Isomorphous Substitution of Trivalent Iron in Mesoporous MCM-48 Silicate Molecular Sieves: Synthesis, Characterization and Catalytic Properties

S.E. Dapurkar, S.K. Badamali, A. Sakthivel and P. Selvam*

Solid State and Catalysis Laboratory, Department of Chemistry,
Indian Institute of Technology−Bombay, Powai, Mumbai 400076

ABSTRACT: Trivalent iron-substituted MCM-48 (FeMCM-48) was synthesized and characterized by various analytical (XRD, N_2 adsorption, TG-DTA and ICP-AES) and spectroscopic (DRUV-VIS, FTIR and ESR) techniques. An NH_3-TPD study suggests the presence of high concentration of moderate Brønsted acid sites. The catalytic performance of the protonated catalyst (H-FeMCM-48) was evaluated for the *tertiary*-butylation of phenol, and the results indicate that the activity for the chosen reaction is comparable or slightly higher than H-FeMCM-41 but lower than their corresponding aluminium and gallium analogues. The observed lower activity is attributed to the low concentration of Brønsted acid sites in the iron analogues. On the other hand, the latter shows much higher *para-tertiary*-butyl phenol selectivity of as compared to many other catalysts reported so far.

INTRODUCTION

The discovery of thermally stable mesoporous silicate molecular sieves [1,2] having one-dimensional hexagonal MCM-41 and three-dimensional cubic MCM-48 structures has attracted significant research interest, and opened up new opportunities in many areas, in particular, heterogeneous catalysis [3-7]. However, much attention has been devoted on the catalytic properties of metal-containing MCM-41 structure because of the ease in preparation of these materials, and only very little attention has been paid on the catalytic properties of metal-incorporated MCM-48 structure [8-13] owing to the difficulty in the synthesis of good quality samples as due to a narrower homogeneity region of the MCM-48 phase [14]. On the other hand, the inherent benefit of three-dimensional pore structure of MCM-48 as well as the associated advantage of the resistance against pore blockage of this phase could serve as an excellent catalyst especially for the conversion of bulkier molecules.

Although the possibility of trivalent iron occupying the tetrahedral site in zeolitic framework has been established long ago, it was only in 1972, McNicol and Pott [15] showed that the iron impurities in faujasite occupy the substitutional framework sites. A detailed synthesis, characterization and catalytic properties of a ferrisilicate analog of ZSM-5 (MFI structure) appeared first in 1985 [16]. Since then, the isomorphous substitution of trivalent iron in the framework structure of many silicate and aluminosilicate topologies has been reported [17-23]. However, the small pore opening of these microporous materials restrict their applications for processes dealing with bulky molecules. Various supported catalysts have also been tried for this purpose; however, the leaching of active metal ions resulted in short lifetime of the catalyst [24]. Although the trivalent iron-substituted mesoporous MCM-41 silicate molecular sieves [25-33] showed promise for large molecules, they too have similar shortcomings of the microporous materials. It is, however, noteworthy here that only very few reports are available on the catalytic properties of mesoporous FeMCM-48 [34-37]. In the present study, we report on the synthesis, characterization and catalytic properties of trivalent iron-substituted mesoporous MCM-48 silicate molecular sieves.

---

* E-mail: selvam@chem.iitb.ac.in

EXPERIMENTAL

Synthesis

FeMCM-48 was prepared is as follows: Initially a mixture 'X' was obtained by adding dil. NaOH to tetraethylorthosilicate under constant stirring for 10 min. A solution 'Y' was then obtained by dissolving 25 wt.% cetyltrimethylammonium bromide (CTAB) surfactant in distilled water and stirred for 20 min. Finally, the mixture 'Y' was added to the mixture 'X' under constant stirring for homogenization. At the end of 25 min. a transparent gel was obtained, which was transferred to Teflon-lined autoclaves and kept in oven at 423 K for crystallization for 7-9 days. The solid product recovered by filtration was repeatedly washed with distilled water and dried at 353 K for 12 h. The as-synthesized sample was calcined at 813 K for 2 h in N_2 and followed by air for 7 h. A number of samples were prepared with the following gel (molar) composition: 1 SiO_2 : 0.25 Na_2O : 0.30 $(CTA)_2O$: 60 H_2O : (0.00 − 0.02) Fe_2O_3. The calcined catalyst was protonated (H-FeMCM-48) by ion-exchange method. For comparison, H-FeMCM-41 was also prepared [26,28].

Characterization

The as-synthesized and calcined samples were systematically characterized by power XRD, TG-DTA, ICP-AES, DRUV-VIS, FT-IR, and ESR techniques. The acidic behavior of the H-FeMCM-48 catalyst was studied by temperature-programmed desorption of ammonia (NH_3-TPD) as per the following procedure outlined earlier [28]. The amount of ammonia desorbed from the catalyst was estimated with the aid of the thermal conducting detector response factor of ammonia.

Catalytic Activity

Tertiary-butylation of phenol was carried out using H-FeMCM-48 catalyst in a homemade fixed-bed flow reactor and the procedure is reported elsewhere [28,38,39]. The various products of the reaction, viz., *p-t*-BP, *o-t*-BP and *2,4*-di-*t*-BP, were identified by gas chromatography (NUCON 5700) with SE-30 column. Further, *m-t*-BP was identified using AT1000 column.

RESULTS AND DISCUSSION

The as-synthesized as well as the calcined FeMCM-48 samples were white in color indicating the absence of dense iron oxy-hydroxy/oxide impurity phases. Figure 1 shows the XRD patterns of FeMCM-48 samples. The diffraction patterns show all the major reflections, which are characteristic of a cubic mesoporous MCM-48 structure [1,2,7]. The calculated average unit cell parameter (a_0) for FeMCM-48 was 84.79 Å, which is higher than the iron–free siliceous MCM-48 (80.7 Å). A similar observation was also noted earlier for Fe-MCM-41 [26,40]. The increase in unit cell parameter could be attributed to the isomorphous substitution of trivalent iron for tetravalent silicon, as the crystal radius of the former (0.63 Å) is larger than the latter (0.40 Å) [41]. An ICP-AES analysis of FeMCM-48 gives 1.2 wt % iron content. The pore volume, surface area, and pore diameter deduced from the N_2 sorption measurement were 0.78 ml g^{-1}, 960 m^2 g^{-1}, and 28 Å respectively. Thus suggesting mesoporous nature of FeMCM-48.
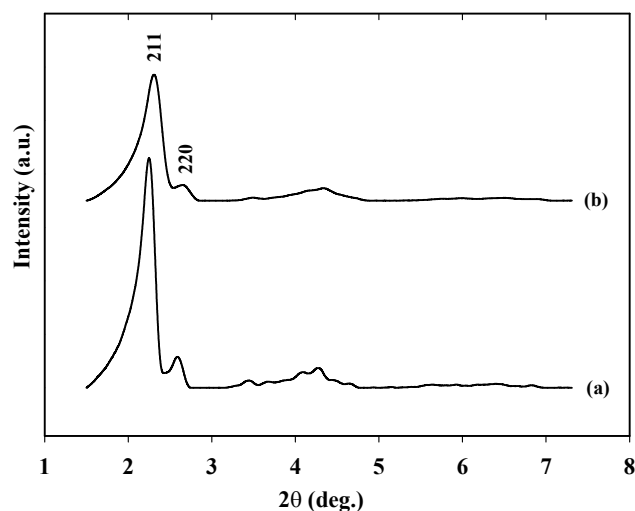

Fig. 1. XRD patterns of as-synthesized: (a) MCM-48 and (b) FeMCM-48.

Fig. 2 shows the DRUV-VIS spectra of various samples. In the case of FeMCM-48, two important absorption bands were observed, i.e., a strong charge transfer (ligand-to-metal)

band in the range 200-330 nm and a broad and weak spin forbidden *d-d* transition band between 330-540 nm. The occurrence of absorption maximum at 255 nm along with a shoulder at 216 nm is assigned to different transitions involving Fe(III) ion in a $[FeO_4]^-$ tetrahedral geometry [26,28]. The broad *d-d* bands, consisting of all possible inter-transitional bands, are also assigned to Fe(III) ions in tetrahedral symmetry. For a comparision, siliceous MCM-48 and Fe_2O_3 spectra are also included in Fig. 2.
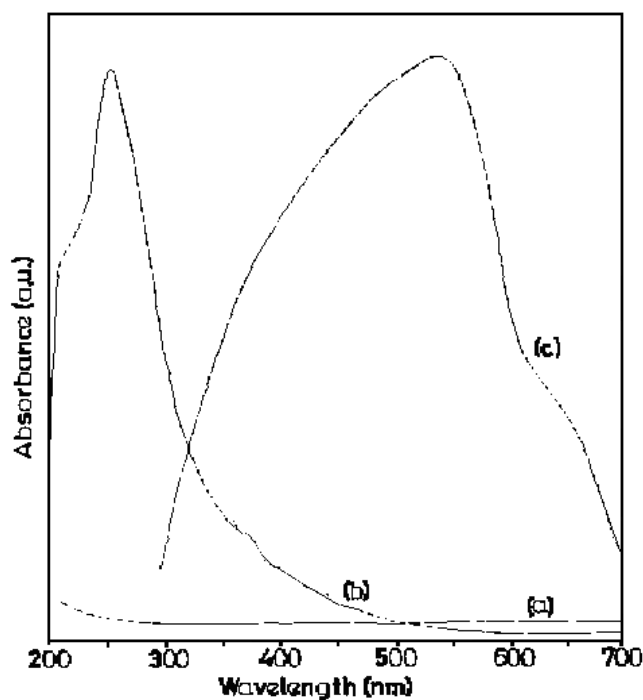

Fig. 2. DRUV-VIS spectra of: (a) as-synthesized MCM-48 (b) FeMCM-48 (c) bulk Fe_2O_3.

The FT-IR spectra of MCM-48 and FeMCM-48 are shown in the Fig. 3. In ferrisilicates, few separate or additional bands appear both in the symmetric and asymmetric vibration region 600-1200 cm^{-1}. Further the bands are shifted to lower wave number compared to its siliceous analogue. The appearance of a band around 660-670 cm^{-1} is consistent with the incorporation of Fe(III) ions in tetrahedral geometry [28,42].

Shown in Fig. 4 and 5 are the ESR spectra of as-synthesized and calcined FeMCM-48 recorded at room temperature and liquid nitrogen temperature. The spectra consists of

three different signals corresponding to the paramagnetic Fe(III) ion different environments. According to the signal assignments reported earlier [17,22] the lower field signals arising at g_{eff} = 4.3 and 7.7 are assigned Fe(III) ions in strongly distorted tetrahedral coordination, i.e., framework substitutional sites. The weak and broad signal appearing at g_{eff} = 2.2 is ascribed to the non-framework superparamagnetic iron oxide particles located inside the pore channels [43,44]. The sharp and intense signal arising at higher field, g_{eff} = 1.99, is attributed to symmetrical Fe(III) in the tetrahedral/octahedral geometry. At this juncture, it also noteworthy here that recently we have reported the successful synthesis of thermally stable trivalent iron-substituted hexagonal mesoporoous aluminophosphate (FeHMA) molecular sieves [45].
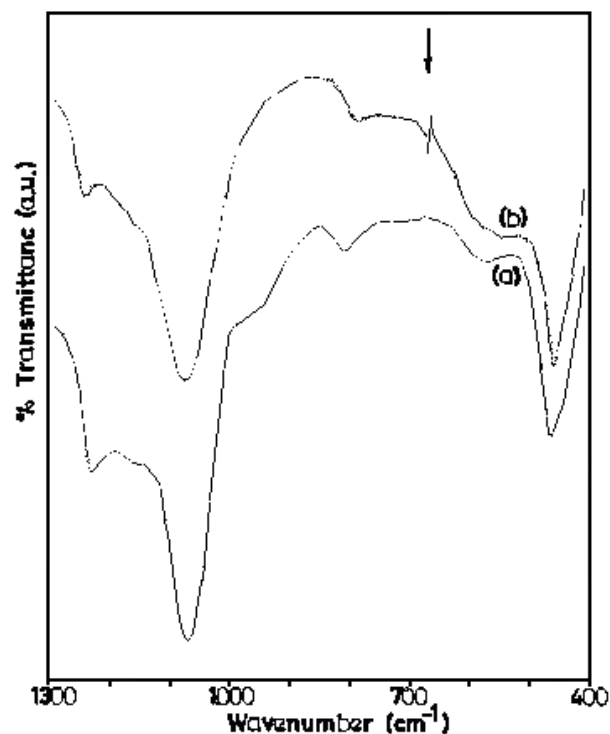

Fig. 3. FT-IR spectra of as-synthesized: (a) MCM-48 (b) FeMCM-48.

Figure 6 displays the NH_3-TPD profile of H-FeMCM-48. The broad pattern indicates a large distribution of different types of acid sites. The profile was deconvoluted using Gaussian function with temperature as variant. The first peak, around 420-440 K, referred to as type (i)

is attributed to surface hydroxyl groups, whereas the next two peaks, viz., type (ii) and type (iii), in the range 450-480 K and 540-600 K originate from moderate structural (Brønsted) acid sites, which is attributed to the presence of tetrahedral iron in two different framework sites. The broad and weak peak around 650-750 K, designated as type (iv), is attributed to weak Lewis acid sites, which may arise from tricoordinated iron in the framework.
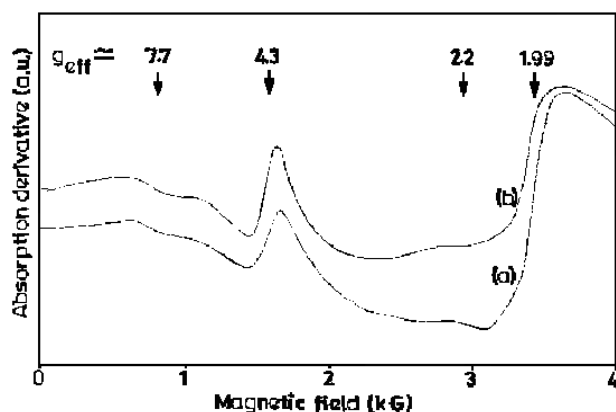

Fig. 4. ESR spectra of as-synthesized FeMCM-48:
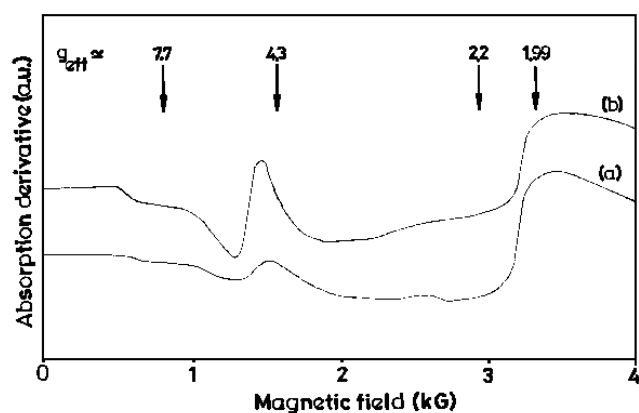(a) 298 K (b) 77 K.

Fig. 5. ESR spectra of calcine FeMCM-48:
(a) 298 K (b) 77 K.

Table 1 presents the results of *tertiary*-butylation of phenol over H-FeMCM-48 under optimized experimental conditions (reaction conditions: T = 448 K; WHSV = 4.8 h^{-1}; TOS = 1.5 h; *t*-BA : Phenol 2 : 1). For a comparison, we have also included the result H-FeMCM-41 [28]. It can be seen from this table that the phenol conversion is higher for H-FeMCM-48 than H-FeMCM-41. However, the activity is lower as compared to their corresponding aluminium and gallium analogues [39,40]. The

observed lower activity could be due to the low concentration of Brønsted acid sites in the iron analogues. In contrast, the iron analogues show much higher selectivity than many other catalysts reported so far.
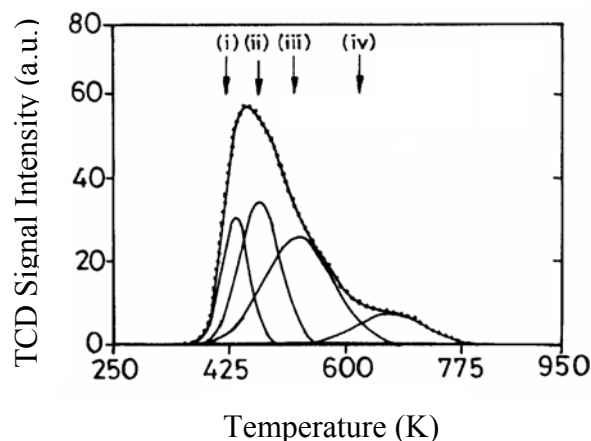

Fig. 6. NH$_3$-TPD profile of H-FeMCM-48.

Table 1. *Tertiary*-butylation of phenol.[†]

	H-FeMCM-41	H-FeMCM-48
Phenol conversion (wt %)	21.1	27.6
Selectivity (wt %)		
o-t-BP	9.5	9.8
m-t-BP	---	---
p-t-BP	87.0	87.8
2,4-di-*t*-BP	3.5	2.4

[†]Reaction conditions: T = 448 K; WHSV = 4.8 h^{-1}; TOS = 1.5 h; *t*-BA : Phenol = 2 : 1.

CONCLUSION

Thus, it can be deduced from the various analytical and spectroscopic studies that trivalent iron substitutes isomorphously in the silicate framework of MCM-48 structure. The extra negative charge generated as a result of this substitution generates acid sites, which is useful as solid acid catalyst. The solid acid catalyst, H-FeMCM-48 is active for chosen reaction and display higher *para*-selectivity for the chosen reaction.

ACKNOWLEDGEMENT

REFERENCES

[1] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, 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. Schelnker, J. Am. Chem. Soc., 114 (1992) 10834.

[2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature, 359 (1992) 710.

[3] A. Sayari, Chem. Mater., 8 (1996) 1840.

[4] A. Corma, Chem. Rev., 97 (1997) 2373.

[5] J.Y. Ying, C.P. Mehnert and M.S. Wong, Angew. Chem. Ind. Ed., 38 (1999) 56.

[6] D. Trong On, D. Desplantier-Giscard, C. Danumah and S. Kaliaguine, Appl. Catal. A, 222 (2001) 299.

[7] P. Selvam, S.K. Bhatia and C. Sonwane, Ind. Eng. Chem. Res., 40 (2001) 3237.

[8] K.A. Koyano and T. Tatsumi, J. Chem. Soc., Chem. Commun., (1995) 145.

[9] W. Zhang and T. J. Pinnavaia, Catal. Lett., 38 (1996) 261.

[10] S.B. Pu, J.B. Kim, M. Seno and M.T. Inui, Micropor. Mater. 10 (1997) 25.

[11] H. Kosslick, G. Lischke, H. Landmesser, B. Parlitz, W. Storek and R. Fricke, J. Catal., 176 (1998) 102.

[12] M. Eswaramoorthy, Neeraj and C.N.R. Rao, Chem. Commun., 615 (1998).

[13] S.E. Dapurkar, A. Sakthivel and P. Selvam, New J. Chem., 27 (2003) 1184.

[14] X. Auvray, C. Petipas, R. Anthore, I. Rico and A. Lattes, J. Phys. Chem., 93 (1989) 7458.

[15] B. D. Mcnicol and G. T. Pott, J. Catal., 25 (1972) 223.

[16] P. Ratnasamy, R. B. Borade, S. Sivasanker, V. P. Shiralkar and S. G. Hegde, Acta Phys. Chem., 31 (1985) 137.

[17] P. Ratnasamy and R. Kumar, Catal. Today, 9 (1991) 239.

[18] R.B. Borade and A. Clearfield, Chem Commun., 1996, 2267.

[19] S. Schubert, H. M. Ziethen, A. X. Trautwein, F. Schmidt, H. Li, J.A. Martens and P. A. Jacobs, Stud. Surf. Sci. Catal., 46 (1989) 735.

[20] J. Das, C. V. V. Satyanaryana, D. K. Chakrabarty, S. N. Piramanayagam and S. N. Shringi, J. Chem. Soc., Faraday Trans., 88 (1992) 3255.

[21] P. E. Dai, R. H. Petty, C. W. Ingram, R. Szostak, Appl. Catal. A, 143 (1996) 101.

[22] Y. S. Bhat, S. Ali, J. Das, B. D. Bhatt and A. B. Halgeri, J. Mol. Catal. A, 111 (1996) 307.

[23] R. Raja, G. Sankar and J. M. Thomas, J. Am. Chem. Soc., 121 (1999) 11926.

[24] M. Stockmann, E. Konietzni, J. U. Notheis, J. Voss, W. Keune and W. E. Maier, Appl. Catal. A, 208 (2001) 343.

[25] Z. Y. Yuan, S. Q. Liu, T. H. Chen, J. Z. Wang and H. X. Li, J. Chem. Soc., Chem. Commun., 1995, 973.

[26] S. K. Badamali and P. Selvam, Stud. Surf. Sci. Catal., 113 (1998) 749.

[27] N. He, S. Bao and Q. Xu, Appl. Catal. A, 169 (1998) 29.

[28] S. K. Badamali, A. Sakthivel and P. Selvam, Catal. Lett., 65 (2000) 153.

[29] M. Stockenhuber, M. J. Hudson and R. W. Joyner, J. Phys. Chem. B, 104 (2000) 3370.

[30] Y. Wang, Q. Zhang, T. Shishido and K. Takehira, J. Catal., 209 (2002) 186.

[31] D. Nicholson and L. Bonneviot, Chem. Mater., 9 (1997) 1716.

[32] A. Tuel, L. Arcon and J. M. M. Millet, J. Chem. Soc., Faraday Trans., 94 (1998) 3501.

[33] Y. Han, X. Meng, H. Guan, Y. Yu, L. Zhao, X. Xu, X. Yang, S. Wu, N. Li and F. Xiao, Micropor. Mesopor.Mater., 57 (2003) 191.

[34] H. Kosslick, G. Lischke, H. Landmesser, B. Parlitz, W. Storek and R. Fricke, J. Catal., 176 (1998) 102.

[35] W. Zhao, Y. Luo, P. Deng and Q. Li, Catal. Lett., 73 (2001) 199.

[36] B.Echchahed, A Moen, D.Nicholson and L.Bonneviot, Chem. Mater., 9 (1997) 1716

[37] Ch. Subrahmanyam, B. Viswanathan and T. K. Varadarajan, J. Mol. Catal. A, 226 (2005) 155.

[38] A. Sakthivel, S.K. Badamali and P. Selvam, Micropor. Mesopor. Mater., 39 (2000) 457.

[39] S.E. Dapurkar and P. Selvam, Appl. Catal. A, 254 (2003) 239; J. Catal., 224 (2004) 178.

[40] P. Selvam and S.E. Dapurkar, Catal. Today, 96 (2004) 135.

[41] R.D. Shannon and C.T. Prewitt, Acta. Crystallogr. B, 25 (1969) 925.

[42] R. Kloetstra, H.W. Zandbergen and H. van Bekkum, Catal. Lett., 33 (1995) 57.

[43] P. Selvam, S.K. Badamali, M. Murugasan and H. Kuwano, Recent Trends in Catalysis, (eds. V. Murugasen, B. Arabindoo, and M. Palanichamy), Narosa, New Delhi, 1999, p.556.

[44] P. Selvam, S.E. Dapurkar, S.K. Badamali, M. Murugesan and H. Kuwano, Catal. Today, 68 (2001) 69.

[45] S.K. Mohapatra, B. Sahoo, W. Keune and P. Selvam, Chem. Commun., 2002, 1466.