

## Significant improvement in the pore properties of SBA-15 brought about by carboxylic acids and hydrothermal treatment

MILAN KANTI NASKAR<sup>1</sup> and M ESWARAMOORTHY<sup>2,\*</sup>

<sup>1</sup>Sol–Gel Division, Central Glass and Ceramic Research Institute, Kolkata 700 032

<sup>2</sup>Chemistry and Physics of Materials Unit and Department of Science and Technology

Unit for Nanoscience, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064

e-mail: eswar@jncasr.ac.in

**Abstract.** A comparative study of the pore properties of SBA-15 samples prepared under non-hydrothermal and hydrothermal conditions, in the absence and presence of carboxylic acids such as succinic, tartaric and citric acids has been carried out. In the absence of carboxylic acid, flake-like and spheroid particles were generally obtained irrespective of the preparative procedures. On the other hand, stirring of the pre-mix induces a rod-like morphology in presence of carboxylic acids. The samples prepared under non-hydrothermal conditions exhibit a higher degree of silicate condensation compared to those synthesized under hydrothermal conditions. SBA-15 samples prepared under hydrothermal conditions show higher values of the *d* (100) spacing independent of the presence of carboxylic acids. Presence of carboxylic acids as well as hydrothermal treatment improves the pore properties of SBA-15.

**Keywords.** SBA-15; mesoporous; carboxylic acids; adsorption; hydrothermal treatment; morphology.

### 1. Introduction

Molecular sieves with large pores have been of great use in carrying out reactions and separation processes involving large molecules.<sup>1,2</sup> While the discovery of MCM-41 is a high point in this area of research,<sup>3,4</sup> many other mesoporous silicas, in particular SBA-15, have also been found to exhibit important features.<sup>5</sup> Thus, SBA-15 has larger pores and thicker walls than MCM-41, in addition to controlled micropores in its walls.<sup>5</sup> The channels in SBA-15 are interconnected to mesopores through micropores.<sup>6</sup> Several variations in the synthesis of SBA-15 have been examined in recent years to improve the characteristic surface properties such as the pore volume and surface area.<sup>7,8</sup> For example, the size of mesopores is enhanced by the addition of hydrocarbons.<sup>9</sup> Addition of organic and inorganic salts to the synthetic mixture has been reported to give rise to exotic particle shapes of SBA-15.<sup>10</sup> SBA-15 silica rods have been synthesized under static conditions in the absence of salts as well.<sup>7</sup> It is found that the surface area and pore volume of SBA-15 are both affected when the material is synthesized under hydrothermal conditions.<sup>8</sup> Pore properties of mesoporous materials also seem to show improvement on

addition of hydroxycarboxylic acids to the synthetic mixture.<sup>11</sup> In view of these findings, we considered it valuable to carry out a comparative study of SBA-15 samples prepared under normal static conditions and by hydrothermal heat-treatment in the presence and absence of hydroxy-carboxylic acids. For this purpose, we have prepared SBA-15 samples in the presence of tartaric and citric acids under hydrothermal and non-hydrothermal conditions, and compared their pore properties with those of a sample prepared with succinic acid as well as of the standard sample prepared in the absence of any carboxylic acids. The results reveal that SBA-15 samples prepared hydrothermally in the presence of succinic, tartaric and citric acids, possess improved pore properties such as surface area and pore volume. This observation could be of value in practical applications.

### 2. Experimental

#### 2.1 Materials and methods

Mesoporous silica SBA-15 was synthesized according to the literature procedure.<sup>5</sup> In a typical preparation, 2 g of pluronic P-123 amphiphilic block-copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) (Aldrich, USA)

\*For correspondence

was dissolved in 15 g of millipore water and 60 g of 2 M HCl under stirring at  $37 \pm 1^\circ\text{C}$  for 1 h. To this solution, 4.25 g of tetraethylorthosilicate (TEOS) (Aldrich, USA), pre-hydrolysed with corresponding carboxylic acids (Merck, India) in water and ethanol mixture (TEOS : organic acid :  $\text{H}_2\text{O}$  :  $\text{C}_2\text{H}_5\text{OH}$  = 1 : 0.1 : 4 : 3), was added under stirring. The stirring was continued at the same temperature for 20 h. The above mixture was heated separately at  $100^\circ\text{C}$  for 24 h under static or hydrothermal conditions. The solid products were collected by filtration followed by calcinations at  $550^\circ\text{C}$  at rate of  $1^\circ\text{C min}^{-1}$  for 6 h in flowing air. The same experiments were also carried under non-stirring conditions for 20 h, followed by non-hydrothermal or hydrothermal heat-treatment.

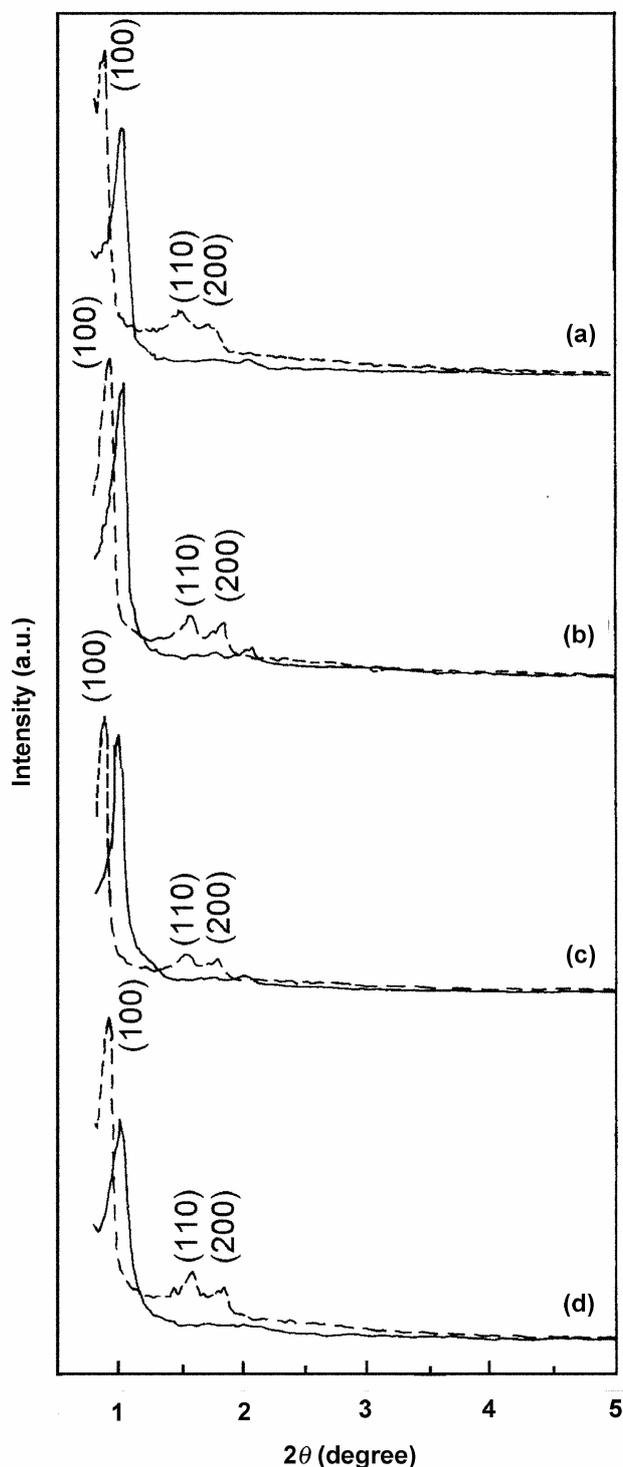
## 2.2 Characterization

SBA-15 mesoporous silica was characterized by a combination of physical techniques. X-ray diffraction (XRD) patterns were recorded using a SEIFERT, XRD 3000TT powder diffractometer system with  $\text{CuK}\alpha$  radiation (40 kV, 30 mA) with 0.01 step size and 1 s step time over the range  $0.8 < 2\theta < 10$ . The Scanning electron microscopy (SEM) images were obtained using a Leica S440i microscope and transmission electron microscopy (TEM) with a JEOL 3010 microscope. BET (Brunauer, Emmett and Teller) specific surface areas were obtained from the nitrogen adsorption experiments measured at 77 K after degassing the samples below  $10^{-3}$  Torr at 473 K for 2 h using an Autosorb-1C (Quantachrome) unit. The pore size distribution was determined from the desorption branch of the isotherm by BJH (Barrett-Joyner-Halenda) method. The total pore volume was calculated as the amount of nitrogen adsorbed at the relative pressure of ca 0.99. Pore wall thickness was calculated as: Pore wall thickness =  $d(100) * 2/\sqrt{3}$  – pore diameter, where  $d(100) * 2/\sqrt{3}$  represents the unit cell parameter and  $d(100)$  is the d-spacing value of the (100) diffraction peak in XRD patterns of the samples.<sup>29</sup>Si MAS NMR was recorded with a Bruker DSX-300 MHz spectrometer. The variation in the size of micelles at the initial stage of pre-mixing was monitored by dynamic light scattering using a Malvern instrument Nanosizer DTS (version 4.10).

## 3. Results and discussion

Figure 1 shows the low angle XRD patterns of SBA-15 prepared in the presence and absence of carbox-

ylic acids under non-hydrothermal and hydrothermal conditions. The values of  $d(100)$  obtained in the pre-

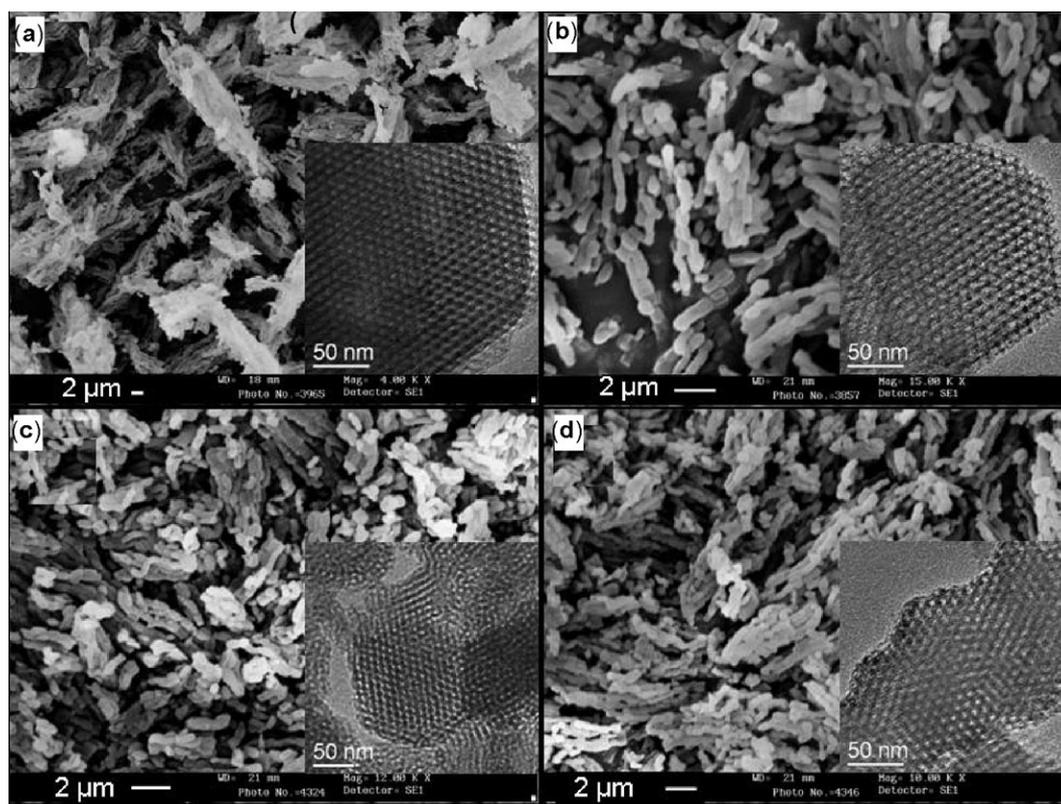


**Figure 1.** X-ray diffraction pattern of SBA-15 synthesized under stirring at  $37 \pm 1^\circ\text{C}$  followed by non-hydrothermal (solid line) and hydrothermal (dashed line) heat-treatment at  $100^\circ\text{C}$ : (a) in absence of an organic acid and in the presence of (b) succinic acid, (c) tartaric acid and (d) citric acid.

**Table 1.** Pore properties of SBA-15 samples<sup>a</sup>.

Sample	$d(100)$ (nm)	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	Pore size (nm)	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Wall thickness (nm)
Standard sample	8.7 (10.2)	455 (609)	4.3 (5.7)	0.59 (0.93)	5.7 (6.1)
Succinic acid	8.5 (9.6)	465 (635)	4.3 (5.7)	0.60 (1.0)	5.5 (5.4)
Tartaric acid	8.8 (9.9)	530 (685)	4.3 (5.7)	0.73 (1.4)	5.8 (5.7)
Citric acid	8.8 (9.8)	533 (690)	4.9 (5.7)	0.76 (1.1)	5.3 (5.6)

<sup>a</sup>Values in parenthesis correspond to the samples prepared under hydrothermal conditions

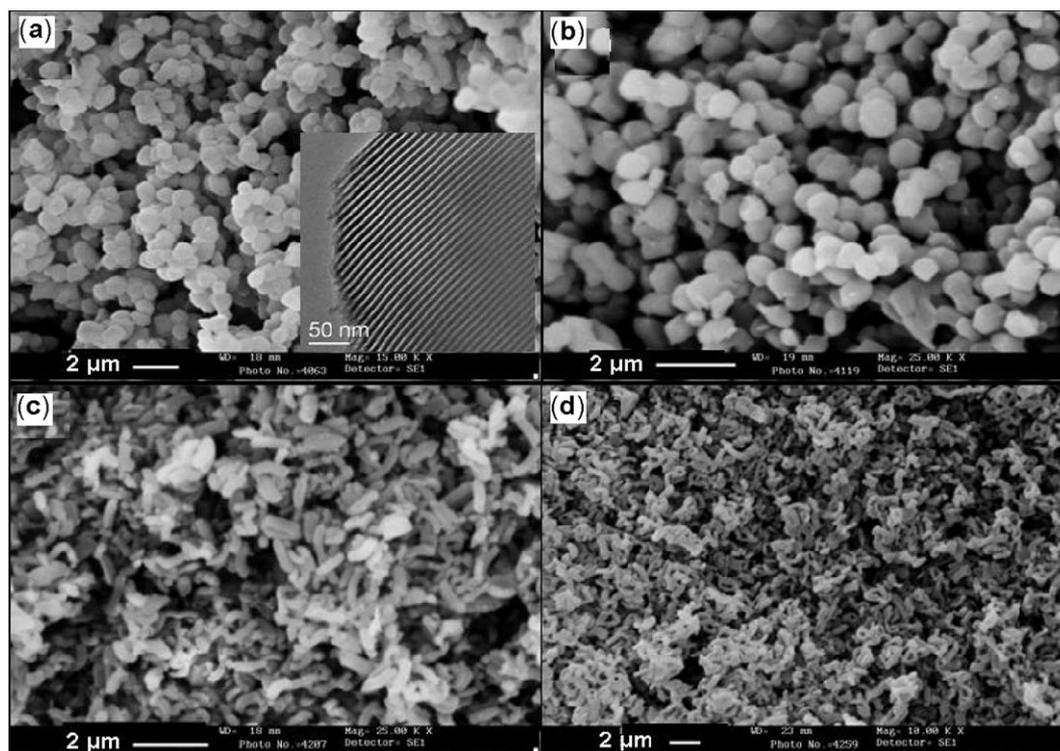


**Figure 2.** SEM images of SBA-15 synthesized under stirring at  $37 \pm 1^\circ\text{C}$  followed by non-hydrothermal heat-treatment at  $100^\circ\text{C}$ : (a) in absence of an organic acid and in the presence of (b) succinic acid, (c) tartaric acid and (d) citric acid. Inset shows TEM images.

sent work matches well with those found in the literature.<sup>5,7</sup> SBA-15 samples prepared in the presence of succinic, tartaric and citric acids, under non-hydrothermal conditions have  $d(100)$  values in the 8.5–8.8 nm ranges while  $d(100)$  values of the samples prepared under hydrothermal conditions are in the range of 9.6–9.9 nm (table 1). The two low intensity peaks associated with the (110) and (200) planes are very small and broad for the sample synthesized under non-hydrothermal condition.<sup>5</sup> These peaks are sharper in the hydrothermally prepared samples, signifying a higher degree of order. The SBA-15 sample prepared

under non-hydrothermal conditions in the absence of any carboxylic acids, shows a wall thickness of 5.7 nm derived from the pore size and the unit cell parameter. The sample prepared under hydrothermal condition exhibits a wall thickness of 6.1 nm (table 1). There appears to be a distinct increase in the wall thickness in hydrothermal preparations. Interestingly, the samples prepared in presence of acids exhibit a wall thickness in the 5.2–5.8 nm ranges, independent of the acid and the method of preparation (table 1).

In the absence of carboxylic acids, the SEM image of the SBA-15 sample shows a flake-like mor-



**Figure 3.** SEM images of SBA-15 synthesized without stirring at  $37 \pm 1^\circ\text{C}$  followed by hydrothermal heat-treatment at  $100^\circ\text{C}$ : (a) in absence of an organic acid and in the presence of (b) succinic acid, (c) tartaric acid and (d) citric acid. Inset shows TEM image.

phology (figure 2a) while in the presence of succinic acid the particles are rod-like (figure 2b) under both non-hydrothermal and hydrothermal conditions when the precursors were pre-mixed under stirring. However, on mixing the precursors without stirring, spheroid morphology is observed under both non-hydrothermal and hydrothermal conditions (figures 3a, b). In the presence of tartaric and citric acids, the SEM images show rod-like morphology independent of whether non-hydrothermal or hydrothermal conditions are employed, as revealed by figures 2c, d and 3c, d. The TEM images show well-ordered hexagonal pore channels in all the SBA-15 samples as can be seen from the insets of figures 2a–d. The TEM images also reveal arrays when viewed perpendicular to the channel axis (see inset of figure 3a).

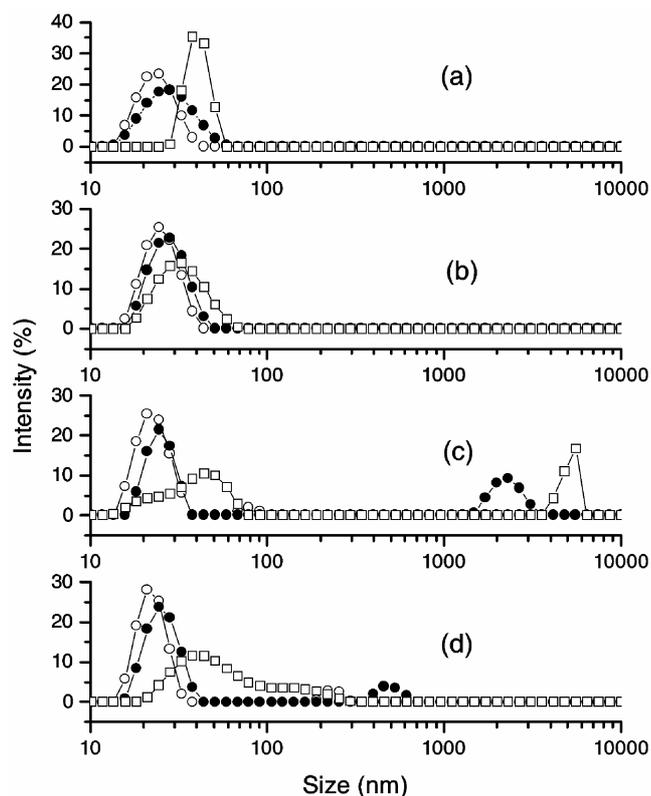
In order to understand the effect of carboxylic acids on the micelle size distribution, DLS experiments were carried out in the presence and absence of acids at different intervals of time (10, 20 and 30 min) after pre-mixing the precursors and the results are given in figure 4. As expected, the average particle size becomes larger in all the cases as the reaction proceeds with time. Notably, an abrupt change in the

particle size is observed in the case of tartaric and citric acids after 20 min of reaction showing a bimodal size distribution. This is consistent with the rod-like morphology observed in SEM. The presence of large number of hydroxyl groups in these acids might favour the interaction of adjacent spherical micelles through hydrogen bonding which organizes to form an elongated rod-like micelles over which the silicate ions condenses.

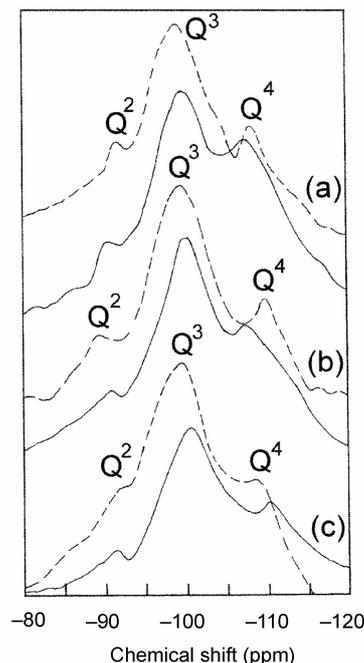
$^{29}\text{Si}$  MAS NMR spectra of the SBA-15 samples prepared in the absence and presence of carboxylic acids under non-hydrothermal and hydrothermal conditions are shown in figure 5. All these samples exhibit prominent signals for the Q<sup>3</sup> ( $\text{Si}(\text{OSi})_3(\text{OH})$ ) and Q<sup>4</sup> ( $\text{Si}(\text{OSi})_4$ ) species around 100 and 110 ppm respectively, with the intensity of the former being higher. It is known that Q<sup>3</sup> is more intense than Q<sup>4</sup> in the mesophases prepared under acidic conditions.<sup>12</sup> A higher intensity of Q<sup>3</sup> indicates a lower degree of condensation of the silicate species. It is also significant that Q<sup>3</sup>/Q<sup>4</sup> ratio of SBA-15 samples prepared under hydrothermal condition (in the absence and presence of carboxylic acids) is higher than that of the same samples prepared under non-

hydrothermal condition. It is possible that at higher pressure, the condensation process may be favourable.

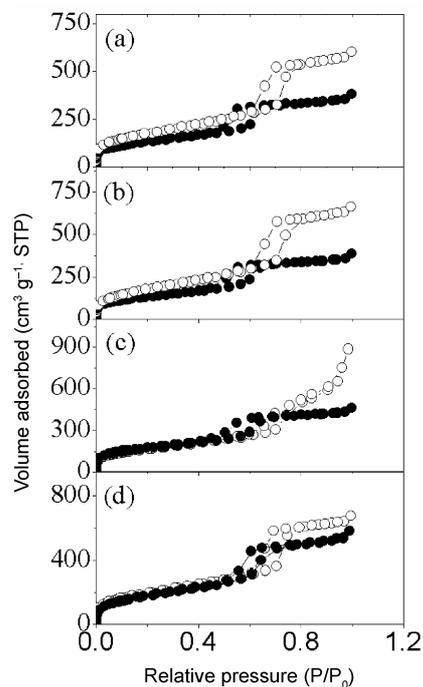
In figure 6, we show the adsorption–desorption isotherms of SBA-15 samples prepared in the presence and the absence of carboxylic acids under non-hydrothermal and hydrothermal conditions. All the samples exhibit typical IV isotherms. The BJH pore size distributions of the samples are shown in figure 7. The BET surface area, pore size and pore volume of the SBA-15 sample prepared under non-hydrothermal conditions in the absence of any carboxylic acid are  $455 \text{ m}^2 \text{ g}^{-1}$ ,  $4.3 \text{ nm}$  and  $0.59 \text{ cm}^3 \text{ g}^{-1}$  respectively (table 1). The sample prepared under hydrothermal conditions exhibits the BET surface area, pore size and pore volumes of  $609 \text{ m}^2 \text{ g}^{-1}$ ,  $5.7 \text{ nm}$  and  $0.93 \text{ cm}^3 \text{ g}^{-1}$  respectively. The BET surface area, pore size and pore volume are relatively higher for hydrothermally treated sample. The SBA-15 samples prepared in the presence of succinic, tartaric and citric



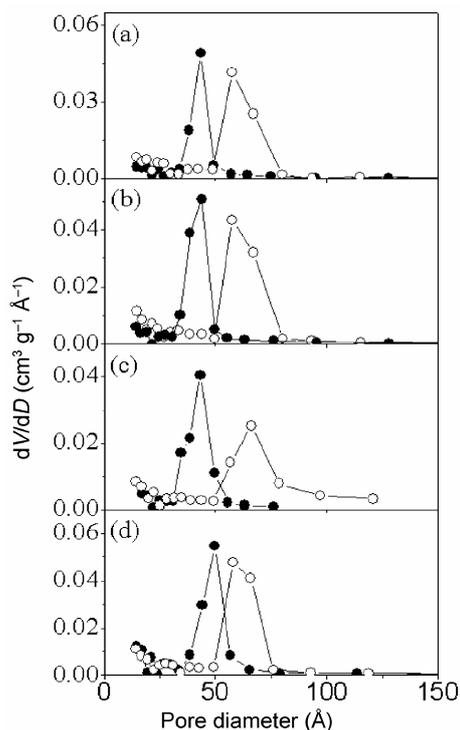
**Figure 4.** Laser particle size measurements of micelles at different time intervals after pre-mixing (a) P123, TEOS, (b) P123, TEOS and succinic acid, (c) P123, TEOS and tartaric acid and (d) P123, TEOS and citric acid at  $37 \pm 1^\circ\text{C}$ .; Open circle represents after 10 min; solid circle represents after 20 min and open square represents after 30 min of reaction.



**Figure 5.**  $^{29}\text{Si}$  MAS solid-state NMR spectra of SBA-15 synthesized under stirring at  $37 \pm 1^\circ\text{C}$  followed by non-hydrothermal (solid line) and hydrothermal (dashed line) heat-treatment at  $100^\circ\text{C}$ : (a) in absence of an organic acid and in the presence of (b) succinic acid and (c) citric acid.



**Figure 6.** Nitrogen adsorption–desorption isotherms of SBA-15 synthesized under stirring at  $37 \pm 1^\circ\text{C}$  followed by non-hydrothermal (solid circles) and hydrothermal (hollow circles) heat-treatment at  $100^\circ\text{C}$ : (a) in the absence of an organic acid and in the presence of (b) succinic acid, (c) tartaric acid and (d) citric acid.



**Figure 7.** BJH pore size distribution curves of SBA-15 synthesized under stirring at  $37 \pm 1^\circ\text{C}$  followed by non-hydrothermal (solid circles) and hydrothermal (hollow circles) heat-treatment at  $100^\circ\text{C}$ : (a) in the absence of an organic acid and in the presence of (b) succinic acid, (c) tartaric acid and (d) citric acid.

acids, under non-hydrothermal conditions exhibit comparable pore size distribution but the BET surface area and pore volume are considerably higher for the samples prepared hydrothermally in the presence of these acids (table 1). Table 1 summarizes the pore properties of SBA-15 samples along with their  $d(100)$  values. The BET surface areas of the samples prepared under non-hydrothermal conditions are in the  $465\text{--}533\text{ m}^2\text{ g}^{-1}$  range for the samples prepared in the presence of succinic, tartaric and citric acids, while the pore volumes are in the  $0.60\text{--}0.76\text{ cm}^3\text{ g}^{-1}$  ranges. These samples when prepared hydrothermally exhibit surface areas in the  $635\text{--}690\text{ m}^2\text{ g}^{-1}$  range and pore volumes in the  $1.0\text{--}1.4\text{ cm}^3\text{ g}^{-1}$  range. The effect of carboxylic acids is noteworthy in that they cause a significant increase in surface area and pore volume (table 1). It is to be noted that the latter would have contributions from the micropores as well.

#### 4. Conclusion

Hydrothermal synthesis of SBA-15 gives rise to higher values of  $d(100)$  both in absence and presence of carboxylic acids. In the absence of carboxylic

acids, flake-like or spheroid particles are observed irrespective of preparative procedures. On the other hand, stirring of the pre-mix induces a rod-like morphology in presence of carboxylic acids both under hydrothermal and non-hydrothermal conditions. The higher  $Q^3/Q^4$  ratio of the SBA-15 samples prepared under hydrothermal conditions indicates a lower degree of condensation of the silicate species. The presence of the  $Q^3$  species further promotes a well-aligned structure through hydrogen bonding and hence a higher order reflected in the second order peaks in XRD patterns. Hydrothermal synthesis of SBA-15 carried out in the presence of carboxylic acids such as succinic, tartaric and citric acids brings out a definitive improvement in the pore properties. Unlike the literature reports, which point out the beneficial effects of hydroxycarboxylic acid, the present studies suggest that even a carboxylic acid such as succinic acid to be equally effective in improving the same properties.

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