

Synthesis of ferrisilicate with the MCM-22 structure

Peng Wu, Hong Lin, Takayuki Komatsu and Tatsuaki Yashima*

Department of Chemistry, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku, Tokyo, 152, Japan

A new ferrisilicate molecular sieve with the MCM-22 structure is synthesized in Al-free form and exhibits low activity as a solid-acid catalyst and significant activity for the selective catalytic reduction of NO with NH₃.

A new zeolite MCM-22 patented recently¹ has been proposed to contain two independent pore systems, both of which are accessed through rings composed of ten tetrahedral (T) atoms.² One of these pore systems consists of large supercages of 12-membered rings. This unique pore structure of the aluminosilicate MCM-22 means it is an interesting catalyst for a wide variety of acid-catalysed reactions.^{3–5}

Isomorphous substitution of other elements for Si or Al into the silica based zeolite framework to prepare the corresponding metallosilicates is an effective way to modify the activity and selectivity of zeolite catalysts. Isomorphous substitution of Ga, Fe, As, Ti, V, Sn, *etc.* into the framework has already been reported. Among these metallosilicates, ferrisilicates have been used as both solid-acid catalysts and oxidation catalysts. The acid strength of MFI type (ZSM-5 type) ferrisilicate is moderate and weaker than that of the Ga and Al analogues.⁶ More importantly, we have reported that MFI type ferrisilicate is a more selective catalyst than Fe³⁺-exchanged ZSM-5 and iron oxide supported on silicalite in the oxidative dehydrogenation of alkanes,⁷ and that it is also an active catalyst for the selective catalytic reduction (SCR) of NO with NH₃ in the presence of O₂.⁸ Ferrisilicates have been synthesized for MFI,⁶ beta,⁹ MOR (mordenite),¹⁰ FER (ferrierite), *etc.*,¹¹ but, as yet, not for the MCM-22 topology. Here, we report for the first time, the synthesis of iron-substituted MCM-22 zeolite and its physicochemical and catalytic properties.

MCM-22 type ferrisilicate (Fe-MCM-22) was synthesized using fumed silicon dioxide (Cab-o-sil M7D) as the source of silicon to obtain an Al-free material (Si/Al > 10000). Hexamethylenimine (HM) and Fe(NO₃)₃·9H₂O were used as the template and iron source, respectively. In a typical synthesis, silicon dioxide and sodium hydroxide were dissolved in an aqueous solution of HM with stirring for 2 h. The resultant mixture was then added dropwise into an aqueous solution of (Fe(NO₃)₃). The mixture was stirred for another 2 h to obtain a clear gel. The pH of the final gel was *ca.* 12 and its molar composition was SiO₂:0.03 Fe₂O₃:0.15 Na₂O:45 H₂O. The gel was then transferred into a Teflon autoclave and heated at 408 K for 11 days under stirring (60 rpm). The resultant solid product was filtered and washed thoroughly with deionized water, dried at 403 K and calcined in air at 753 K for 5 h to remove the template. The Na form of the zeolite thus obtained

was transformed into the H form by ion exchange with 0.1 M NH₄NO₃ followed by calcination in air at 723 K for 2 h. A reference sample of the Al analogue, Al-MCM-22, was synthesized according to ref. 12. These two samples were characterized with XRD, IR, N₂ adsorption and catalytic studies.

Fe-MCM-22 was nearly white, indicating the absence of iron oxides within the crystals. The XRD pattern of Fe-MCM-22 was very similar to that of its aluminosilicate analogues reported previously¹² except that the relative peak intensities were somewhat different (Fig. 1). Its framework IR spectrum was also similar to that of Al-MCM-22. Upon substitution of Fe for Al, some vibration bands were shifted to lower wavenumbers which can be taken as evidence that Fe ions are present in the tetrahedral framework sites since Si–O–Fe vibrations are weaker than those of Si–O–Al. The internal asymmetric vibration has been reported to show a larger shift than the external one upon the substitution of Fe for Al in beta and MOR.^{9,10} However, the extent of the shift of these two vibrations was reversed for MCM-22 (Table 1), which may be due to the unique structure of the MCM-22 zeolite. From N₂ adsorption experiments, Fe-MCM-22 had a comparable micropore volume and specific surface area to Al-MCM-22. These data were also similar to those reported for MCM-22 aluminosilicates⁴ and is a clear indication that Fe-MCM-22 has a high degree of crystallinity.

If trivalent Fe³⁺ ions are incorporated into the silicate framework, Si(OH)Fe hydroxy groups must be generated when Fe-MCM-22 was exchanged into the H form. Fig. 2 shows IR spectra of both H-form Fe-MCM-22 and H-form Al-MCM-22 in the hydroxy region. For Al-MCM-22 [Fig. 2(a)], the bands at 3748 cm⁻¹ (external silanols), 3730 cm⁻¹ (internal silanols), 3663 cm⁻¹ (associated with extraframework Al species) and 3621 cm⁻¹ [the structural Si(OH)Al hydroxy groups] were

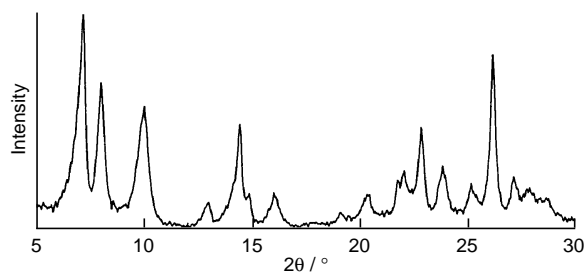


Fig. 1 X-Ray diffraction pattern of Fe-MCM-22

Table 1 Physicochemical and catalytic properties of Fe-MCM-22 and Al-MCM-22

	Si/M ratio in gel	N ₂ adsorption		v _{asym} /cm ⁻¹		Catalytic activity/mol%	
		Micropore/ ml g ⁻¹	Surface area/ m ² g ⁻¹	External	Internal	<i>o</i> -Xylene ^a isomerization	Toluene ^b methylation
Fe-MCM-22	15	0.197	544	1229	1089	6.1	23.9
Al-MCM-22	15	0.203	551	1244	1092	67.5	81.6

^a *o*-Xylene isomerization: cat., 0.4 g; W/F = 7.2 g h mol⁻¹; T = 573 K; He, 20 ml min⁻¹; time on stream (TOS) = 1 h. ^b Toluene methylation: cat., 0.4 g; W/F = 6.8 g h mol⁻¹; T 573 K; MeOH–toluene molar ratio = 2 : 1; He, 20 ml min⁻¹; TOS = 1 h.

clearly distinguished. Fe-MCM-22 [Fig. 2(b)] exhibited a characteristic band at 3637 cm^{-1} . This band was removed completely after pyridine adsorption followed by desorption at 423 K, while a band due to pyridinium ions was observed at 1550 cm^{-1} . This allows us to assign the band at 3637 cm^{-1} to structural Si(OH)Fe groups with Brønsted acidity. Hence, the above results are considered as strong proof of the incorporation of Fe^{3+} ions in the framework. The higher wavenumber of Si(OH)Fe groups suggests that the Brønsted acidity of Fe-MCM-22 is much weaker than that of Al-MCM-22 and Fe-

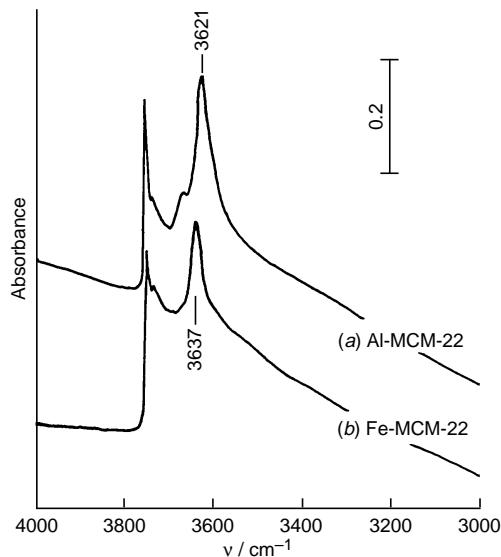


Fig. 2 IR spectra in the hydroxy region

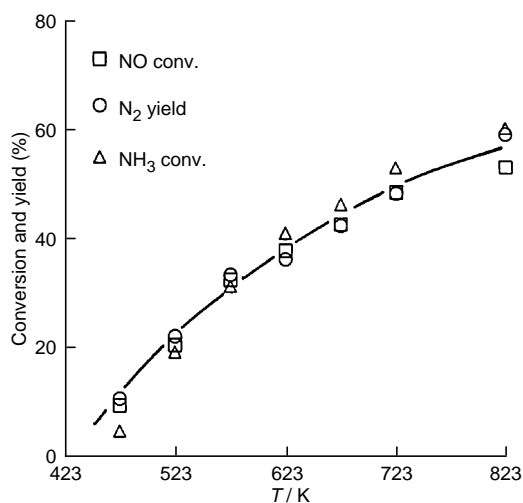


Fig. 3 NO reduction over Fe-MCM-22 with NH_3 in the presence of O_2 . Reaction conditions: cat. 0.1 g; feed, NO (0.1%), NH_3 (0.1%), O_2 (2%), He (balance); total flow rate, 500 ml min^{-1} .

MCM-22 showed very low activity for *o*-xylene isomerization (catalysed by Brønsted-acid sites having at least medium strength), while it exhibited a relatively higher activity for toluene methylation (proceeds even over weak Brønsted-acid sites) at the same reaction temperature (Table 1).

Further, Fe-MCM-22 was also tested for the selective catalytic reduction of NO with NH_3 in the presence of O_2 . It is obvious from Fig. 3 that Fe-MCM-22 is an effective catalyst for NO reduction with NH_3 as a reductant. The activity of Fe-MCM-22 was even *ca.* 10% higher than that of MFI-type ferrisilicate (Si/Fe = 25) below 600 K (the temperature region where NO reduction occurred selectively for MFI-type ferrisilicate). It should be noted that Al-MCM-22 only showed NO conversion of less than 5% at the temperatures studied. Thus, the active sites must be the framework Fe^{3+} ions, as reported previously for MFI type ferrisilicate.⁸ NO conversion, N_2 yield and NH_3 conversion correlated well with each other even at high temperatures, indicating that the reduction of NO by NH_3 occurred selectively. This result also verifies that extraframework Fe species are negligible in Fe-MCM-22 since we have observed that iron oxide species supported on MFI type silicalite exhibits activity for the oxidation of NH_3 by O_2 to form NO but no activity for the reduction of NO.⁸ As Fe-MCM-22 can be synthesized with relatively high Fe content (Si/Fe = 15), it is anticipated that more active catalysts for SCR of NO can be obtained by exchange with other transition-metal ions into Fe-MCM-22.

To summarize, a new ferrisilicate possessing the MCM-22 structure has been hydrothermally synthesized. Fe-MCM-22 is a weak solid acid but is an effective catalyst for the selective reduction of NO.

Footnote

* E-mail: Komatsu@chem.titech.ac.jp

References

- M. K. Rubin and P. Chu, *US Pat.*, 4439409, 1990.
- M. E. Leonowicz, J. A. Lawton, S. L. Lawton and M. K. Rubin, *Science*, 1996, **264**, 1910.
- K. J. Del Rossi and Jr. Huss, *US Pat.*, 5107047, 1992; Jr. A. Huss, G. W. Kirker, K. M. Keville and R. T. Thomson, *US Pat.*, 4992615, 1991.
- R. Ravishanker, T. Sen, V. Ramaswamy, H. S. Soni, S. Ganapathy and S. Sivasanker, *Stud. Surf. Sci. Catal.*, 1994, **84**, 331.
- M. A. Asensi, A. Corma and A. Martínez, *J. Catal.*, 1996, **158**, 561.
- C. T.-W. Chu and C. D. Chang, *J. Phys. Chem.*, 1985, **89**, 1569.
- Md. A. Uddin, T. Komatsu and T. Yashima, *J. Catal.*, 1994, **146**, 468; Md. A. Uddin, T. Komatsu and T. Yashima, *J. Catal.*, 1994, **150**, 439.
- Md. A. Uddin, T. Komatsu and T. Yashima, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3275.
- R. Kumar, A. Thangaraj, R. N. Bhat and P. Ratnasamy, *Zeolites*, 1991, **11**, 42.
- A. J. Chandwadkar, R. N. Bhat and P. Ratnasamy, *Zeolites*, 1990, **10**, 85.
- R. B. Borade and A. Clearfield, *Chem. Commun.*, 1996, 2267.
- A. Corma, C. Corell and J. Pérez-Pariente, *Zeolites*, 1995, **15**, 2.

Received, 18th November 1996; Com. 6/07769B