



## Synthesis, Characterization and Catalytic Studies of Mn-MCM-48

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High quality MCM-48 was hydrothermally synthesized using different silica sources-fumed silica and tetraethylorthosilicate. A comparison of the XRD pattern of the pre- and post treated samples clearly shows the definite well ordered structural pattern in the post treated MCM-48 samples. This is also confirmed from the SEM and TEM images of the sample. The Mn-MCM-48 was also synthesized by ion-exchange and calcinations of the previously prepared MCM-48 with permanganate solution. The EPR analysis shows that the manganese is reduced from  $Mn^{7+}$  to  $Mn^{2+}$  during calcinations and may be in the extra framework octahedral sites of the framework structure. The surface area of the mesoporous material was determined from  $N_2$  adsorption isotherm plot. An epoxidation of styrene study with Mn-MCM-48 shows 87 % conversion in 5 h.

**Key Words:** Mesoporous, Mn-MCM-48, Epoxidation.

### INTRODUCTION

The rapidly growing number of publications about the synthesis, modification and characterization of MCM-48 reflects the growing interest in these mesoporous silica amongst scientist and technologists<sup>1,2</sup>. These mesoporous materials discovered by Mobil<sup>3</sup> and designated as M 41S has cubic structural lattice and belongs to the space group  $Ia3d^{4,5}$ . However compared to MCM-41 with one dimensional hexagonal array of pore channels, MCM-48 has three dimensional pore networks. The unique pore size (2 nm-4 nm) and high surface area (1000-1500  $m^2/g$ )<sup>6</sup> make these mesoporous materials attractive to study adsorption, separation, ion-exchange and size and shape selective catalysis and as host structure for nanowires and nanomaterials<sup>7-9</sup>. As catalyst MCM-48 has more advantage over MCM-41, because of the presence of three dimensional pores, which allow faster diffusion through the channel and makes it more resistant towards pore blocking. The principal difficulty of MCM-48 as reported is the structural instability<sup>10</sup>. However it has been reported<sup>11</sup> that post treatment can increase its structural stability of the MCM-48. Further incorporation of small amount of transition metal does not affect its structure but increases its catalytic property. In view of the above properties of MCM-48, we have attempted to synthesize MCM-48 using different silica sources. We have successfully synthesized Mn-MCM-48 by both pre and post synthesis process and its catalytic activity was studied in epoxidation reactions of styrene.

### EXPERIMENTAL

The MCM-48 were synthesized using fumed silica (Aldrich 99.8 %), tetraethylorthosilicate (TEOS) (Merck 98 %), *N*-cetyl-*N,N,N*-trimethylammoniumbromide (CTAB) (Merck), sodium hydroxide (Merck) and ammonium hydroxide (Merck). The IR spectra of the compounds were taken in KBr pellet with a Perkin Elmer RX I FT-IR instrument. The XRD of the powder samples were recorded between  $1^\circ$ - $10^\circ$   $2\theta$  values with a Bruker powder diffractometer with  $CuK_\alpha$  radiation. The SEM image of the samples was recorded with a LEO (Carl Zeiss) microscope. EPR were recorded with a JES-FA 200 ESR spectrometer instrument at room temperature. The surface area of the catalyst was determined with micromeritics-tristar-3000 instrument after degassing the sample at 373 K for 1 h and then degassing at 523 K for 3 h. The catalytic reactions were carried out in liquid phase by addition of appropriate reactants with the activated catalysts Mn-MCM-48 (0.2 g) and the reaction products were withdrawn periodically and analyzed by GC-MS (Perkin Elmer Clarus-600).

**Synthesis of Mn-MCM-48:** The hydrothermal synthesis of Mn-MCM-48 consists of two steps. In the first step, the required amount of deionized water, ethanol and aqueous ammonia were stirred vigorously at 300 K. Then the required amount of *N*-cetyl-*N,N,N*-trimethyl ammonium bromide were added to the mixture in small lots and then the tetraethyl-orthosilicate was added slowly and stirred for 5 h. The molar

ratio of the synthesis mixture was TEOS:CTAB:H<sub>2</sub>O:ethanol:NH<sub>4</sub>OH = 1:0.4:174:0.4:12.5. The white gel produced was filtered and washed with distilled water. In the second step, 0.05 M *tris*-acetylaceto manganese(III) and the white gel was added slowly to a 2% CTAB solution with constant stirring for one hour and the pH was maintained at 8.5. Then the gel was transferred to an autoclave and heated to 383 K for 72 h. Finally the product was filtered, washed with distilled water and dried. One part of the product was calcined at 813 K for 6 h by initial slow heating at 5 °C per min in a programmable muffle furnace. [Mn(acac)<sub>3</sub>] was synthesized as reported<sup>12</sup>.

The Mn-MCM-48 was also prepared by ion-exchange of 0.1 g calcined MCM-48 with 20 mL of 0.05 molar KMnO<sub>4</sub> for 4 h<sup>13</sup>. The product was filtered, washed with distilled water and dried.

## RESULTS AND DISCUSSION

**IR study:** The IR spectra of the Mn-MCM-48 samples (Fig. 1) shows stretching vibration of silanol Si-OH at 3450 cm<sup>-1</sup> and the bending vibration of H<sub>2</sub>O at 1636 cm<sup>-1</sup>, the asymmetric and symmetric vibrations of Si-O at 1097 cm<sup>-1</sup> and 805 cm<sup>-1</sup> respectively.

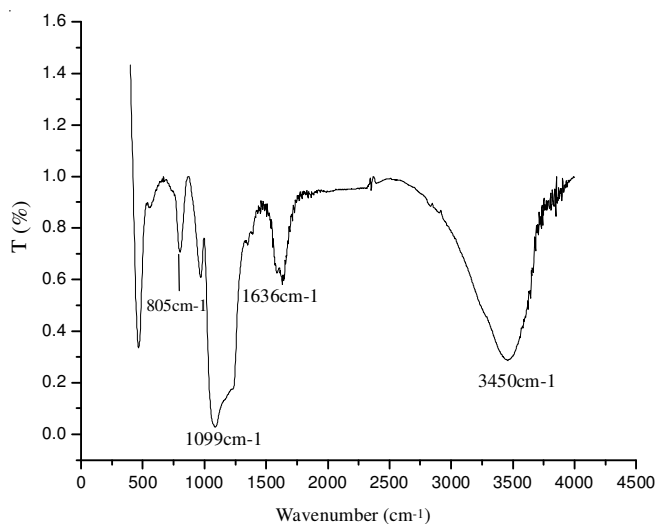


Fig. 1. IR spectra Mn-MCM-48

**DRS study:** The DRS of Mn-MCM-48 showed (Fig. 2) a large absorption at about 320 nm, which may be due to the charge transfer from O<sup>2-</sup> to Mn<sup>2+</sup> in octahedral coordination and the band at 380 nm may be attributed to the octahedral coordination of Mn in the extra framework. But in case of MCM-48 such characteristic absorbance were not observed. This demonstrates the incorporation of Mn in the MCM-48 materials.

**XRD study:** The XRD of Mn-MCM-48 (Fig. 3) shows the typical low-angle *hkl* reflections characteristic of the cubic lattice *Ia3d* and shows that the formation of network for cubic array has started but lacks long range order and may be of noncrystalline nature. As shown in figure a very strong peak at *d* = 39.14 Å (211 plane) was observed. Other weak peaks may be indexed at *d* = 23.8 Å (400 plane), 20.6 Å (420 plane), 19.02 Å (332 plane) and 18.8 Å (422 plane). The characteristic *d*<sub>220</sub> peak of MCM-48 is obtained at 32.07 Å in the sample.

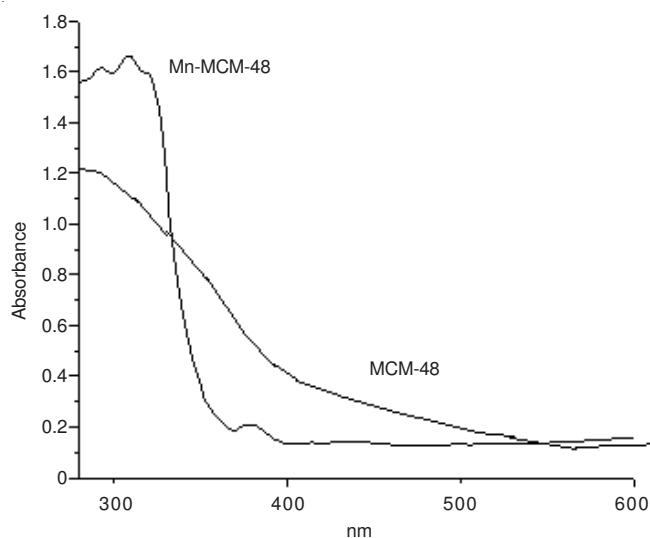


Fig. 2. DR UV-VIS spectra of Mn-MCM-48

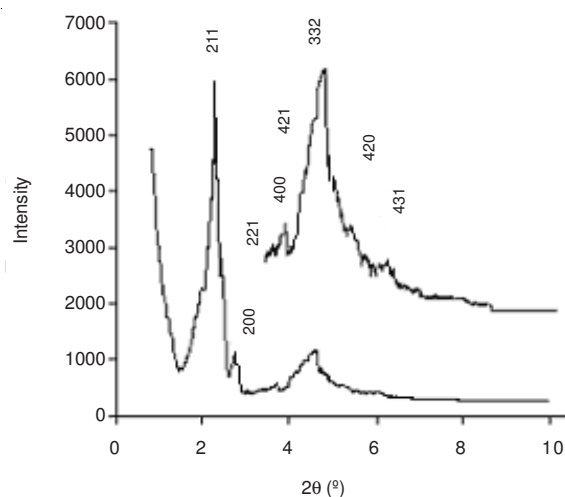


Fig. 3. XRD of Mn-MCM-48

**SEM study:** The SEM of Mn-MCM-48 (Fig. 4) shows that the particles are free standing with some aggregation. The particles are nearly spherical shaped. A closed look reveals the unique cylindrical morphology<sup>14</sup>.

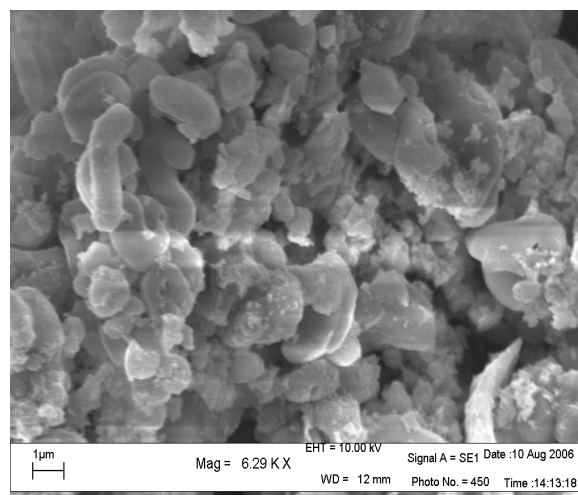


Fig. 4. SEM of Mn-MCM-48

**EPR study:** The room temperature EPR of the Mn-MCM-48 shows (Fig. 5) a signal centered at  $g = 2.03$ . The six well resolved hyperfine line originate from  $Mn^{2+}$  coupled to its own nuclear spin ( $^{55}Mn$ ,  $I = 5/2$ ) and because of significant zero field interaction the sextet lines are not equal in spacing and line height. The manganese atoms may be present at extra framework sites in octahedral symmetry. The EPR analysis also confirms that the manganese is reduced from  $Mn^{7+}$  to  $Mn^{2+}$  during calcinations. This is in conformity with results reported by others<sup>15-17</sup>.

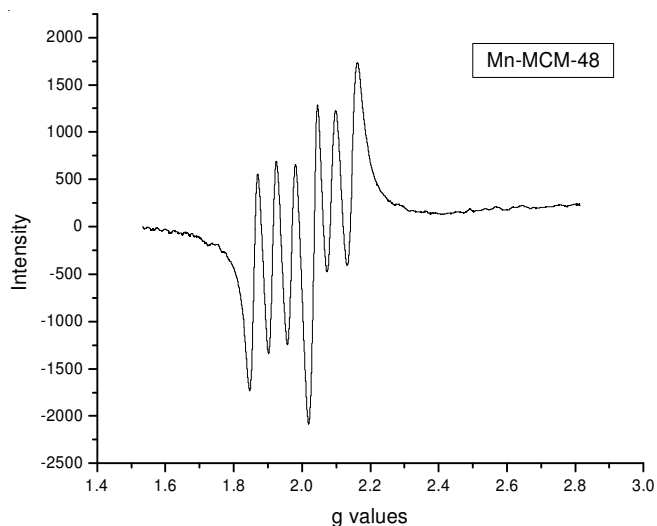


Fig. 5. EPR of Mn-MCM-48

**Nitrogen adsorption/desorption isotherm:** The hysteresis loop of the Mn-MCM-48 in the nitrogen adsorption isotherm (Fig. 6) at a relative pressure  $P/P_0 = 0.0-0.35$  is due to capillary condensation of nitrogen within the pores and at the pressure  $P/P_0 = 0.5-1.0$  is due to interparticle porosity. The BET surface area was  $510 \text{ m}^2\text{g}^{-1}$ . The BJH adsorption average pore diameter (4V/A) was 2.75 nm and BJH desorption average pore diameter (4V/A) was 2.5 nm.

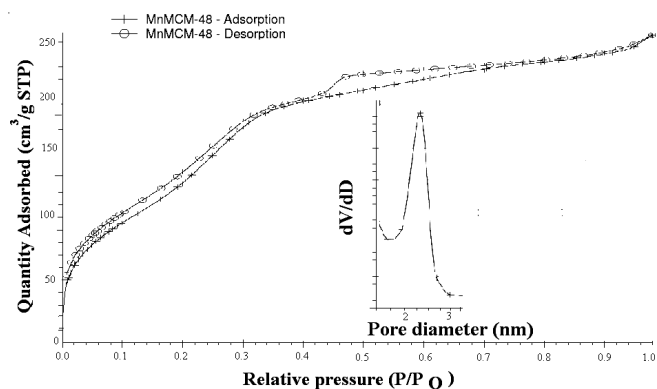
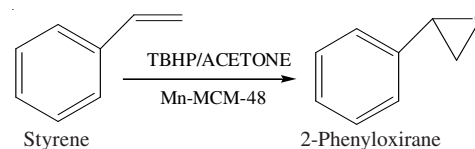


Fig. 6. Nitrogen adsorption/desorption isotherm of Mn-MCM-48

**Catalytic activity of Mn-MCM-48:** The epoxidation reaction of styrene was carried out by refluxing of 2 mL of styrene with 1.5 mL of TBHP in 3 mL of acetone and 0.2 g of catalyst for 5 h (Scheme-I). The products were identified by GC-MS and the percentages of yield were calculated (Table-1) at different time intervals.



Scheme-I

TABLE-1  
PRODUCT YIELD (%)

Time (h)	1	2	3	4	5
Product (%) yield (2-phenyloxirane)	34	49	66	87	87

From the table, it can be seen that the product formation increases upto 87 % in 4 h. It has been reported<sup>18,19</sup> that titanium silicate-1 (TS-1) gives 85 % and *Tris*(d,d-dicampholyl-methanato) iron(III) complex  $[Fe(dcm)_3]$  gives 90 % yield of the styrene oxide. Our catalyst Mn-MCM-48 also gives similar results.

### Conclusion

High quality Mn-MCM-48 can be synthesized with fumed silica as well as tetraethylorthosilicate. The manganese atoms may be present at extra framework sites in octahedral symmetry. The incorporation of Mn increases the catalytic activity towards epoxidation reactions.

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