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SHORT COMMUNICATION

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

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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_2 adsorption sites. The apparent activation energies (17.5-21.8 $kcal \cdot mol^{-1}$) of desorption determined from O_2 TPD measurements reveal that the extent of interactions between the Si-OH defects and the adsorbed O_2 molecules becomes weaker with decreasing Al content in the zeolite.

Key words : MFI Zeolites, Internal Silanol Groups, O_2 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 physicochemical 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_2 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_4F and TPABr [Chezeau et al., 1989]. As-synthesized samples were calcined in flowing O_2 at 823 K for 12 h, refluxed twice in 1.0 M NH_4NO_3 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_α 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_2 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_2 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_2 (20 $cm^3 \cdot min^{-1}$) was passed over

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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_2. Finally, the TPD curves were obtained in flowing He (30 $cm^3 \cdot min^{-1}$) 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_2 alone by a Balzers MSC 200 mass spectrometer.

RESULTS AND DISCUSSION

Fig. 1 shows the TPD curves of O_2 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 $K \cdot min^{-1}$. All MFI samples used in obtaining the TPD curves in Fig. 1 were prepared by the conventional method which includes the addition of OH^- 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_2 adsorption sites is developed when the Al content in MFI zeolites is gradually lowered.

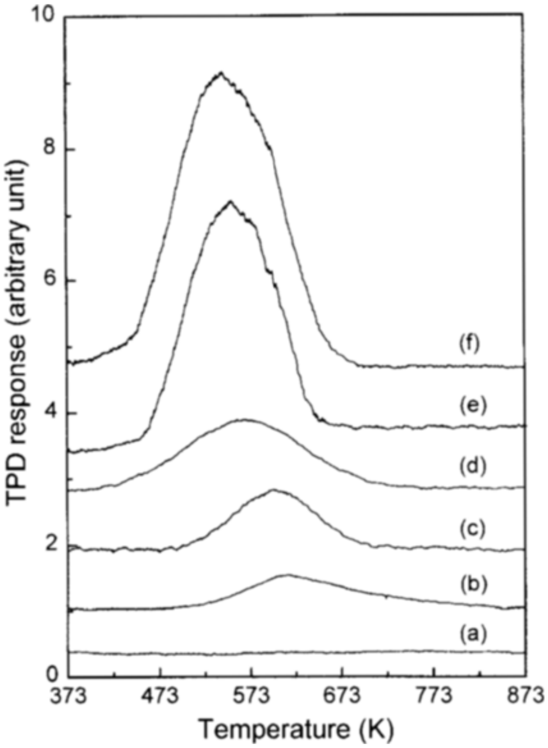

Fig. 1. O_2 TPD curves from the proton form of MFI zeolites with different Si/Al ratios: (a) MFI(I), (b) MFI(II), (c) MFI(III), (d) MFI(IV), (e) MFI(V), and (f) MFI(VI) samples. The heating rate is 20 $K \cdot min^{-1}$.

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_M) of desorption peaks has been used to determine heats of desorption that are mediately related to the acid strength distribution. The amounts of desorbed O_2 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_2 molecules becomes larger with decreasing Al content in the MFI zeolite. Therefore, it is most likely that the desorption peaks in Fig. 1 are not due to O_2 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_M 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_2 adsorbed at room temperature on the proton form of MFI zeolites with different Si/Al ratios

Sample	Si/Al ratio	BET surface area[a] ($m^2 \cdot g^{-1}$)	T_M[b] (K)	V_d[c] ($cm^3 \cdot g^{-1}$)	No. of O_2 molecules ($10^{18} \cdot g^{-1}$)	E_d[d] ($kcal \cdot mol^{-1}$)
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)[e]	>18000	416	-	-	-	-

[a] BET surface areas calculated from N_2 adsorption data.
[b] The temperature at maximum of desorption peaks in TPD curves that were recorded at a heating rate of 20 $K \cdot min^{-1}$.
[c] The amount of desorbed O_2.
[d] The apparent activation energy of desorption.
[e] Prepared in the presence of F^- ions.

ed acid site [Pine et al., 1984]. Thus, if the desorption peaks in parts b-f of Fig. 1 originate from O_2 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_2 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^- ions in the synthesis mixture. It has been repeatedly shown that the amount of internal Si-OH defects in MFI zeolites is greatly reduced by using F^- ions instead of OH^- 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^- ions. Therefore, it is most likely that the reason why MFI samples synthesized by using OH^- ions as mineralizing agents exhibit desorption peaks (Fig. 1) is the presence of internal Si-OH defects serving as O_2 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^{-1} 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.

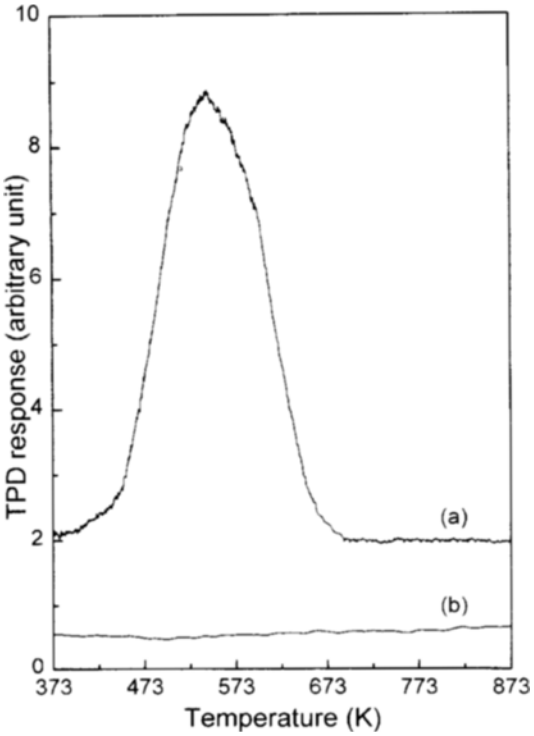

Fig. 2. O_2 TPD curves from pure-silica MFI zeolites prepared by (a) conventional and (b) fluoride methods. The heating rate is 20 K·min^{-1}.

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

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

where b is the linear heating rate, V_d is the amount of base at saturation, K_o is the preexponential factor in the desorption rate expression, and R is the gas constant. Therefore, the E_d value can be determined from the plots of ($2 \log T_M - \log b$) vs. $1/T_M$ when the T_M is measured as a function of b. This analysis has been applied to the O_2 TPD peaks from five MFI zeolites with Si/Al ratios from 27 to ∞. The T_M values of the respective desorption peaks become higher with increasing b from 5 to 30 K min^{-1}, while their V_d values remain almost unchanged. Fig. 3 shows plots of ($2 \log T_M - \log b$) vs. $1/T_M$ for the O_2 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_d 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_d value of O_2 desorption it shows. As a result, the pure-silica MFI(VI) sample was found to have the lowest E_d value (17.5 kcal·mol^{-1}) among the MFI zeolites studied here. This indicates that the interaction of O_2 with internal Si-OH groups decreases with decreasing Al content in the zeolite. In addition, it should be noted that the E_d values (17.5-21.8 kcal·mol^{-1}) listed in Table 1 are higher than those (12.0-18.2 kcal·mol^{-1}) of O_2 adsorbed on the paramagnetic de-fect centers in aluminophosphate molecular sieves [Kim et al., 1997], and are even higher than the energies (0.5-10.0

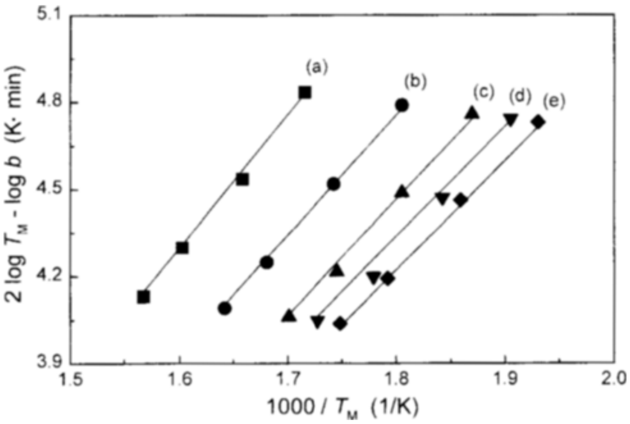

Fig. 3. Plots of (2 log T_M – log b) vs. $1/T_M$ for the TPD peaks of O_2 from (a) MFI(II), (b) MFI(III), (c) MFI(IV), (d) MFI (V), and (e) MFI(VI) samples.

kcal·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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REFERENCES

Breck, D. W., "Zeolite Molecular Sieves", Wiley, New York (1974).

Chester, A. W., Chu, Y. F., Dessau, R. M., Kerr, G. T. and Kresge, C. T., "Aluminum-independent Cation Exchange of Internal Siloxy Groups in ZSM-5 and ZSM-11", *J. Chem. Soc., Chem. Commun.*, 289 (1985).

Chezeau, J. M., Delmotte, L., Guth, G. L. and Soulard, M., "High-Resolution Solid-State ^{29}Si and ^{13}C NMR on Highly Siliceous MFI-Type Zeolites Synthesized in Nonalkaline Fluoride Medium", *Zeolites*, **9**, 78 (1989).

Corma, A., "Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions", *Chem. Rev.*, **95**, 559 (1995).

Cvetanovic, R. J. and Amenomiya, Y., "Application of a Temperature-Programmed Desorption Technique to Catalyst Studies", *Adv. Catal.*, **17**, 103 (1967).

Dessau, R. M., Schmitt, K. D., Kerr, G. T., Woolery, G. L. and Alemany, L. B., "On the Presence of Internal Silanol Groups in ZSM-5 and the Annealing of These Sites by Steaming", *J. Catal.*, **104**, 484 (1987).

Engelhardt, G. and Michel, D., "High-Resolution Solid-State NMR of Silicates and Zeolites", Wiley, Chichester, 1987.

Farneth, W. E. and Gorte, R. J., "Methods for Characterizing Zeolite Acidity", *Chem. Rev.*, **95**, 615 (1995).

Hong, S. B., Kim, S. J. and Uh, Y. S., "Formation of Paramagnetic Defect Centers in Aluminophosphate Molecular Sieves", *J. Am. Chem. Soc.*, **118**, 8102 (1996).

Jacobs, P. A. and Martens, J. A., "Synthesis of High-Silica Aluminosilicate Zeolites", Elsevier, Amsterdam (1987).

Kim, S. J., Kim, M. H., Hong, S. B., Uh, Y. S. and Choi, Y. S., "Adsorption of Oxygen on the Paramagnetic Defect Centers in Aluminophosphate Molecular Sieves", *Catal. Lett.*, **44**, 165 (1997).

Moser, W. R., Thompson, R. W., Chiang, C. C. and Tong, H., "Silicon-Rich H-ZSM-5 Catalyzed Conversion of Aqueous Ethanol to Ethylene", *J. Catal.*, **117**, 19 (1989).

Pauling, L., "The Nature of the Chemical Bond", Cornell University Press, Ithaca, 3rd ed. (1974).

Pine, L. A., Maher, P. J. and Wachter, W. A., "Prediction of Cracking Catalyzed Behavior by a Zeolite Unit Cell Size Model", *J. Catal.*, **85**, 466 (1984).

Venuto, P. B., "Organic Catalysis over Zeolites: a Perspective on Reaction Paths within Micropores", *Microporous Mater.*, **2**, 297 (1994).

Woolery, G. L., Alemany, L. B., Dessau, R. M. and Chester, A. W., "Spectroscopic Evidence for the Presence of Internal Silanols in Highly Siliceous ZSM-5", *Zeolites*, **6**, 14 (1986).