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**RESEARCH ARTICLE**

# Tailoring of Morphology and Texture of Mesoporous Molecular Sieve MCM-41 by using Different Silica Sources

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## *Abstract*

Highly ordered pure-silica MCM-41 material possessing well-defined morphology has been successfully synthesised. Attempts have been made for the synthesis of highly ordered MCM-41 using different silica sources such tetraethylorthosilicate (TEOS), sodium silicate and fumed silica. By studying the effect of various silica sources on the morphology and texture of MCM-41, a fast, convenient, scalable, facile and cost-effective methodology was developed. The synthesised samples were characterised by XRD, $N_2$-physisorption, SEM and TEM.

## INTRODUCTION

Porous materials have gained high importance in the field of applied science and engineering. These materials are mainly characterized by their porosity. IUPAC, classification is associated with three pore size regimes, such as:

- Microporous, smaller than 2 nm
- Mesoporous, between 2 and 50 nm
- Macroporous, larger than 50 nm[1]

Syntheses of porous materials are essential to the development of innovative high performance products. Microporous and mesoporous solids are used in catalysis, gas separation, soil remediation, water management, hydrothermal vents, oil recovery and the removal of metal and organic contaminants from process streams[2,3]. First time in 1992, scientists from Mobil Oil Corporation, U.S. were successful in development of ordered MCM-41 mesoporous materials of the M41S family[4].

- MCM-41 which has a hexagonal arrangement of one-dimensional pore channels
- MCM-48 which has a three dimensional cubic pore structure
- MCM-50 which is lamellar structure in the non-calcined form.

Following the discovery of mesoporous materials, the synthesis of hierarchically ordered structures has generated a great deal of effort to control simultaneously morphology and texture. Reaction parameters such as solvent, temperature, aging, drying, stirring rates, pH, silica precursor, surfactant type, and the ratio of surfactant to silica play an important role in tailoring the final shape and size of the internal structure for specific applications.[5-10]

Among these mesoporous molecular sieves, MCM-41 is the most important for potential application in catalysis, adsorption, separation, sensing, medical usage, bio-medicals, ecology, electronic technologies, electro-optical devices and nanotechnology[11,12].

In the present paper, we have describe a detailed study of the effects of the various silica sources on the morphology and texture of MCM-41 silica spheres prepared in a water medium with liquor ammonia as catalyst at very low surfactant concentrations (0.15).

## 2. Methods and Materials:

### 2.1 Chemicals:

Cetyltrimethyl ammonium bromide (Spectrochem), Aqueous ammonia (25 wt. %, Fisher Scientific), Tetraethyl orthosilicate (TEOS, Aldrich), Sodium silicate (Loba Chemie) and Fumed silica (Kemphasol). All chemicals were AR grade hence they were used without further purification.

### 2.2 Experimental procedure:

The mesoporous silica, MCM 41 was synthesized by hydrothermal method. In the typical synthesis, cetyltrimethyl ammonium bromide dissolved in double distilled water. In this solution a fixed amount of (9.52 g) of aqueous ammonia (25 wt %) was added. Further silica source was added dropwise under vigorous stirring to get white precipitate. The molar composition of the resultant gel was $1SiO_2$: 0.152CTAB: $2.8NH_3$: $141.2H_2O$. This gel was stirrered for 2 hr in the autoclave at 373K then after it was filtered and washed several times. The obtained filter cake was dried at 373 K for 12 hr. In temperature control furnace the obtained power was calcined at 823 K for 5.5 hr at the rate of $1^0$/min to expel the template.

### 2.3 Charactarization:

The synthesized Si-MCM-41 and its modified forms were characterized by different tools to identify phase purity, morphological and structural parameters such as:

- Power X-ray diffraction: The powder patterns were obtained using Cu Kα radiation on a Rigakau diffractometer. The samples were scanned for 2θ from 1 to $10^0$
- N2-physisorption: Surface areas and pore diameters of the samples were determined from $N_2$-adsorption-desorption isotherms using a commercial volumetric adsorption apparatus (Omnisorp 100 CX, Coulter Corporation, USA). Approximately 100-150 mg of the calcined sample was degassed at $400^0$C for 5h at $10^{-5}$ Torr, prior to surface area measurements. The sample was then cooled to 77K using liquid nitrogen and the sorption of nitrogen was carried out at different equilibrium pressures.
- Electron Microscopy (SEM/TEM): The crystallite size and morphology of the as-synthesized and calcined samples were determined by a scanning electron microscope (Model JEOL JSM 5200)

## 3. Result and discussion:

The time dependant study was carried out for synthesis of good quality of MCM-41 using different silica sources *i.e.* fumed silica, sodium silicate and tetraethyl ortho silicate.

The synthesized sample that has shown highest $a_o$ (unit cell parameter) value was selected and labeled as MCM-41-XX where XX indicates silica source used [FS - fumed silica, SS – sodium silicate and TS – tetraethyl ortho silicate]. Figure 1 shows the powder XRD pattern of MCM-41-TS, MCM-41-FS and MCM-41-SS. The synthesis time required to obtain MCM-41 phases with highest $a_o$ values using different silica sources are provided in Table 1.

On the basis of time required to obtain highly ordered MCM-41, the silica source reactivity trend observed in the present studies was: TEOS > fumed silica > sodium silicate. A rapid hydrolysis process of tetraethyl ortho silicate assisted by efficient condensation may be responsible for achieving high ordering degree within the shorter synthesis period as compared to other silica source materials.

From Figure 1, the XRD patterns of MCM-41-FS, MCM-41-SS and MCM-41-TS showing four reflections which can be assigned to the hexagonal lattice of the mesoporous materials. The (100), (110) and (200) reflections are well resolved in all the samples. In case of MCM-41-TS along with three reflections, a fourth diffraction peak with a notable lower intensity, corresponding to (210) reflections, was also observed. This indicates that an excellent quality of MCM-41 has been obtained when TEOS is used as a silica source.

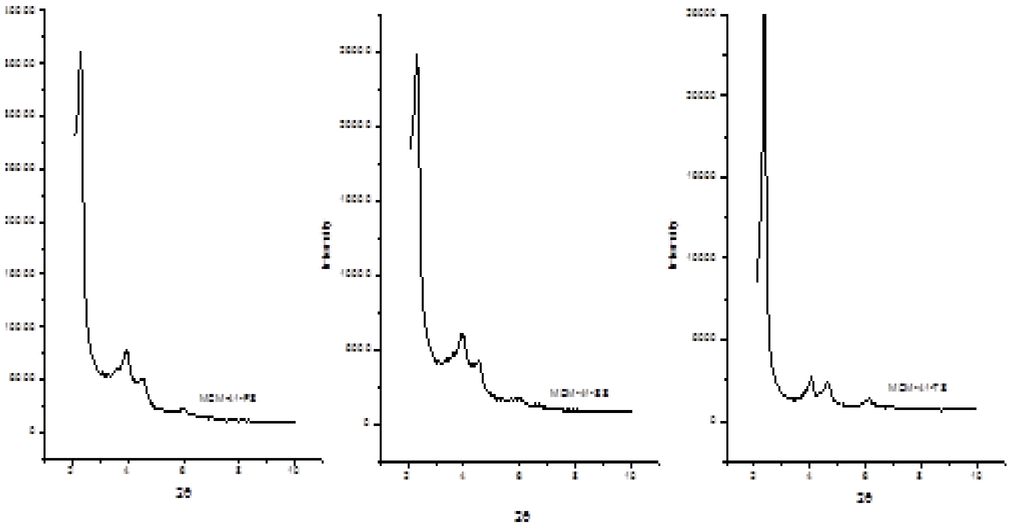
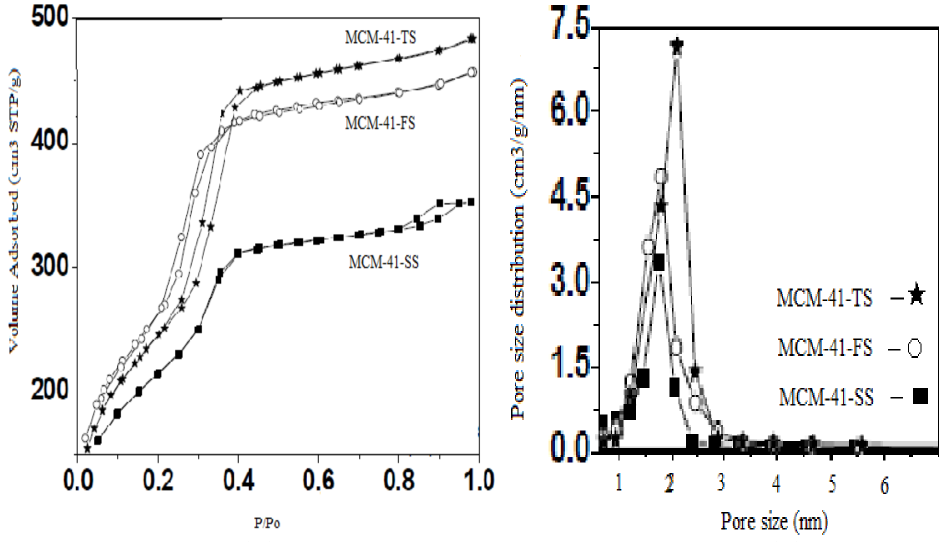


**Figure 1: The XRD pattern of (A) MCM-41-FS, (B) MCM-41-SS and (C) MCM-41-TS**

Also MCM-41-TS was found to be highly ordered while MCM-41-FS and MCM-41-SS lack sharp higher diffraction angle peaks, which indicate poor orderness and presence of some contribution due to amorphous matter. Since the quality of the product depends on the fraction of $Q^4$ [Si (OSi)4] units in the gel[13]. Among these three sources, the gel prepared using tetra ethyl ortho silicate may contain lower proportion of $Q^4$ units. Thus lower degree of silica polymerization in the gel seems to be respossible for synthesizing high quality MCM-41. Therefore, it can be concluded that, lower the degree of silica polymerization in the gel, higher the quality of product formed.

All the calcined MCM-41-TS, MCM-41-SS and MCM-41-FS samples were subjected for their textural/structural characteristics. Nitrogen adsorption and desorption isotherms are given in Figure 2 while the Figure 2 (B) depicts the pore size distribution curves obtained from desorption branch and BJH method. The data concerning their specific pore volume, specific surface area, average pore diameter and the wall thickness are also summarized in Table 1.



(A) (B)

**Figure 2: (A) Nitrogen adsorption and desorption isotherm of MCM-41 samples synthesised using different silica source and (B) Pore size distribution**

All samples exhibit pronounced steep condensation step for relative pressures 0.2 to 0.4 arising from condensation of nitrogen inside the primary mesopores which is typical type IV adsorption-desorption isotherm. The condensation step on the isotherms is steep particularly for MCM-41-TS and MCM-41-FS as compared to

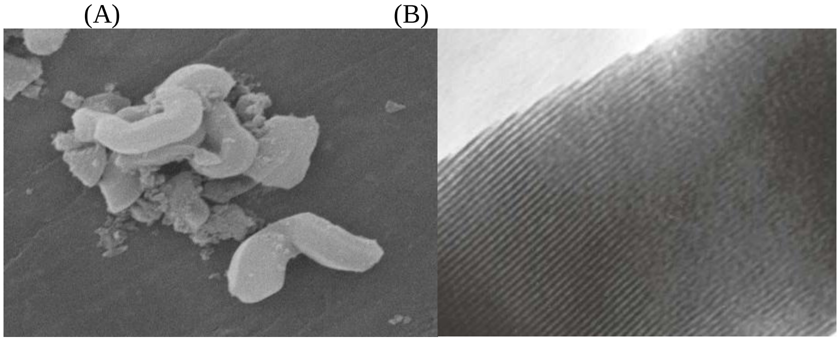
MCM-41-SS. Gradual development of hysteresis loops was observed for samples MCM-41-TS and MCM-41-FS. The change in the shape of hysteresis loop was found to be consistent with increase in the primary mesopore size. The quality of the product was found to affect the width of hysteresis loops and steepness of the condensation. In addition to this, the appearance of hysteresis loops below relative pressure of 0.40 may be partly attributed to the instability of liquid nitrogen meniscus for nitrogen adsorption studies. Sample MCM-41-TS has narrow pore size distribution as compared to other samples.

The unit cell parameter of MCM-41-TS is higher as compared to MCM-41-FS and MCM-41-SS. Specific surface area is also higher for MCM-41-TS. The mutual inverse proportion was observed between BET specific surface area and wall thickness. This can be justified on the basis of definition of specific surface area. Since it takes into account the weight of the sample, the material with higher wall thickness will certainly have lower specific surface area. Moreover, the specific surface area and pore volume were found in direct proportion in these samples. The wall thickness was calculated by difference between the unit cell parameter and the pore diameter.

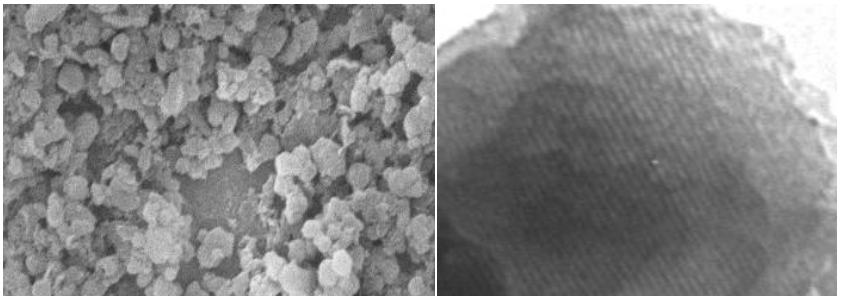
**Table 1: Effect of silica source on structural and textural properties of MCM-41**

| Sample designation | Inter planar spacing $d_{100}$ (Å) | Unit cell parameter $a_0$ (Å) | Hydrothermal synthesis time (h) | Spe. surface area ($m_2$/g) | Pore diameter (Å) | Pore volume (ml/g) | Wall thickness (Å) |
|---|---|---|---|---|---|---|---|
| MCM-41-FS | 36.10 | 41.73 | 24 | 936 | 23.53 | 0.60 | 18.2 |
| MCM-41-SS | 34.47 | 39.84 | 48 | 1015 | 22.94 | 0.65 | 16.9 |
| MCM-41-TS | 37.99 | 43.91 | 2 | 1062 | 27.2 | 0.68 | 16.71 |

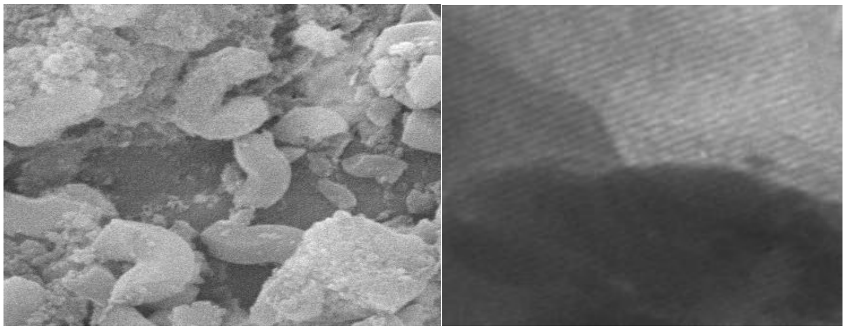
The SEM and TEM micrographs of MCM-41-FS, MCM-41-SS and MCM-41-TS are illustrated in Figure 3. The morphology of the particles was found to be influenced by the silica source used. The MCM-41-FS and MCM-41-SS have shown worm like morphology whereas MCM-41-TS has shown the presence of fused particles. This may be due to the fast hydrolysis of tetraethyl ortho-silicate. It is clearly evident from TEM images of MCM-41 samples prepared with different silica sources that well-ordered MCM-41 materials can synthesize using the fumed silica, sodium silicate and tetraethyl ortho-silicate.



MCM-41-FS



MCM-41-TS



MCM-41-SS

**Figure 2.19: (A) SEM micrographs and (B) TEM micrographs of MCM-41 samples synthesised using different silica sources**

## 4. Conclusion:

Thus, here we can conclude that using TEOS as silica source excellent quality of MCM-41 is synthesised. We also have showed that the silica source plays key role on the texture and the morphology of mesoporous MCM-41. The developed synthesis methodology is fast, convenient and easily scalable to produce large quantity. Also it is a cost effective methodology as high quality of MCM-41 synthesised within a short period time. One of the drawback of the MCM-41 synthesised using sodium silicate as silica source is that presence of $Na^+$ in mesoporous silica is often undesirable with respect to stability and in some cases unfavourable to the incorporation of hetero atoms. Thus, using TEOS silica source, purely siliceous MCM-41 synthesised which is used further for post synthesis modification by metal ion exchange to act as catalysts in various industrial processes.

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