Spectroscopic Investigation of Fe(III) in FeMCM-41

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ABSTRACT: A series of Fe(III) containing mesoporous MCM-41 molecular sieves (FeMCM-41) have been synthesized hydrothermally. The samples were characterized systematically by various spectroscopic and analytical techniques in order to study the location, coordination, stability and oxidation state of iron within the matix. Here we report on the spectroscopic information, which is particularly being inferred from EPR, ^{29}Si MAS NMR, Mössbauer and Magnetic susceptibility studies. Analysis of EPR signal indicated that Fe(III) is present in two different tetrahedral sites along with octahedral coordination. During template removal, Fe(III) is partly dislodged from the framework and migrates to non-framework and/or extra-framework sites, irrespective of calcination temperature. ^{29}Si MAS NMR studies revealed that paramagnetic Fe(III) is present in the direct vicinity of $[SiO_4]$ tetrahedral and therefore results in broadening of spectral lines. Absences of side spinning bands are attributed to the uniform dispersion of Fe_xO_y within the matrix. The observed isomer shift value of <0.3mm/sec in the Mössbauer spectrum supported the tetrahedral coordination of Fe(III). Further, the appearance of sexset pattern is attributed to the superparamagnetic Fe_xO_y nanoparticles. The coexistence of paramagnetic and superparamagnetic Fe(III) in FeMCM-41 is also inferred from magnetic susceptibility studies.

INTRODUCTION

It is of considerable interest to develop molecular sieve based solid acid catalysts that may replace the conventionally used hazardous non-selective homogeneous catalysts for alkylation, acylation, benzoylation and sulfonation etc [1]. The traditionally used catalysts (e.g., HF, H_2SO_4, $AlCl_3$, $FeCl_3$, BCl_3 etc.) pose several problems of high toxicity, spent acid disposal, use of more than stoichiometric amounts and difficult separation and recovery. However, the application of zeolite/zeolite based solid acid catalysts offer high efficiency, robustness, shape selectivity as well as environmentally benign chemical process [2]. Among the solid acid catalysts, isomorphously substituted trivalent iron in zeolite/zeolitic materials are interesting owing to numerous diversified applications. The synthesis, characterization and potential catalytic ability of various microporous ferrisilicate molecular sieves are reviewed elsewhere [3]. The advent of mesoporous materials (M41S family) in 1992 [4, 5] and their widespread applications [6-8] has given a new dimension to the molecular sieve science and

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technology. Especially the pore size tuning has overcome the limitation of diffusional constraints for bulkier molecules. Further, the possible insertion of heteroatoms into the mesoporous framework has broadened the scope of heterogeneous catalysis. Trivalent iron substituted mesoporous MCM-41 (FeMCM-41) exhibits excellent activity as a selective acid catalyst [9] as well as oxidation catalyst [10-11]. The study of the active sites in ferrislicates is often challenging due to the complex Fe(III) chemistry under synthesis conditions [3]. Nevertheless, Fe(III) being a paramagnetic ion (d^5 system) a variety of techniques can be employed to probe the Fe(III) sites in ferrisilicate molecular sieves. In continuation to our earlier work on FeMCM-41 [12-14] and MCM-48 [15] materials, further we intend to report on the location, coordination and stability of Fe(III) sites, which is inferred from a combination of appropriate spectroscopic investigations.

EXPERIMENTAL

Synthesis and Characterization

The FeMCM-41 samples were synthesized hydrothermally and systematically characterized by various techniques such as powder XRD, TG-DTA, BET surface area, FT-IR, DR UV-VIS, EPR, TPD-NH$_3$ as reported earlier [12,14]. The samples were, further studied by ^{29}Si MAS NMR, Mössbauer and magnetic susceptibility measurements. The number within the parentheses represents the silicon-to-iron content in molar gel composition.
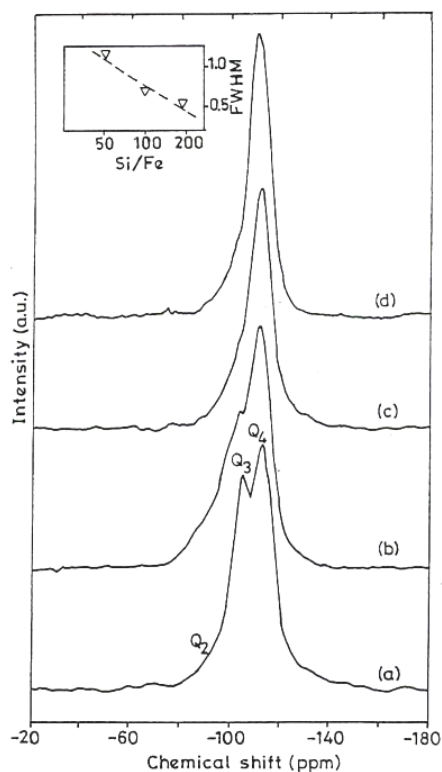
RESULTS AND DISCUSSION

A characteristic EPR spectrum of FeMCM-41(50) sample (calcined at different temperatures), NH$_4^+$-exchanged as well as in the H$^+$-form is included in Figure 1. As it can be seen three signals observed at three different g_{eff}-values (4.3, 2.0 and 2.2) are attributed to Fe(III) in distorted tetrahedral, symmetrical tetrahedral/octahedral coordination and Fe$_x$O$_y$ nanoparticles, respectively [9]. Interestingly, it

has been observed that upon calination partial dislodgement of Fe(III) occur from the framework [14] and it occupies the inner surface as Fe$_x$O$_y$ particles. Therefore, we have attempted to calcine the samples at different temperatures. However, it was difficult to prevent the dislodgement. This is quite understandable, as larger trivalent iron (crystal radii = 0.63 Å) is comparatively unstable in the tetrahederal framework of tetravalent silicon (crystal radii = 0.40 Å). The distorted geometry results in broad EPR signal, observed between magnetic field strength of 2.1–3.1 kgauss (Figure 1a-d). It was further noticed that upon NH$_4^+$ ion-exchange the signal intensities are decreased, indicating dislodgement of Fe(III) from framework sites, owing to the hydrolysis of Si–O–Fe or Si–O–Si linkages. Despite of partial dislodgement, in the protonated form (H$^+$-FeMCM-41) significant amount of Fe(III) still remains in the tetrahedral coordination and exhibits moderate-to-strong acidity [10]. However, interpretation of EPR result is not straightforward as the EPR signal is highly sensitive to slight distortion of Fe(III) coordination [16] and hence needs further investigation.
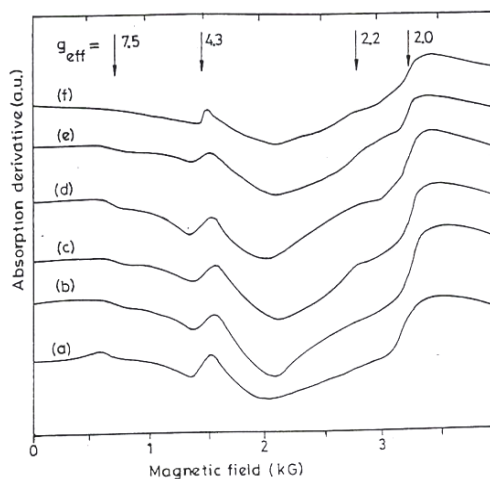
Figure 1. EPR spectra of FeMCM-41(50) calcined at : (a) 823 K; (b) 773 K; (c) 723 K; (d) 673 K; (e) NH$_4^+$-FeMCM-41(50) and (f) H$^+$-FeMCM-41(50).
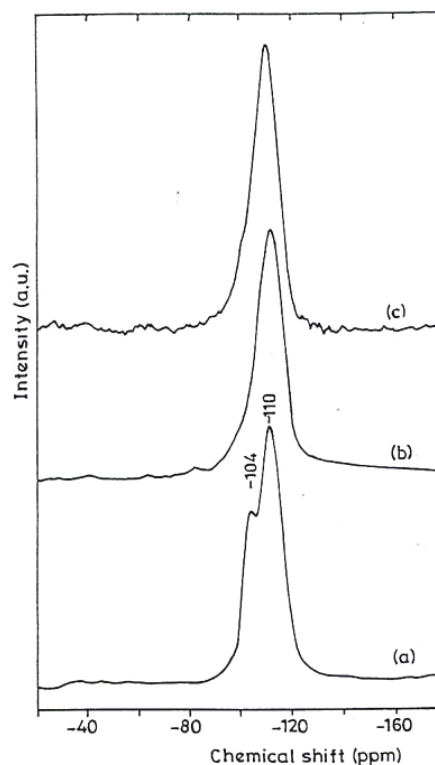
^{29}Si MAS NMR spectra of as-synthesized and calcined FeMCM-41samples with varying Si/Fe content are shown in Figure 2 and 3, respectively. For a comparison the spectrum of siliceous MCM-41 is included.

that the full width at half maxima (FWHM) of [29]Si signal increases linearly with increasing iron content in FeMCM-41 (see inset, Figure 2) implying a uniform dispersion and high degree of spatial ordering of Fe(III) species [16].

Figure 2. ^{29}Si MAS NMR spectra of as-synthesized: (a) MCM-41; (b) FeMCM-41(50); (c) FeMCM-41(100) and (d) FeMCM-41(200).

Figure 3. ^{29}Si MAS NMR spectra of calcined: (a) MCM-41; (b) FeMCM-41(200) and (c) FeMCM-41(100).

The as-synthesized MCM-41 exhibits signals at −103 ppm and −109 ppm assigned to $Q_3(\equiv Si\text{-}OH)$ and $Q_4(Si(-OSi)_4)$ sites respectively [17]. However, the intensity of Q_3 signal in FeMCM-41 is considerably decreased along with line broadening. Such behaviour indicates a direct interaction between paramagnetic Fe(III) and Q_3 sites (nuclear-electron coupling), i.e., as a consequence the relaxation time is shortened. This observation is in accordance with the earlier reports and attributed to the isomorphous substitution [16, 18-20]. The presence of a shoulder at −103 ppm, clearly observed in all samples is tentatively assigned to Si(–O–Fe) linkage. Further, it can also be seen from figure
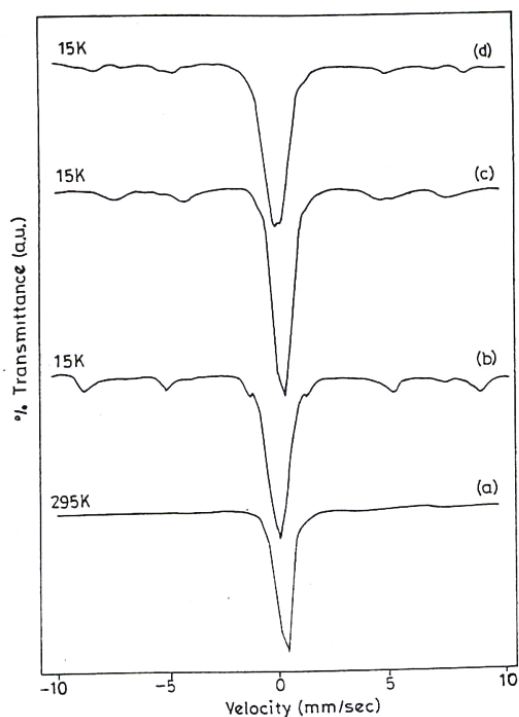
Sample having the highest iron content (i.e., Si/Fe=50) shown significant line broadening along with good signal intensity for Q_3 sites. Presumably, the insertion of Fe(III) in the silicon framework distorts the $[SiO_4]^{4-}$ geometry, and disfavours the condensation of silanol groups as observed in FeMCM-48 [20]. A close inspection of the spectra of calcined samples revealed that the broadening is smaller than the as-synthesized analogues suggesting that part of the Fe(III) ions have remained in the framework [19]. The absence of spinning side bands in all these samples is due to weak dipole-dipole interactions or due to high dispersion of Fe(III) species [21].
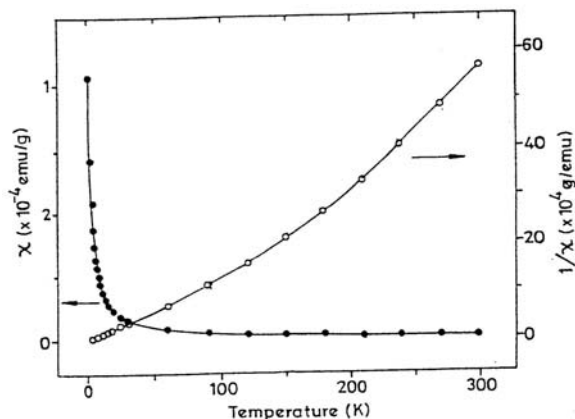
Mössbauer spectra of different as-sythesized FeMCM-41 samples are shown in Figure 4. The room temperature spectrum of FeMCM-41(50) showed a singlet with isomeric shift value of 0.26 mms^{-1} and quadrupole splitting, < 0.5 mms^{-1}, relative to metallic iron.

of different FeMCM-41 samples are composed of both quadrupole doublets and sex-set pattern corresponding to paramagnetic and superparamagnetic Fe(III) species, respectively.

Figure 4. Mössbauer spectra of as-sythesized: (a) FeMCM-41(50); (b) FeMCM-41(50); (c) FeMCM-41(100) and (d) FeMCM-41(200).

Figure 5. Temperature dependence of magnetic susceptibility of FeMCM-41(50).

The temperature dependence of the normal (χ) and reciprocal ($1/\chi$) susceptibilities is shown in Figure 5. The low temperature (<150 K) part of the Curie-Weiss fit, i.e., straight line passing through the origin is indicative of paramagnetic Fe(III) [22]. However, the upward bending of the curve at higher temperature (>150 K) is attributed to the dependence of spontaneous magnetization on temperature. That suggests the magnetic behaviour departs from paramagnetic nature due to the interaction between iron oxy-hydroxy clusters. These interpretations well support the coexistence of paramagnetic and superparamagnetic Fe(III) species in mesoporous FeMCM-41 [25].

This indicates presence of paramagnetic Fe(III) in tetrahedral coordination. However, the spectrum recorded at 15 K showed a six-line pattern along with a strong quadrupole doublet. The presence of doublet pattern is attributed to the high spin Fe(III) in the tetrahedral framework. On the other hand, the sexset pattern is typical characteristics of superparamagnetic particles at low temperature. This observation is in accordance with Kundig et al. [22]. However, close inspection of the spectrum suggests that there may be two sets of six magnetic hyperfine resonance lines. This arises due to the formation of FeO(OH) and Fe_2O_3 nanoparticles from the precipitated $Fe(OH)_3$ under reaction (alkaline) conditions [23, 24]. The low temperature spectra

CONCLUSION

The study of various measurements led us to the conclusion that paramagnetic Fe(III) substitutes isomorphously into the silicate framework of MCM-41 and remains both in distorted and symmetrical tetrahedral geometry. Fe(III) is also present in octahedral coordination (extra-framework positions) within the matrix. Tetrahedral Fe(III) sites are in direct vicinity of silicon tetrahedral and thermally unstable, therefore, partly dislodged during calcination.

Apart from this, Fe(III) is also present as superparamagnetic (oxy-hdroxy)nanoparticles and highly dispersed within mesopores.

ACKNOWLEDGEMENT

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