Studies on the Structure and Acid Properties of GaMCM-41 Mesoporous Molecular Sieve

Kazu Okumura,* Kyoichi Nishigaki, and Miki Niwa
Department of Meterials Science, Faculty of Engineering, Tottori University, Koyama-cho, Tottori 680-0945

(Received March 2, 1998; CL-980152)

GaMCM-41 was synthesized and the structure and acid properties were investigated. Powder X-ray diffraction and nitrogen adsorption isotherm proved high uniform hexagonal structure of the synthesized GaMCM-41. Temperature programmed desorption (TPD) of ammonia and octane cracking indicated that the GaMCM-41 possessed strong acid sites in comparison with AlMCM-41.

Much attention has been paid to MCM-41 molecular sieve with unidimensional hexagonal mesopore since it was developed by researchers in Mobil oil corporation.[1,2] Many kinds of metals were tried to be incorporated into the MCM-41 framework to add new character.[3] As for generation of acid sites, researchers' interests were mainly focused on aluminum MCM-41 to generate acid sites. However, reports on gallium MCM-41 are relatively insufficient[4,5] and detailed acid properties are not known. Here, we report the acid properties of GaMCM-41 in comparison with AlMCM-41 as well as structural characterization.

GaMCM-41 and AlMCM-41 samples were synthesized in a similar manner reported by Ryoo and Kim.[6] The detailed procedure, gel equilibrium adjustment method, has already been reported elsewhere.[7] Following is the outline of the procedure. Tetradecyltrimethylammonium bromide was used as the template. $NaAlO_2$ and $Ga(NO_3)_3$ were sources for Al and Ga metals, respectively. The hydrothermal reaction was conducted at 373 K under the static conditions for 5 days, while adjusting the pH of gel to 11. The as-synthesized samples were calcined in a nitrogen stream for 1 h at 813 K, then the carrier gas was switched to oxygen and the calcination was continued for 10 h, after the temperature was increased at a heating rate of 2 K min^{-1}. The calcined samples were ion-exchanged with 0.5 M ammonium nitrate solution for 1 day at room temperature. Thus obtained NH_4^+ form samples were calcined in air at 723 K to obtain the H-form of Ga or AlMCM-41. Chemical composition of the H-form Ga or AlMCM-41 samples were analyzed by ICP. The strength and amount of the acid sites were estimated from temperature programmed desorption (TPD) of ammonia. Measurement procedure was previously reported.[8] It should be noted that before the TPD experiment, water vapor was exposed to the MCM-41 samples at 373 K which had been equilibrated with NH_3 to remove weakly adsorbed NH_3. Mass spectrometer was used to monitor the desorbed NH_3. A conventional type of pulse reactor was used for octane cracking. Before the reaction, 10 mg of sample was pretreated under a He stream at 773 K for 1 h. The reaction was conducted at 723 K with injection of 1 mm^3 of octane, and the cracked products were analyzed by GC with a silicone SE-30 column.

Structural characterization of H-form GaMCM-41 was carried out by nitrogen adsorption and powder X-ray diffraction measurements. Nitrogen adsorption of all the synthesized samples showed typical type IV isotherm with a sharp inflection due to the capillary condensation, suggesting the uniform mesopore structure of the synthesized GaMCM-41. Powder X-ray diffraction patterns of H-form GaMCM-41 were presented in Figure 1. Four well resolved peaks indexed to the (100), (110), (200), and (210) reflections were observed. Formation of GaMCM-41 with the uniform hexagonal structure was thus confirmed. Table 1 lists several structural parameters determined by the nitrogen adsorption isotherm and the X-ray diffraction experiment, as well as acid amount and NH_3/Ga ratio calculated from the desorbed NH_3 in the NH_3 TPD experiments.

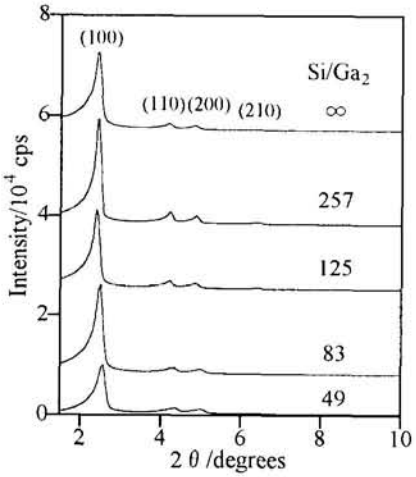

Figure 1. Powder X-ray diffraction of H-form GaMCM-41 with different Si/Ga_2 ratio.

Table 1. Chemical composition, structural parameters and acid amount of the H-form GaMCM-41

Si/Ga_2 ratio[a]	Ga content[a] /mol kg^{-1}	d_{100} spacing[b] /nm	Surface Area /m^2 g^{-1}	Acid Amount[c] /mol kg^{-1}	NH_3/Ga ratio
49	0.545	3.45	1172	0.446	0.82
83	0.345	3.59	927	0.357	1.03
125	0.233	3.66	915	0.194	0.83
257	0.123	3.67	846	0.104	0.85
∞	0	3.66	888	-	-

[a]Ga content was analyzed by ICP using H-form samples.
[b]Calculated from powder X-ray diffraction.
[c]Calculated from NH_3 TPD.

The NH_3/Al ratio was close to one, implying that one Ga atom originated one acid site and nearly all of the Ga atoms was exposed on the surface. Similarly, Al content agreed well with desorbed amount of NH_3 on AlMCM-41. As for *d*-spacing, it decreased with increasing Ga content, which was directly observed in the peak position shift toward higher angle along with increase in Ga content in the X-ray diffraction patterns (Figure 1). In the case of AlMCM-41, increase in *d*-spacing was observed with increasing Al concentration[7] due to the longer bond length of Al-O than that of Si-O. However, the observation of

GaMCM-41 is unusual, because Ga-O is much longer than Si-O. This is possibly explained by a steric hindrance around Ga atom in the MCM-41 framework, which reflected on the *d*-spacing change.

Figure 2 shows NH_3 TPD spectra of H-form AlMCM-41 (a) and GaMCM-41 (b). Maximum NH_3 desorption peak appeared

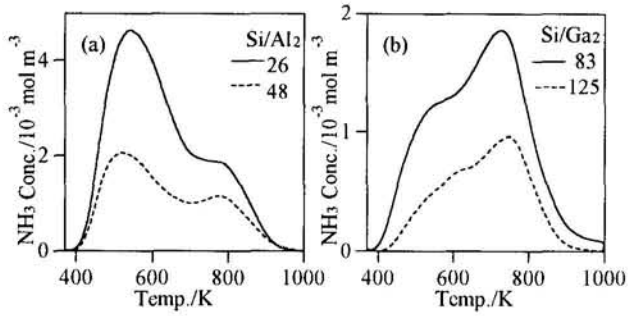

Figure 2. NH_3 TPD spectra of (a) AlMCM-41 and (b) GaMCM-41.

at 540 K on AlMCM-41, accompanied by a small peak at 790 K. The desorption peak at 540 K may be intrinsic to the Al kept in the MCM-41 framework, while the peak at 790 K may be due to the extra-framework aluminum; because, the destruction of the AlMCM-41 structure causes the decrease in the former peak and the increase in the latter peak. Figure 2 (b) shows the NH_3 desorption spectra of GaMCM-41. An NH_3 desorption peak appeared at 750 K, which was by 210 K higher than the desorption peak for AlMCM-41. These results represent that GaMCM-41 samples possess much stronger acid sites than AlMCM-41.

In Figure 3, the dependence of amount of octane cracking on Al or Ga concentration of MCM-41 samples is shown. Linear relationship between activity and metal concentration was observed on both Al and GaMCM-41 samples. However, in consistent with the NH_3 TPD experiment, GaMCM-41 showed cracking activity 4 times as high as AlMCM-41, compared at the same metal concentration. This supports that GaMCM-41 has stronger acid sites than AlMCM-41. Several researchers compared the acid strengths of Ga- and Al-zeolites, ZSM-5[9-11] and beta zeolites.[12] They reported that the acid strength of gallosilicate was slightly weaker than aluminosilicate. Therefore the tendency in acid strength of MCM-41 is opposite to the zeolite case. At this stage, the reason for the generation of such strong acid sites on GaMCM-41 is not clear. One possible explanation may be made by the steric hindrance around Ga as suggested by powder X-ray diffraction. However other

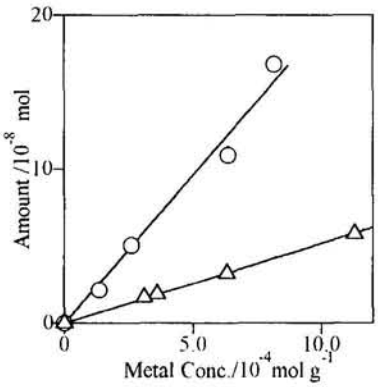

Figure 3. Amount of products in the octane cracking over GaMCM-41(○) and AlMCM-41(△) against the metal concentration. Reaction conditions: temperature, 723 K; flow rate, 15 ml min^{-1}; octane, 1 μl; catalyst weight, 10 mg.

investigations, including MAS NMR and XAFS studies, are necessary for confirmation.

References

1 J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Loenowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
2 C.T. Kresge, M.E. Leonowics, W.J. Roth, J.C. Vartuli, and J.C. Beck, *Nature*, **359**, 710 (1992).
3 Corma, *Chem. Rev.*, **97**, 2373 (1997).
4 C.-F. Cheng, M.D. Alba, and J. Klinowski, *Chem. Phys. Lett.*, **250**, 328 (1996).
5 C.-F. Cheng, H. He, W. Zhou, J. Klinowski, J.A.S. Gonçalves, and L.F. Gladden, *J. Phys. Chem.*, **100**, 390 (1996).
6 J.M. Kim, J.H. Kwak, S. Jun, and R. Ryoo, *J. Phys. Chem.*, **99**, 16742 (1995).
7 J.-H. Kim, M. Tanabe, and M. Niwa, *Microporous Mater.*, **10**, 85 (1997).
8 K.R. Reddy, N. Araki, and M. Niwa, *Chem. Lett.*, **1997**, 637.
9 M.A. Camblor, J. Pérez-Pariente, and V. Forenés, *Zeolites*, **12**, 280 (1992).
10 C.T-W. Chu and C.D. Chang, *J. Phys. Chem.*, **89**, 1569 (1985).
11 M. Sigl, S. Ernst, J. Weitkamp, and H. Knözinger, *Catal. Lett.*,**45**, 27 (1997).
12 S.G. Hegde, R.A. Abdullah, R.N. Bhat, and P. Ratnasamy, *Zeolites*, **12**, 951 (1992).