

Comprehensive characterization of highly ordered MCM-41 silicas using nitrogen adsorption, thermogravimetry, X-ray diffraction and transmission electron microscopy

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Received 6 August 2000; received in revised form 27 November 2000; accepted 28 November 2000

Abstract

Highly ordered MCM-41 silicas were synthesized using a new procedure and their structures were thoroughly characterized. Using the new synthesis method and the previously reported similar one, the pore diameter of MCM-41 can be tailored from 3.1 to 4.9 nm with about 0.35 nm increments and reproducibility usually better than ± 0.1 nm using surfactants of different chain length. The surfactant content and structural parameters of MCM-41 synthesized using the same single surfactant or surfactant mixture were highly similar for different silica:surfactant molar ratios in the synthesis mixture. Moreover, the silica:surfactant molar ratio in as-synthesized MCM-41 was quite independent of the chain length of the surfactant used and approximately equal to 8. This may be related to the well-defined synthesis conditions imposed by the pH adjustment procedure employed. The results indicate that the silica:surfactant ratios in starting mixtures suitable for the synthesis of high-quality MCM-41 under the present synthesis conditions should not exceed about 8 to avoid contamination with amorphous silica. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: MCM-41 synthesis; Mesoporous silica; Nitrogen adsorption; Thermogravimetry; Mesopore structure characterization

1. Introduction

The synthesis and properties of ordered mesoporous materials (OMMs) [1–5] have been extensively

studied during the last decade with the particular interest in the prospective applications of these highly promising materials [6–8]. It is now generally accepted [7] that the synthesis of silica-based OMMs, such as MCM-41 [2], usually involves the formation of ion pairs between the oligomeric silicate species and surfactant ions, and the subsequent self-assembly of these ion pairs into ordered silicate–surfactant composites [3]. It is also

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known that the charge density matching at the silicate–surfactant interface is a crucial parameter which determines the structure of the self-assembled silicate–surfactant composites [3,6,7]. However, some important problems related to the synthesis of OMMs are still far from being fully understood. In particular, there are some indications that the structure type of silicate–surfactant composites and/or the silica:surfactant molar ratio in the product depend on the silica:surfactant molar ratio in the synthesis gel [9–11], although some other studies showed no such dependence [12,13]. The current study addresses the aforementioned problem by providing extensive characterization results for MCM-41 materials synthesized using a new procedure, which involves the use of surfactants with different chain lengths under well-defined synthesis conditions imposed by pH adjustment.

2. Experimental

2.1. Materials

The synthesis of MCM-41 silica was performed with mixed surfactants system consisting of alkyltrimethylammonium bromide ($C_nH_{2n+1}N(CH_3)_3Br$, C_nTMABr for brevity; n denotes the number of carbon atoms in the alkyl chain of the surfactant) and alkyltriethylammonium bromide ($C_nH_{2n+1}N(CH_2CH_3)_3Br$, C_nTEABr), similar to our previous reports [14,15], but the silica:surfactant ratio and mixing mode of the starting mixture were modified. An aqueous solution of sodium silicate (11.3 wt.% $Na_2Si_4O_9$ and 88.6 wt.% H_2O) was used as the silica source as in Refs. [13,14]. In the cases where n was less than or equal to 16, the silica source and the surfactant solution were prepared at room temperature, while reactants for $n > 16$ were heated (328 K for $n = 18$, 333 K for $n = 20$ and 338 K for $n = 22$).

The silica source was rapidly added to a polypropylene bottle containing the surfactant solution, and immediately the bottle was vigorously shaken by hand for about 3–5 min. Mixing was continued for 1 h at the temperature used for the preparation of reactants using a magnetic stirrer.

The starting mixture after the magnetic stirring was heated in an oven at 373 K under static conditions for 24 h. The mixture was cooled to the initial reactant temperature, and the pH of the mixture was adjusted to 10 with acetic acid. The reaction mixture after the pH adjustment was heated for 48 h at 373 K. Then, the pH was adjusted again to 10 with acetic acid at the initial reactant temperature, and heating at 373 K was repeated once again for 48 h. Precipitated MCM-41 products were filtered before cooling and washed with doubly distilled cold water, in order to remove the surfactants that do not participate in the formation of mesostructures. The products were dried in an oven at 373 K before use, or calcined at 823 K in air after extraction of the remaining surfactants with an EtOH/HCl mixture as reported previously.

The silica:surfactant and $C_nTMA^+ : C_nTEA^+$ molar ratios in the synthesis gel for the MCM-41 samples are listed in Table 1. The MCM-41 samples are denoted as C_n or C_n-m , where m is a number used to distinguish different samples prepared using the same surfactant and different silica:surfactant ratios. MCM-41 samples were also prepared as described in Refs. [14,15], including uncalcined (water-washed), ethanol/HCl extracted, and calcined samples synthesized using a mixture of $C_{18}TMA^+$ and $C_{18}TEA^+$ surfactants, the samples being denoted as MCM-41-UC, -EX, and -C, respectively.

2.2. Measurements

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer (500 W) using $Cu K\alpha$ radiation. Nitrogen adsorption measurements were carried out using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, calcined and solvent-extracted samples were outgassed for 2 h at 473 K, whereas the as-synthesized samples were outgassed for several hours at room temperature in the degas port of the adsorption analyzer. Weight change curves were recorded on a TA Instruments TGA 2950 high-resolution thermogravimetric analyzer under nitrogen flow using a high-resolution mode with a maximum heating rate of $5 K min^{-1}$. High-resolution transmission

Table 1
Selected properties of the synthesis gels and the resultant MCM-41 samples

Sample	SiO ₂ :surf initial ratio	C _n TMA ⁺ :C _n TEA ⁺ initial ratio	d_{100}^A (nm)	d_{100} (nm)	Weight loss 373–823 K (%)	Residue at 1270 K (%)	SiO ₂ :surf ratio – as-synthesized
C12	2.8:1	1:0	3.52	3.38	31	63	8.9:1
C14	3:1	1:0	3.84	3.71	34	60	8.5:1
C16-1	1:1	0.8:0.2	4.03	3.91	42	54	7.0:1
C16-2	2:1	0.8:0.2	4.09	3.92	39	56	7.8:1
C16-3	3:1	0.8:0.2	4.11	4.01	39	55	7.7:1
C16-4	3.2:1	0.8:0.2	4.20	3.98	37	58	8.5:1
C16-5	4:1	0.8:0.2	4.14	3.96	38	56	7.8:1
C16-6	5:1	0.8:0.2	4.05	3.96	38	56	8.1:1
C16-7	6:1	0.8:0.2	4.03	4.03	39	56	7.8:1
C18	3.5:1	0.66:0.34	4.39	4.22	46	50	6.5:1
C20	3.8:1	0:1	4.70	4.44	44	53	8.3:1
C22	4:1	0:1	5.02	4.90	44	52	8.8:1

SiO₂:surf initial ratio – molar ratio of silica to surfactant in the synthesis gel; C_nTMA⁺:C_nTEA⁺ initial ratio – molar ratio of alkyltrimethylammonium to alkyltriethylammonium in the synthesis gel; d_{100}^A and d_{100} – XRD (100) interplanar spacing for the as-synthesized and calcined sample; Weight loss 373–823 K and Residue at 1270 K – thermogravimetric weight loss from 373 to 823 K, and residue at 1270 K; SiO₂:surf ratio – as-synthesized – molar ratio of silica to surfactant in as-synthesized sample estimated from TGA.

electron microscopy (HRTEM) images were acquired using a JEOL JEM-3010 TEM as described elsewhere [15].

2.3. Calculations

The specific surface area was calculated using the standard BET method [16]. The total pore volume (the volume of pores of diameter below about 200 nm) was estimated from the amount adsorbed at a relative pressure of about 0.99 [16]. The primary mesopore volume, external surface area, and micropore volume were evaluated using the α_s plot method [16–18]. Pores are classified herein on the basis of their diameter as micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) [16]. Ordered mesopores are referred to as primary mesopores, whereas other mesopores and macropores (up to about 200 nm) are referred to as secondary pores. The primary mesopore diameter and pore wall thickness of MCM-41 were evaluated from the XRD unit cell parameter and primary mesopore volume using the geometrical method [15,18]. The pore size distribution was calculated using the BJH algorithm [19] calibrated to accurately reproduce the pore diameter, and

pore volume of MCM-41, as proposed by Kruk, Jaroniec, and Sayari [18]. The silica:surfactant molar ratio in the as-synthesized samples was evaluated from the TGA data assuming that (i) the residue at 1270 K is composed of SiO₂ only, (ii) the weight of surfactant in the sample is equal to 95% of the weight loss between 373 and 823 K (the 5% adjustment from 100% was made in attempt to account for the water release as a result of framework condensation), and (iii) in the case of mixed surfactants, their molar ratio in as-synthesized samples is equal to that in the synthesis gel. The assumptions (i) and (ii) appear well-supported in light of TGA and elemental analysis results reported in Refs. [9,20].

3. Results and discussion

XRD patterns for the calcined MCM-41 samples featured from 4 to 6 well-resolved reflections (some of them are not visible in Fig. 1 because of the intensity scale used) despite the fact that the patterns were recorded on a simple powder diffractometer using rather short counting times (15 min for scan from 2θ from 1.2° to 10°) and

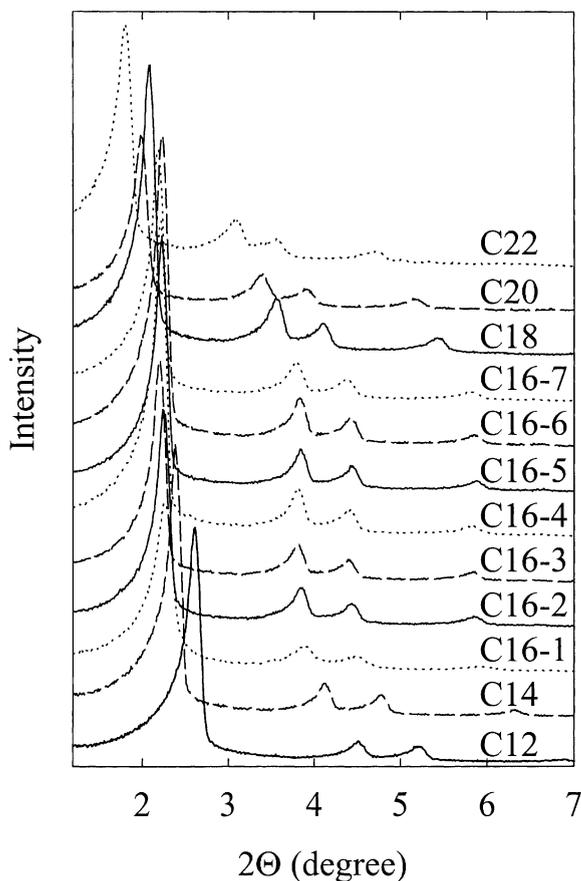


Fig. 1. Powder XRD patterns for calcined MCM-41 samples.

therefore the background noise was relatively large. Similarly well-resolved patterns were recorded for as-synthesized samples and there was no evidence of XRD reflections other than those characteristics of two-dimensional hexagonal MCM-41 phase, thus precluding the possibility of the presence of ordered impurities, for instance lamellar phase. The resolution of the XRD patterns for the samples synthesized using different silica:surfactant ratios (C16-*m* samples) was similar, the only exception being the lowest silica:surfactant ratio, for which the XRD pattern was less well-resolved. Under the conditions used, the MCM-41 phase was obtained independently from the silica:surfactant ratio in the synthesis gel, as already reported for MCM-41 prepared using similar synthesis procedure [13]. Several other researchers reported similar results [11,12], but

Vartuli et al. [9] were able to obtain different silicate-surfactant phases simply by varying the silica:surfactant ratio.

The unit cell parameters for the MCM-41 materials were dependent on the chain length of the surfactant used and covered a wide range of values (Table 1). For C16 MCM-41 prepared using different silica:surfactant ratios, the unit cell size was approximately constant, but the intensity of XRD reflections was significantly different (although our data are not sufficient for a quantitative comparison), being the highest for a sample prepared using silica:surfactant ratio of 3.2:1. For all samples under study, the unit cell contraction upon calcination was small (below 6%, see Table 1).

Nitrogen adsorption isotherms and pore size distributions for the MCM-41 samples are shown in Figs. 2 and 3. The capillary condensation

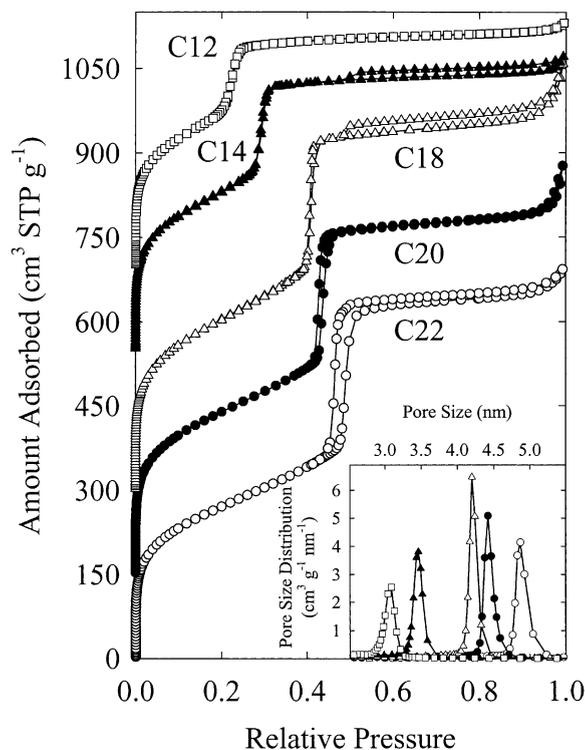


Fig. 2. Nitrogen adsorption isotherms and pore size distributions of calcined MCM-41 samples synthesized using surfactants of different chain lengths. The adsorption isotherms for C20, C18, C14, and C12 samples were offset vertically by 150, 300, 550, and 700 cm^3 STP g^{-1} , respectively.

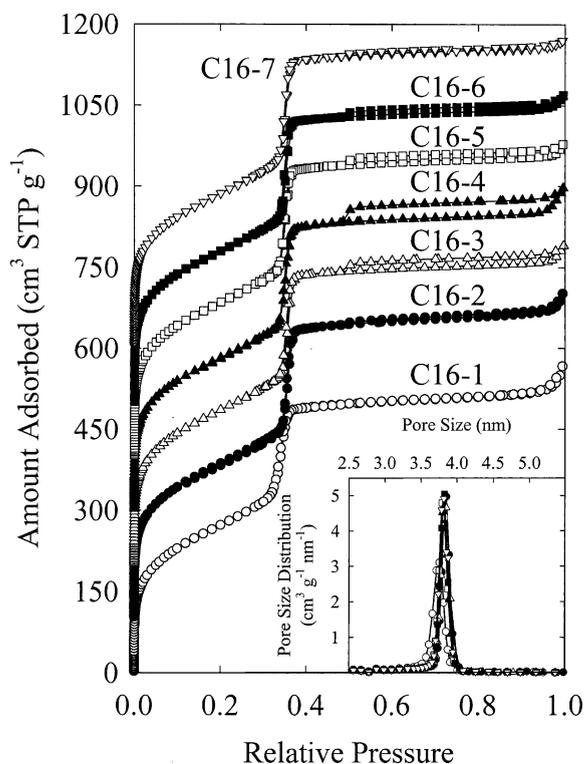


Fig. 3. Nitrogen adsorption isotherms and pore size distributions of calcined MCM-41 samples synthesized using surfactants with hexadecyl alkyl chains. The adsorption isotherms for C16-2, -3, -4, -5, -6, and -7 samples were offset vertically by 100, 200, 300, 400, 500, and 600 $\text{cm}^3 \text{STP g}^{-1}$, respectively.

pressure systematically increased with the increase in the surfactant alkyl chain length, as already reported (see Ref. [15] and references therein), which reflects the gradual pore size increase. In the case of C16 MCM-41, adsorption capacity and the width of the pore size distribution were largely independent of the silica:surfactant molar ratio in the synthesis gel, although the large relative amount of surfactant (1:1 ratio) resulted in slightly decreased adsorption capacity accompanied with some loss of pore size uniformity. The calcined samples exhibited similar BET specific surface areas (about $1000 \text{ m}^2 \text{ g}^{-1}$) and their primary mesopore size systematically increased in accord to the alkyl chain length of the surfactant used in the synthesis (about 0.35 nm increase per two additional carbon atoms in the alkyl chain) (see Table 2). The pore sizes were very close to those reported earlier [15] for MCM-41 samples prepared using a similar synthesis procedure involving surfactants with the same alkyl chain length [14]. The differences usually were below 0.1 nm with the largest being only 0.16 nm. This indicates that using the synthesis procedure reported herein or that described in Ref. [14], one can synthesize MCM-41 materials of custom-tailored pore size with about 0.35 nm increments and reproducibility of about ± 0.1 nm. It is also interesting to note that the primary mesopore sizes calculated using the two

Table 2
Structural properties of the calcined MCM-41 samples

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_t ($\text{cm}^3 \text{ g}^{-1}$)	w_d (nm)	w_{KJS} (nm)	b_d (nm)	V_p ($\text{cm}^3 \text{ g}^{-1}$)	S_{ex} ($\text{m}^2 \text{ g}^{-1}$)
C12	950	0.66	3.10	3.07	0.95	0.61	30
C14	1020	0.79	3.53	3.46	0.92	0.73	30
C16-1	990	0.85	3.74	3.76	0.95	0.75	50
C16-2	1040	0.91	3.82	3.84	0.89	0.82	40
C16-3	1040	0.90	3.91	3.84	0.91	0.83	30
C16-4	1020	0.91	3.87	3.81	0.91	0.81	30
C16-5	1030	0.88	3.86	3.81	0.90	0.83	30
C16-6	1010	0.87	3.84	3.82	0.92	0.81	30
C16-7	1040	0.88	3.93	3.80	0.91	0.83	20
C18	1100	1.13	4.20	4.20	0.87	0.94	80
C20	1040	1.12	4.40	4.42	0.94	0.92	70
C22	980	1.06	4.88	4.86	1.01	0.94	60

S_{BET} – BET specific surface area; V_t – total pore volume; w_d – primary mesopore diameter calculated using the geometrical method; w_{KJS} – primary mesopore diameter calculated using BJH method calibrated as proposed by Kruk, Jaroniec and Sayari (KJS) [18]; b_d – pore wall thickness calculated using the geometrical method assuming hexagonal pore geometry; V_p – primary mesopore volume; S_{ex} – external surface area.

methods employed herein exhibited excellent agreement with differences usually smaller than 0.1 nm. The primary mesopore volume in general increased as the surfactant chain length increased, the only exception being C18 MCM-41 with the pore volume larger than that of C20 and C22 samples. The MCM-41 samples exhibited small or moderate external surface areas and secondary pore volumes (differences between the total pore volume and primary mesopore volume) and had no detectable microporosity. The pore wall thickness was similar for all samples.

Except for C18 MCM-41, weight losses in the temperature range of the surfactant decomposition (373–823 K) had a tendency to increase as the length of the surfactant alkyl chain increased, whereas residues at 1270 K tended to decrease (Table 1). The weight losses and residues were similar for the samples prepared using hexadecylammonium surfactants with different silica:surfactant molar ratios in the synthesis gel. In all cases, there was a good correlation between the primary mesopore volume and the weight loss corresponding to the surfactant decomposition, which clearly indicated that the as-synthesized MCM-41 samples did not undergo any appreciable collapse upon calcination, and their contamination with any silicate:surfactant phase, which would collapse upon calcination, is highly unlikely. This in turn suggests that rectangular-shaped hysteresis loops observed at relative pressures above 0.5 for some of the samples, such as for C14, C16-4, and C18, have a different origin from that of the triangular-shaped hysteresis loops commonly observed for MCM-41 contaminated with lamellar phase which collapsed upon calcination [21]. The origin of the rectangular-shaped hysteresis loops is not fully clear, but the recent study showed that similar hysteresis loops may arise from the presence of defects (void spaces) inside the MCM-41 particles [22].

The silica:surfactant molar ratio for the as-synthesized MCM-41 materials under study was found to be relatively constant (about 8, see Table 1), being quite independent from the silica:surfactant ratio in the synthesis gel and from the chain length/headgroup size of the surfactants. Similar

silica:surfactant ratios in MCM-41 were obtained for samples prepared using the previously reported similar synthesis procedure [14]. Silica:surfactant ratio is known to change as a result of the pH adjustment [23]. One can speculate that the repeated pH adjustment procedure imposes well-defined conditions in the synthesis gel, thus facilitating the formation of materials with well-defined silica:surfactant ratios. Having this in mind, one can consider formation of MCM-41 under well-defined conditions as a kind of a stoichiometric reaction, although the polymeric nature of the silicate framework and the micellar nature of surfactant species may certainly be quite forgiving as far as the deviations from the stoichiometry are concerned.

As already reported for MCM-48 templated using surfactants of different alkyl chain length [24], the maxima on weight change derivatives for as-synthesized MCM-41 samples shifted to some extent to higher temperature as the surfactant alkyl chain length increased. For the samples synthesized using alkyltriethylammonium surfactants or their mixtures, considerable weight losses were observed at about 700 K, whose extent clearly increased as the molar ratio of the large head-group surfactant in the synthesis gel increased. Thus, the decomposition of part of alkyltriethylammonium surfactant appears to take place at temperatures considerably higher than those for alkyltrimethylammonium. Apparently, the large head-group surfactant undergoes Hoffmann elimination (the major mechanism of alkylammonium surfactant decomposition [2]) less readily than the smaller head-group surfactant does.

In order to gain further insight into the properties of MCM-41 materials, as-synthesized, solvent-extracted and calcined samples synthesized using the previously reported procedure [13] were studied. Similarly to MCM-48 [24], as-synthesized (surfactant-containing) MCM-41 had inaccessible primary mesoporosity and its secondary porosity resembled that of the surfactant-free materials, as seen from the higher-pressure parts of nitrogen adsorption isotherms (Fig. 4). The surfactant-containing MCM-41 has a relatively hydrophobic external surface, thus indicating its extensive cov-

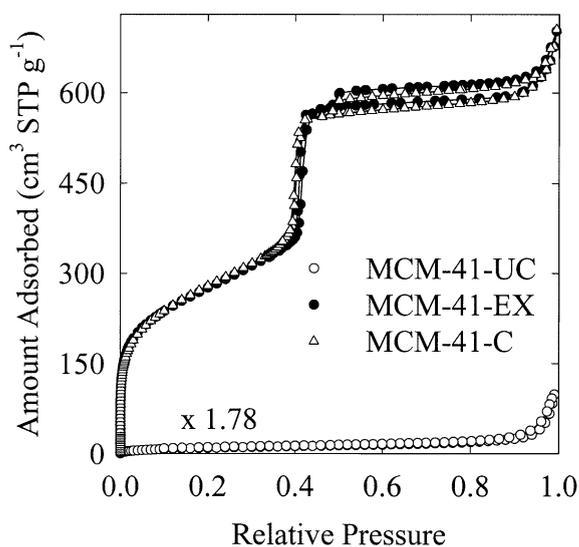
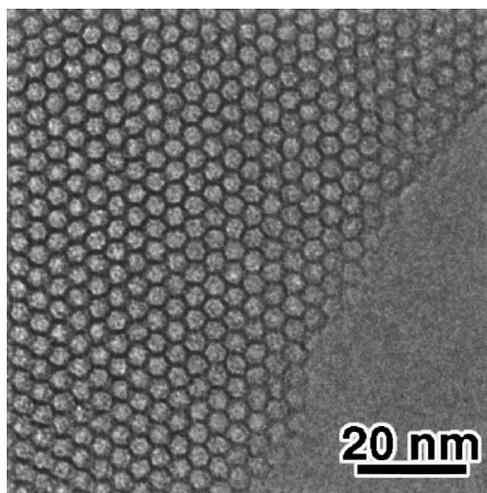
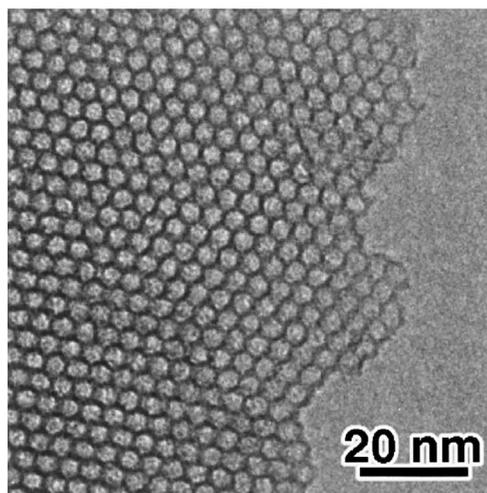


Fig. 4. Comparison of nitrogen adsorption isotherms for as-synthesized uncalcined, template-extracted uncalcined, and calcined MCM-41 sample. The amount adsorbed for the as-synthesized sample was recalculated for the mass of the silica in the sample.

erage with electrostatically bonded surfactant ions with alkyl chains exposed to exterior of the particles [15,24]. As seen from HRTEM, calcination did not have any major effect on the degree of structural ordering and the pore shape, the latter being approximately hexagonal (Fig. 5). The finding about the hexagonal pore shape for MCM-41 samples studied (which may or may not be a general feature of all MCM-41 samples) is very important in some applications of MCM-41 as a model adsorbent (for instance in specific surface area and statistical film thickness calculations [15]). Nonetheless, in many other cases, a circular pore model is clearly a good approximation. Ethanol/HCl-extracted samples usually exhibited low content of residual surfactant (below 2–3 wt.%, based on TGA data). Despite of the presence of residual surfactant and larger degree of hydroxylation, some of the extracted samples had larger adsorption capacity and in general had larger pore sizes than those of the calcined materials (see Fig. 5). This lends credence to HRTEM results, which indicate that the silica pore walls of MCM-41 and FSM-16 thicken as a result of calcination [15,25].



C14MCM-41 as-synthesized



C14MCM-41 calcined

Fig. 5. HRTEM images of as-synthesized and calcined C14 MCM-41 synthesized as described in Ref. [14].

Acknowledgements

M.J. acknowledges the donors of the Petroleum Research Fund administered by the American Chemical Society for a partial support. R.R. acknowledges a partial support from KOSEF (961-0305-037-2). O.T. thanks CREST, JST for financial support.

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