M</sub> <sup>b</sup> (K)	V <sub>d</sub> <sup>c</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	No. of O <sub>2</sub> molecules (10 <sup>18</sup> ·g <sup>-1</sup> )	E <sub>a</sub> <sup>d</sup> (kcal·mol <sup>-1</sup> )
MFI(I)	14	379	-	-	-	-
MFI(II)	27	383	633	0.10	2.6	21.8
MFI(III)	50	398	603	0.12	3.1	19.6
MFI(IV)	150	400	571	0.16	4.3	19.2
MFI(V)	450	400	551	0.27	7.2	18.1
MFI(VI)	>18000	410	538	0.29	7.7	17.5
MFI(VII) <sup>e</sup>	>18000	416	-	-	-	-

<sup>a</sup>BET surface areas calculated from N<sub>2</sub> adsorption data.

<sup>b</sup>The temperature at maximum of desorption peaks in TPD curves that were recorded at a heating rate of 20 K·min<sup>-1</sup>.

<sup>c</sup>The amount of desorbed O<sub>2</sub>.

<sup>d</sup>The apparent activation energy of desorption.

<sup>e</sup>Prepared in the presence of F<sup>-</sup> ions.

ed acid site [Pine et al., 1984]. Thus, if the desorption peaks in parts b-f of Fig. 1 originate from O<sub>2</sub> adsorbed on Brønsted acid sites, they should appear in a higher temperature region with decreasing Al content. On the other hand, it is well-known that the number of terminal Si-OH groups on zeolite crystal surfaces varies as a function of crystal size [Breck, 1974]. In general, the smaller the crystal size, the larger the number of terminal Si-OH groups. The scanning electron microscopy reveals that the average crystal size of MFI zeolites used in obtaining the TPD curves in Fig. 1 becomes larger with decreasing Al content. Thus, the pure-silica MFI(VI) sample is the largest of all MFI zeolites and is composed of single, cubic crystals of approximately 20 μm. By contrast, the MFI(I) sample with the highest Al content consists of twined, slightly elongated prisms of 1-3 μm in crystal length. Recall that the TPD curve of the MFI(I) sample in Fig. 1a gives no noticeable desorption peaks, although this material has the highest concentration of terminal Si-OH groups among the MFI samples studied here. This led us to rule out the possibility that the Si-OH groups at the external surface of the zeolite crystals are responsible for the desorption peaks in Fig. 1.

Fig. 2 shows the TPD curves of O<sub>2</sub> on two pure-silica MFI zeolites that were synthesized using TPA cations together with and without NaOH, respectively. Fig. 2a is the same as Fig. 1f, which was obtained from the pure-silica MFI zeolite prepared with TPABr and NaOH. This curve exhibits one distinct desorption peak around 540 K. As seen in Fig. 2b, however, no detectable desorption peaks are observed from the pure-silica MFI sample prepared in a fluoride medium without adding OH<sup>-</sup> ions in the synthesis mixture. It has been re-

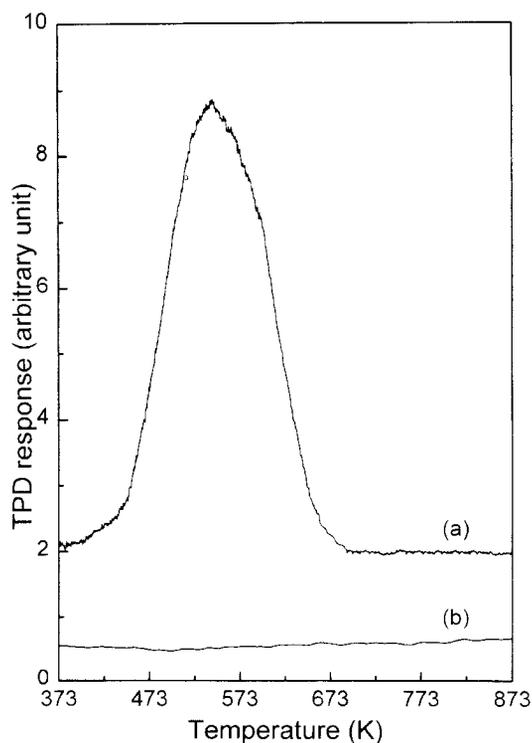


Fig. 2. O<sub>2</sub> TPD curves from pure-silica MFI zeolites prepared by (a) conventional and (b) fluoride methods. The heating rate is 20 K·min<sup>-1</sup>.

peatedly shown that the amount of internal Si-OH defects in MFI zeolites is greatly reduced by using F<sup>-</sup> ions instead of OH<sup>-</sup> ions as mineralizing agents [Chezeau et al., 1989]. This suggests that the absence of any noticeable desorption peaks in Fig. 2b may be due to the very small defect concentration in the pure-silica MFI sample prepared in the presence of F<sup>-</sup> ions. Therefore, it is most likely that the reason why MFI samples synthesized by using OH<sup>-</sup> ions as mineralizing agents exhibit desorption peaks (Fig. 1) is the presence of internal Si-OH defects serving as O<sub>2</sub> adsorption sites in these materials. On the other hand, the amount and nature of internal Si-OH defects in MFI zeolites are known to depend strongly on their framework Al content [Woolery et al., 1986; Dessau et al., 1987]. An early infrared spectroscopic study on MFI zeolites with different Si/Al ratios demonstrate that a broad band appearing in the region of 3,300-3,500 cm<sup>-1</sup> originates from internal Si-OH defects forming hydrogen bonds and that this band becomes stronger with its simultaneous shift to a higher wavenumber region, as the Si/Al ratio systematically varies from 35 to 13,000 [Woolery et al., 1986]. This clearly indicates that with decreasing Al content in the zeolite the number of internal Si-OH defects increases gradually, while the opposite arises in the strength of hydrogen bonds between internal Si-OH groups. Then, if such is the case, this may explain why the area and position of desorption peaks in Fig. 1 depend strongly on the Si/Al ratio of MFI zeolites.

It is well-established that the T<sub>M</sub> values of the desorption peaks in TPD curves are related to the apparent desorption energy (E<sub>d</sub>) of adsorbates. Considering only first-order interactions, the relationship between E<sub>d</sub> and T<sub>M</sub> can be expressed by the following equation [Cvetanovic and Amenomiya, 1967]:

$$2 \log T_M - \log b = E_d / 2.303RT_M + \log (E_d V_d / RK_o) \quad (1)$$

where b is the linear heating rate, V<sub>d</sub> is the amount of base at saturation, K<sub>o</sub> is the preexponential factor in the desorption rate expression, and R is the gas constant. Therefore, the E<sub>d</sub> value can be determined from the plots of (2 log T<sub>M</sub> - log b) vs. 1/T<sub>M</sub> when the T<sub>M</sub> is measured as a function of b. This analysis has been applied to the O<sub>2</sub> TPD peaks from five MFI zeolites with Si/Al ratios from 27 to ∞. The T<sub>M</sub> values of the respective desorption peaks become higher with increasing b from 5 to 30 K·min<sup>-1</sup>, while their V<sub>d</sub> values remain almost unchanged. Fig. 3 shows plots of (2 log T<sub>M</sub> - log b) vs. 1/T<sub>M</sub> for the O<sub>2</sub> TPD peaks from these five MFI zeolites. Notice that all the plots are characterized by straight lines, which is consistent with Eq. (1). The E<sub>d</sub> values determined from the slopes of plots in Fig. 3 are also given in Table 1. These data clearly show that the smaller the Al content the zeolite has, the lower the E<sub>d</sub> value of O<sub>2</sub> desorption it shows. As a result, the pure-silica MFI(VI) sample was found to have the lowest E<sub>d</sub> value (17.5 kcal·mol<sup>-1</sup>) among the MFI zeolites studied here. This indicates that the interaction of O<sub>2</sub> with internal Si-OH groups decreases with decreasing Al content in the zeolite. In addition, it should be noted that the E<sub>d</sub> values (17.5-21.8 kcal·mol<sup>-1</sup>) listed in Table 1 are higher than those (12.0-18.2 kcal·mol<sup>-1</sup>) of O<sub>2</sub> adsorbed on the paramagnetic defect centers in aluminophosphate molecular sieves [Kim et al., 1997], and are even higher than the energies (0.5-10.0

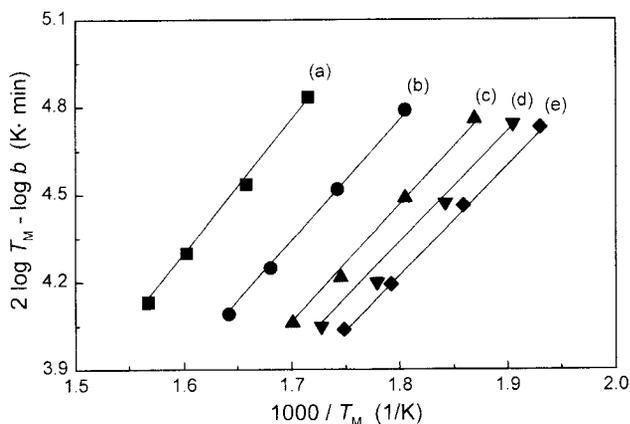


Fig. 3. Plots of  $(2 \log T_M - \log b)$  vs.  $1/T_M$  for the TPD peaks of  $O_2$  from (a) MFI(II), (b) MFI(III), (c) MFI(IV), (d) MFI(V), and (e) MFI(VI) samples.

$\text{kcal}\cdot\text{mol}^{-1}$ ) of conventional hydrogen bonds [Pauling, 1974]. This suggests that the interaction of the adsorbed  $O_2$  molecules with the internal Si-OH defects in MFI zeolites is strong enough to form 'hydrogen-bonded complexes' rather than 'van der Waals complexes'. To obtain further evidence supporting the speculation given above, we are investigating the interaction of  $O_2$  with internal Si-OH groups in MFI zeolites by using variable-temperature infrared spectroscopy.

In conclusion, results from the TPD measurements demonstrate that the adsorption of nonpolar  $O_2$  molecules at room temperature on the proton form of MFI zeolites gives rise to the hydrogen bonding interactions between the  $O_2$  adsorbates and the internal Si-OH groups in these zeolites. The strength of such interactions is found to become weaker with increasing Al content in the zeolite.

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