ORDERED NANOPORE SILICATES (IITM-56):
SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

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Mesoporous molecular sieves are special class of materials with ordered arrays of uniform pores, high surface areas and large pore volumes. These periodic silica/silica-based materials are promising for variety applications including catalysis, adsorption and separation processes. Two most common types involve MCM-41 and SBA-15 has ordered structures consisting of two dimensional hexagonal arrays of uniform mesoporous. SBA-15 has larger pores, thicker walls and higher thermal stability as compared to other mesoporous silicas including MCM-41. However, it is of interest to make materials with a combination of moderate pore size and thicker wall structure. Therefore, in this investigation, an attempt has been made to prepare materials with desired characteristics using oligomeric alkyl poly ethylene oxide (Brij-56) surfactant template. We report here, for the first time, a novel mesoporous silicate material, designated as IITM-56, with a (moderate) pore size of 38.4 Å and a wall thickness of 21 Å. XRD pattern of IITM-56 depicts structure which is typical characteristics of MCM-41/SBA-15. TG studies of IITM-56 show a 49% weight loss in conjunction with exothermic transition (DTA) suggestive of mesoporous nature of the material. This further confirmed by N₂ sorption measurements, which indicate type IV isotherm with capillary condensation at 0.3-0.4 (P/P₀).

Keywords: mesoporous silicate, MCM-41, SBA-15, IITM-56.

INTRODUCTION

In ordered porous solids, the reactant molecules interact not only on the surface but also inside the pore walls of the materials. This property of enhancement in reaction sites is of immense importance and hence, in recent years, there is a great urge in exploiting these materials for a variety of applications. In this regard, the conventional microporous materials (zeolites) are suitable only to molecules of limited size and that causes diffusivity problems for large molecules while mesoporous materials can very well be used for such purpose (Taguchi and Schüth, 2005). Thus, periodic silica/silica-based nanoporous materials are promising for variety applications including catalysis, adsorption and separation processes. Although a majority of the studies have been focused on MCM-41 type materials (Selvam et al., 2001), there has been continued interest in developing new mesophases owing to its low surface acidity and hydrothermal stability. Among the numerous phases, the structure based on SBA-15 seems to be promising although the mesopore organization is similar to that of MCM-41 but with larger pore diameters, micropores and thicker walls (Selvam et al., 2010a). The SBA-15 can be synthesized in various morphologies as linear silicate oligomers are mainly generated in acidic medium and that poly (alkylene oxide) tri-block co-polymer (Pluronic P-123) is as template. Although SBA-15 exhibits very good textural properties and hence has got greater advantage of tunable pores but due to its larger pore size, side reactions often occur leading poor selectivity of products (Gao et al., 2005). Therefore, there is a necessity to make materials with a combination of moderate pore size and thicker wall structure such that the material will have high selectivity and also greater hydrothermal stability. In this investigation, an attempt has been made to
prepare mesoporous silicates, designated as IITM-56, with desired characteristics using Brij-56 surfactant as structure directing agent.

EXPERIMENTAL

Mesoporous IITM-56 silicates were prepared as per the following procedure: At first, Brij-56 surfactant was dissolved in water and 2M hydrochloric acid, and stirred at room temperature to obtain a homogeneous solution. To this solution, calculated amount of TEOS was added and again stirred at 50°C for 24 h. The mixture was then transferred into a Teflon-lined autoclave and kept at 100°C for 24 h. The reaction vessel was cooled to room temperature and the product obtained was filtered, washed and dried at 60°C for 6 h, referred as as-synthesized IITM-56, followed by calcination 550°C for 6 h at a heating rate of 1°C/min, referred as calcined IITM-56. The samples were systematically characterized by various analytical and spectroscopic techniques.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of both as-synthesized and calcined IITM-56. The well resolved diffraction peaks can be indexed based on 2D-hexagonal symmetry (Zhao et al., 1998). The unit cell parameters calculated from the XRD data are 6.15 and 5.94 nm for the as-synthesized and calcined samples, respectively. Calcination of the as-synthesized IITM-56 gives rise to relatively low shrinkage and an increase of diffraction intensity which is indicative of the framework stability in a similar way to that of SBA-15 and MCM-41.

![Figure 1. XRD patterns of IITM-56: a) as synthesized; b) calcined](image-url)
Figure 2 depicts the electron diffraction and high resolution TEM micrographs of IITM-56, which confirms the hexagonal topography along 100 direction (Figure 2a). The HRTEM images of IITM-56 also show well ordered hexagonal arrays of mesopores with one dimensional channels indicating 2D-hexagonal mesostructure both in parallel and perpendicular directions (Figure 2b & 2c). Figure 3 presents the TG-DTA traces of as-synthesized IITM-56, which shows typical four-stage weight loss characteristic of mesoporous materials: a small loss at 100°C corresponds to removal of water and/or adsorbed gas molecules; the second and third weight loss at 150-300°C is due to oxidative degradation of surfactant molecules; the fourth-stage weight loss at 450°C is due to the condensation/dehydroxylation of silanol groups in agreement with MCM-41 and SBA-15 (Jaroniec et al., 2000).

![Figure 2. a) Electron diffraction; b) and c) HRTEM of IITM-56](image)

Figure 2. a) Electron diffraction; b) and c) HRTEM of IITM-56

![Figure 3. TG-DTA of as synthesized IITM-56: (—) TG; (- - -) DTA.](image)

Figure 3. TG-DTA of as synthesized IITM-56: (—) TG; (- - -) DTA.

Figure 4 illustrates the FT-IR spectra of both as-synthesized and calcined IITM-56 samples. The band at 972 cm$^{-1}$ is due to the $\nu_{\text{Si-OH}}$ stretching vibration of the hydrogen-bonded silanol groups. The stretching vibrations $\nu_{\text{OH}}$ of the surface silanol groups and
adsorbed water and their bending mode $\delta_{O-H}$ is seen as broad peak 3100 and 3800 cm$^{-1}$ region and at 1630 cm$^{-1}$ respectively. The bands corresponding to $\nu_{as}(\text{Si-O-Si})$ and $\nu_{s}(\text{Si-O-Si})$ appear at 1050 and 800 cm$^{-1}$ respectively. The bands due to symmetric and asymmetric stretching modes of $-\text{CH}_2$ group of the template are seen below 3000 cm$^{-1}$ and the corresponding bending mode at 1400 cm$^{-1}$. The absence of bands in these regions in the calcined sample infers the loss of surfactant molecules upon calcination (Pastore et al., 2010).

Figure 4. FT-IR Spectra of IITM-56: a) as synthesized; b) calcined

Table 1. Structural and textural properties of various mesoporous silicates

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_0$ (nm)</th>
<th>SBET ($m^2 g^{-1}$)</th>
<th>D (nm)</th>
<th>$V_p$ ($cm^3 g^{-1}$)</th>
<th>hw (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IITM-56</td>
<td>5.94</td>
<td>772</td>
<td>3.84</td>
<td>0.98</td>
<td>2.1</td>
</tr>
<tr>
<td>MCM-41</td>
<td>4.30</td>
<td>897</td>
<td>2.90</td>
<td>1.24</td>
<td>1.4</td>
</tr>
<tr>
<td>SBA-15</td>
<td>10.18</td>
<td>663</td>
<td>6.48</td>
<td>1.06</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Figure 5 shows the $^{29}$Si MAS-NMR of as-synthesized and calcined IITM-56. The samples show two main signals; a strong signal centered at $\sim -110$ ppm, assigned to $Q^4$ site [Si(OSi)$_4$], and $\sim -100$ ppm corresponding to $Q^3$ site [Si(SiO)$_3$(OH)]. The stronger intensity of $Q^4$ as compared to $Q^3$ indicates complete condensation of silanol groups of the mesoporous matrix (Zhao et al., 1998). Figure 6 gives the $N_2$ sorption isotherms of IITM-56 which show a type IV pattern typical characteristic of mesoporous channel. A well-defined step occurs at a relative pressure of 0.3-0.4, corresponding to capillary condensation of $N_2$, indicative of the uniformity of the pores and pore size similar to
MCM-41. Textural properties of IITM-56, SBA-15 and MCM-41 were tabulated in Table 1. It is clear from this table that IITM-56 has wall thickness similar to SBA-15 and pore size similar to MCM-41. Such a desired characteristic of the silicate materials is achieved mainly due to the choice of surfactant (Brij-56); as it has C16 carbon chain similar to CTAB and ethylene oxide units similar to pluronic P-123.

![29Si MAS NMR of IITM-56: a) as synthesized; b) calcined](image1)

**Figure 5.** $^{29}\text{Si MAS NMR of IITM-56: a) as synthesized; b) calcined}$

![N$_2$ sorption isotherms and pore size distribution of IITM-56](image2)

**Figure 6.** N$_2$ sorption isotherms and pore size distribution of IITM-56
CONCLUSION

In summary, a nanoporous silica IITM-56 with advantages of both MCM-41 and SBA-15 was successfully synthesized and was systematically characterized. IITM-56 with its large pore volume, high surface area and the presence of silanol groups can lead to homogeneous dispersion of active species when used as support material. Further, IITM-56 can also be used as hard template for the preparation of ordered mesoporous carbon, NCCR-56 (Selvam et al., 2010b) in a similar way to that of SBA-15 and MCM-41, respectively for the preparation of CMK-3 (Ryoo et al., 1999) and NCCR-1 (Selvam et al., 2008).

REFERENCES


