

Expanding the Pore Size of MCM-41 Silicas: Use of Amines as Expanders in Direct Synthesis and Postsynthesis Procedures

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New opportunities are discussed for the pore-size engineering of mesoporous silicas using amines as swelling agents. It was shown that *N,N*-dimethylhexadecylamine (DMHA) is a convenient expander allowing for the synthesis of large-pore MCM-41 in mild conditions. Their pore size increased and the structural ordering decreased as the amount of the amine in the synthesis gel increased. The material with the largest pore size attained (7.7 nm) exhibited narrow pore-size distribution, very large primary mesopore volume, but a disordered pore system. Other amines, such as trioctylamine and tridodecylamine, were also found to be suitable for preparation of large-pore MCM-41 but not as efficient as DMHA. Addition of dimethyldecylamine (DMDA), dimethyloctylamine (DMOA), and small trialkylamines to the synthesis gel did not lead to the pore size enlargement but decreased the structural uniformity and in some cases resulted in development of microporosity. It was also demonstrated that it is possible to induce up to 3-fold enlargement of pore size of as-synthesized MCM-41 by treating it in an aqueous emulsion of an appropriate amine, such as DMHA, DMDA, and DMOA. This novel synthesis approach allowed us to prepare materials with pore sizes up to 11 nm, pore volumes up to 2.4 cm³/g, large surface areas (about 1000 m²/g), and narrow pore-size distributions. Although it was possible to achieve a limited pore-size increase (ca. 20%) with retention of the hexagonal structure, more significant enlargement was accompanied by loss of ordering. Structural features of materials restructured under different conditions, such as temperature, treatment time, and nature of the amine used, are described, and structural changes during the pore size enlargement are discussed.

Introduction

Since their discovery in the early nineties,¹ MCM-41 and related mesoporous molecular sieves attracted much attention. This strong interest stems from a number of remarkable facts: (1) These materials, with MCM-41 in particular, exhibit a pore system with adjustable sizes within a wide range that expands the range of zeolitic micropores. (2) They may be prepared under a variety of experimental conditions in terms of pH, composition, type of precursors and templates, temperature, and time. (3) They exhibit a number of desirable physical properties such as high surface area and pore volume, high thermal stability, and ease of surface modifications.

The development of strategies for the synthesis of materials with controllable pore sizes within as wide a range as possible has been targeted by many research groups.^{1–19} Listed in Table 1 are recently developed techniques for the synthesis of silicas with narrow pore-size distributions, pore dimensions ranging from small mesopores (2–4 nm) to macropores (> 50 nm), and often periodic structures. Several approaches, such as the use of surfactants with different chain lengths, oligomers, and polymers, as well as swelling agents, were inspired by known behavior of surfactant and polymer solutions.^{1–7,13–19} Other methods use high temperature (ca. 423–438 K) during direct synthesis or postsynthesis treatment to enlarge the pore size of

TABLE 1: Recently Developed Methods for Synthesis of Silicas with Narrow Pore-Size Distributions and Tailored Pore Sizes

pore size (nm)	method	ref
2–5	use of surfactants of different chain lengths as templates: charged (usually alkyltrimethylammonium) neutral (usually amines)	1, 2 3
4–10	use of charged surfactants and expanders: aromatic hydrocarbons alkanes trialkylamines alkyldimethylamines	1, 2, 4 5 6, 7 7
4–7	hydrothermal postsynthesis treatment: in mother liquor in water	8, 9 2
2.5–6.6	high-temp synthesis	10–12
4–11	water–amine postsynthesis treatment	7
2–30	use of oligomers and polymers as templates	13–17
> 50	emulsion templating	18
> 200	colloidal crystallization	19

preformed materials.^{7–12} In many of these synthesis approaches, application of swelling agents plays an important role.^{1,2,4–7,16,17} In particular, aromatic hydrocarbons were used by Mobil scientists to expand the upper limit of the pore-size range available for MCM-41 materials from 4 to 10 nm.¹ Likewise, Stucky and co-workers used aromatics to obtain ordered polymer-templated SBA-15 silicas with pore sizes larger than 10 nm.^{16,17} Moreover, Klinowski et al. suggested that the swelling action of hexadecyldimethylamine (DMHA) generated

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in-situ from decomposition of cetyltrimethylammonium ions was responsible for unit-cell enlargement of MCM-41 in high-temperature conditions.¹⁰ We showed⁷ that DMHA also forms during the hydrothermal restructuring in the mother liquor^{8,9} and suggested that the swelling action of DMHA is a common driving force of unit-cell enlargement processes observed for cetyltrimethylammonium-templated MCM-41 in high-temperature (about 423 K) conditions.¹² The micelle-expanding properties of DMHA were quite unexpected, since long-chain neutral amines were shown to be facile structure directing agents, rather than expanders, in the synthesis of HMS mesoporous silicas with narrow pore-size distributions.³ So, although the engineering of MCM-41 pore sizes by using many organic additives, including aromatics, linear hydrocarbons, alcohols, ethers, carboxylic acids, glycols, ketones, and amides²⁰ as well as trialkylamines,⁶ was explored in some detail, the potential usefulness of long-chain amines as auxiliary organics was overlooked. From our studies of high-temperature pore-size enlargement of MCM-41, it was inferred that DMHA is a good swelling agent and our attempts to confirm this hypothesis led us to development of two successful new synthesis procedures.⁷ First, when DMHA or other amines were added to the synthesis gels, the preparation of large-pore MCM-41 materials was possible at moderate temperature (343 K), since there was no need for high temperature to generate the swelling agent via surfactant decomposition. Moreover, we provided evidence that the amine can actually penetrate into preformed noncalcined MCM-41 materials and act as a swelling agent, thus showing a novel pathway for the synthesis of large-pore materials via postsynthesis treatments using proper swelling agents. As it was briefly described in our preliminary report,⁷ both of these methods gave rise to materials with narrow pore-size distributions, large pores, and exceptionally high pore volumes. In the current contribution, a detailed description is provided for materials prepared under a wide range of conditions in the presence of various amines using these two new approaches. The structural changes during the postsynthesis pore-size enlargement in the presence of amines are discussed, and perspectives of future work are outlined.

Experimental Section

All experiments using postsynthesis treatment in emulsions of amines were carried out on the same batch of the MCM-41 silica, except for treatments with hexadecyldimethylamine (DMHA) for short contact times (<24 h), which were performed using two other small batches prepared in the same conditions. All these batches were prepared as described earlier^{8,9} using a synthesis gel with the following composition: 1:0.33:0.17:0.17:17 SiO₂-TMAOH-CTMABr-NH₄OH-H₂O, where TMAOH and CTMABr denote tetramethylammonium hydroxide and cetyltrimethylammonium bromide, respectively. Cab-O-Sil silica (30 g) was mixed manually with 50 g of water. Then, 51.3 g of 25% TMAOH aqueous solution was added under vigorous magnetic stirring. Another mixture comprised of 30.4 g of CTMABr, 54.7 g of water, and 9.75 g of concentrated ammonia was prepared under stirring. Both of these mixtures were transferred into a Teflon-lined autoclave, stirred for 30 min, and then heated statically at 343 K for 3 days. The obtained precipitate was filtered out, washed thoroughly with deionized water, and dried at 333 K. Subsequently, 0.8 g MCM-41 batches were subjected to treatment in an emulsion of 0.5 g of amine in 30 g of water.⁷ The treatments were carried out for a desired period of time from 6 h to 10 days (usually 3 days) at temperatures in the range from 343 to 413 K using dimethyl-

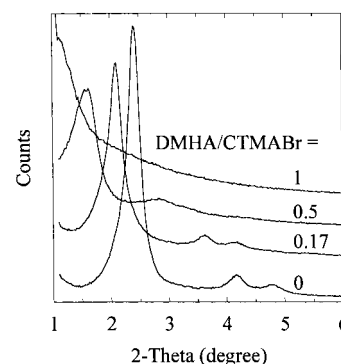


Figure 1. Powder X-ray diffraction patterns for samples prepared in direct synthesis with different DMHA/CTMABr molar ratios.

hexadecylamine (DMHA), dimethyldodecylamine (DMDA), or dimethyloctylamine (DMOA). The obtained samples were calcined in flowing air at 823 K for 5 h.

The direct synthesis of MCM-41 with amines as swelling agents was carried out using the same gel composition as above, except for the addition of different amines, such as DMHA, DMDA, DMOA, trioctylamine (TOA), tridodecylamine (TDDA), trimethylamine (TMA), and triethylamine (TEA). The amine was added to the surfactant-water-ammonia mixture. The amine:CTMABr ratio was varied from 0.05 to 1 for DMHA, was equal to 0.5 for TOA, TDDA, TMA, and TEA, and varied up to 1 for DMDA and DMOA. The synthesis gel was heated at 343 K for 3 days. The obtained samples were separated and calcined as described above.

Nitrogen adsorption measurements were performed using an ASAP 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA). Before the adsorption analysis, the samples were outgassed for 2 h at 473 K in the degas port of the adsorption apparatus. XRD spectra were acquired on a Siemens D5000 diffractometer using nickel-filtered Cu K α radiation.

The BET specific surface area²¹⁻²⁴ was calculated on the basis of nitrogen adsorption data in the relative pressure range from 0.04 to 0.2. The total pore volume was evaluated from the adsorbed amount at a relative pressure of about 0.99.²²⁻²⁴ The external surface areas and the primary mesopore volumes for materials obtained using the direct synthesis procedure were calculated using the α_s -plot method as described elsewhere.^{9,23} The pore-size distributions were obtained from adsorption branches of the isotherms using the BJH method²⁵ with the corrected Kelvin equation and the statistical film thickness curve reported recently.²¹ In the case of large-pore materials synthesized via the postsynthesis restructuring in emulsions of amines, the primary mesopore volume was estimated on the basis of the BJH incremental pore size distributions, unless noted otherwise. For the materials, which exhibited clear XRD patterns characteristic of the MCM-41 phase, the pore size was also calculated from the XRD interplanar spacing and primary mesopore volume on the basis of geometrical considerations.^{23,26,27}

Results and Discussion

Synthesis of Large-Pore MCM-41 Using Long-Chain Amines as Expanders. This work provided direct evidence that some amines are strong micelle expanders. XRD patterns of samples prepared using different DMHA/surfactant ratios are shown in Figure 1. It can be seen that the interplanar spacing d_{100} increases significantly as the amount of DMHA increases. The sample prepared using a DMHA:CTMABr ratio of unity exhibited a d_{100} spacing of 7.6 nm vs 3.7 nm in the absence of

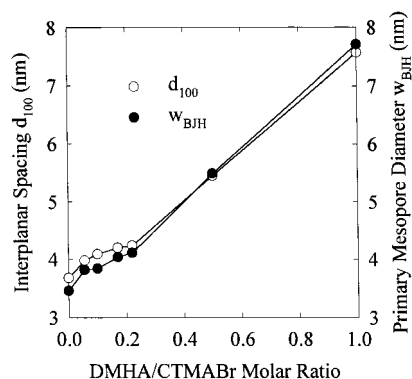


Figure 2. Influence of the DMHA:CTMABr molar ratio in the gel used for direct synthesis of MCM-41 and (i) the (100) interplanar spacing and (ii) primary mesopore size calculated using the BJH method.

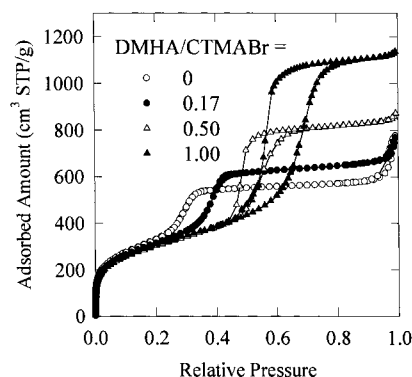


Figure 3. Nitrogen adsorption isotherms for samples prepared in direct synthesis procedure using different DMHA:CTMABr molar ratios.

DMHA. This strong relationship between DMHA:CTMABr and d_{100} is well-illustrated in Figure 2. From inspection of XRD spectra it is inferred that the structural ordering of the obtained materials gradually decreases as the interplanar spacing increases. As shown in Figure 1, the sample with d_{100} distance of 4.20 nm exhibited an excellent structural ordering. The XRD spectrum of the sample with d_{100} distance of 5.45 nm also showed a pattern typical for MCM-41 materials. The spectrum featured a prominent (100) peak and coalesced, but still distinct, (110) and (200) reflections as well as a noticeable increase in intensity at the 2θ angle, at which (210) peak would be expected. The material with d_{100} distance of 7.6 nm exhibited a single weak XRD peak at very low angles, indicating a large unit-cell size and a rather low degree of structural ordering. This is consistent with TEM and nitrogen adsorption data for this sample, which indicated disordered structure and narrow pore-size distribution, respectively.⁷

Figure 3 shows representative nitrogen adsorption isotherms for samples prepared in the presence of different amounts of DMHA. The shift toward higher relative pressures of the adsorption step corresponding to nitrogen condensation in primary mesopores is consistent with the occurrence of larger pores. Moreover, despite the gradual departure from a well-ordered hexagonal structure, the PSDs of samples with the largest pores (5.5 and 7.7 nm) remained relatively narrow (see Figure 4).

Table 2 shows that the unit-cell enlargement is almost solely due to increasing pore sizes, the wall thickness being almost constant. The pore size increased from 3.5 to 7.7 nm as the DMHA/CTMABr ratio approached unity. Moreover, as shown in Table 2, the two large-pore (5.5 and 7.7 nm) materials had remarkably large primary mesopore volumes (1.19 and 1.66 cm³/

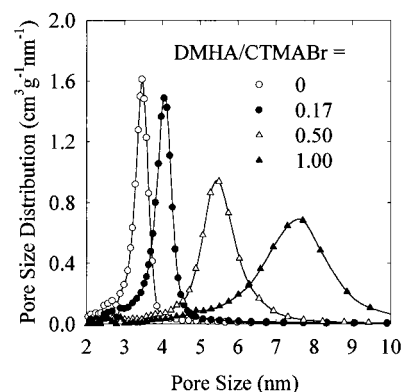


Figure 4. Pore-size distributions calculated using the BJH method for samples prepared in direct synthesis procedure using different DMHA:CTMABr molar ratios.

TABLE 2: Structural Properties of MCM-41 Materials Synthesized Using Amines as Expanders in Direct Synthesis Procedure^a

amine	amine: CTMABr	d_{100} (nm)	S_{BET} (m ² /g)	V_t (cm ³ /g)	V_p (cm ³ /g)	S_{ex} (m ² /g)	w_d (nm)	b_d (nm)	w_{BJH} (nm)
none		3.68	1210	1.15	0.80	90	3.57	0.68	3.46
DMHA	0.055	3.98	1060	1.27	0.76	130	3.82	0.78	3.82
DMHA	0.1	4.09	1080	1.32	0.76	130	3.93	0.80	3.84
DMHA	0.17	4.20	1150	1.13	0.88	140	4.14	0.71	4.04
DMHA	0.22	4.24	1140	1.16	0.90	130	4.19	0.71	4.11
DMHA	0.5	5.45	1100	1.33	1.19	90	5.62	0.67	5.49
DMHA	1	7.6 ^b	1120	1.78	1.66	70	8.1 ^b	0.6 ^b	7.7
TOA	0.5	5.51	1180	1.37	1.23	100	5.71	0.65	5.28
TDDA	0.5	5.38	1210	1.43	1.29	100	5.61	0.60	5.08
TMA	0.5	3.53	1250	1.01	0.75	100	3.38	0.70	3.30
TEA	0.5	3.34	1370	0.82	0.76	50	3.20	0.66	3.10

^a DMHA, *N,N*-dimethylhexadecylamine; TOA, trioctylamine; TDDA, tridodecylamine; TMA, trimethylamine; TEA, triethylamine; amine: CTMABr, molar ratio of amine to CTMABr; d_{100} , XRD (100) interplanar spacing; S_{BET} , BET specific surface area; V_t , total pore volume; V_p , primary mesopore volume; S_{ex} , external surface area; w_d and b_d , primary mesopore size and pore wall thickness calculated using geometrical considerations; w_{BJH} , BJH pore size. ^b Weak peak on XRD spectrum; d_{100} , w_d , and b_d may be inaccurate.

g, respectively) and large specific surface areas (about 1100 m²/g). For comparison, large-pore samples prepared in the presence of CTMABr at high temperature via direct synthesis¹² or postsynthesis hydrothermal treatment⁹ exhibited pore volumes not exceeding 1.04 cm³/g. Huge values of pore volumes suggest that the samples prepared in the presence of DMHA have relatively thin pore walls, which in turn might be considered as an indication of their lower stability. Calculation based on the geometrical model^{26,27} using XRD interplanar spacing and primary mesopore volume assessed from adsorption data gave pore wall thicknesses of only 0.67 nm for the material with 5.5 nm pores. Despite the presence of such thin walls, the calcined samples showed a good stability in ambient air in comparison to materials with much smaller pores prepared directly using more common procedures. Indeed, after about 1 year of storage in the calcined form, nitrogen adsorption data provided no evidence of structural degradation for the large-pore materials, whereas some of the materials with smaller pores prepared in similar conditions without the use of amines suffered a noticeable loss of structural uniformity after storage in similar conditions.

The synthesis of large-pore MCM-41 was also accomplished in the presence of TOA and TDDA in the synthesis gel. The resulting materials had large primary mesopore volumes (1.28 and 1.35 cm³/g, respectively) but exhibited lower structural ordering in comparison to the samples prepared using DMHA,

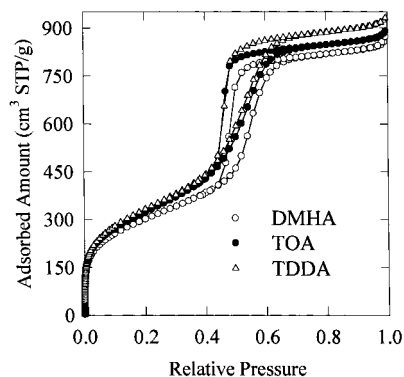


Figure 5. Nitrogen adsorption isotherms for MCM-41 samples prepared in direct synthesis procedure using dimethylhexadecylamine (DMHA), trioctylamine (TOA), and tridodecylamine (TDDA) with amine:CTMABr molar ratio of 0.5.

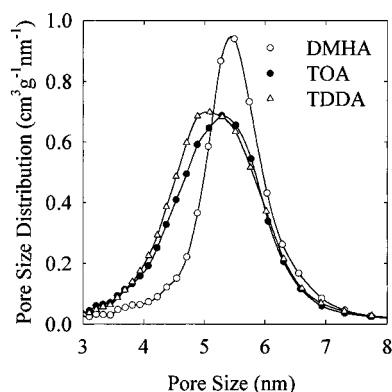


Figure 6. Pore-size distributions calculated using the BJH method for MCM-41 samples prepared in direct synthesis procedure using dimethylhexadecylamine (DMHA), trioctylamine (TOA), and tridodecylamine (TDDA) with amine:CTMABr molar ratio of 0.5.

which manifested itself in the presence of broader capillary condensation steps and wider hysteresis loops on adsorption isotherms (Figure 5) as well as broader peaks on the pore-size distributions (Figure 6).

In contrast to DMHA, dimethylalkylamines with shorter alkyl chains, such as DMDA and DMOA, were not found to be suitable additives for the preparation of large-pore MCM-41. Their use in relatively large amounts (amine:CTMABr molar ratio of 0.5 and 1) in the synthesis gel led to the development of microporosity and to extremely nonuniform porous structures. Moreover, addition of a small amount of DMDA (amine:CTMABr = 0.1) afforded a material without evidence of microporosity but with small pore size and broad pore-size distribution. Similar MCM-41 samples were obtained in the presence of trimethylamine and triethylamine, as no pore enlargement was observed (see data in Table 2) and the structures were less ordered than materials prepared in the presence of amine-free synthesis gels. Thus, DMHA with a single long alkyl chain was found to be the most effective expander in comparison to amines with single shorter alkyl groups (DMDA, DMOA) or with three shorter alkyl groups (TOA, TDDA) as well as in comparison to small trialkylamines.

Postsynthesis Pore-Size Enlargement in Aqueous Emulsions of Amines. If the in situ formation of DMHA is responsible for the pore-size enlargement of MCM-41 under high-temperature conditions, one can expect that it might be possible to induce pore-size enlargement using a postsynthesis treatment in aqueous emulsions of DMHA and, possibly, other amines. On the basis of this idea, we were able to prepare

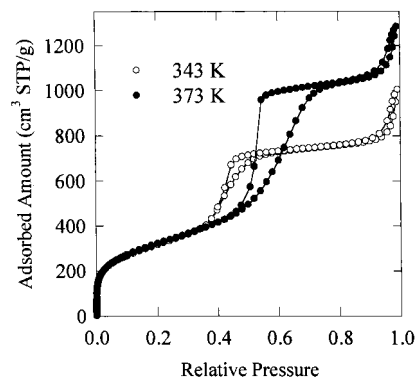


Figure 7. Nitrogen adsorption isotherms for silicas prepared via postsynthesis restructuring of 3.5 nm MCM-41 material in aqueous emulsion of DMHA at 343 and 373 K.

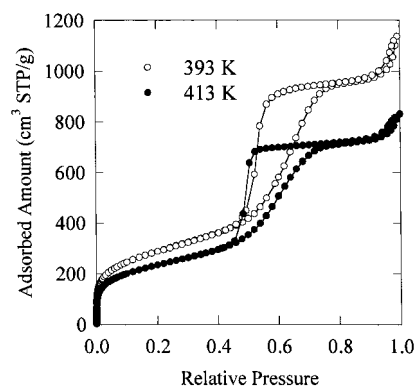


Figure 8. Nitrogen adsorption isotherms for silicas prepared via postsynthesis restructuring of 3.5 nm MCM-41 material in aqueous emulsion of DMHA at 393 and 413 K.

mesoporous silicas with narrow pore-size distributions, with large pore sizes and surface areas, and with exceptionally high mesopore volumes.⁷ Samples treated in the presence of DMHA will be discussed first. MCM-41 used as a starting material was prepared at 343 K for 3 days as described above and was used in noncalcined form. Sample used in most of the treatments originated from the same batch, which had primary mesopore size and volume of about 3.5 nm and 0.8 cm³/g, respectively. Short contact times (2–20 h) with water–DMHA emulsion at 373 and 393 K led to a significant pore size enlargement. However, the pore-size distributions (PSDs) of the obtained materials were very broad and, in some cases of treatments at 373 K, PSDs were bimodal with a fraction of more or less uniform pores of a size slightly larger than that of the nonrestructured material but also with a broad range of much larger pores.²⁶ It is important to note here that 12 h of treatment in distilled water at 393 K did not lead to any pore-size change, so the presence of the amine was clearly responsible for the swelling action observed. The pore-size enlargement was usually accompanied with partial or complete loss of the structural ordering, but in most cases there was no appreciable change in the specific surface area. Moreover, there was no evidence of formation of micropores. Longer treatment times (e.g., 3 days) gave rise to materials with monodisperse systems of significantly enlarged pores. Nitrogen adsorption isotherms for the samples treated at 373, 393, and 413 K for 3 days (Figures 7 and 8) exhibited pronounced but broad steps of capillary condensation in primary mesopores. The pore size distributions (PSDs) were centered at about 6 nm, monodisperse, but quite broad (see Figure 9). In this case, the pore size was not significantly affected by the treatment temperature, but the pore volume was the highest (above 1.5 cm³/g) for the material prepared at the

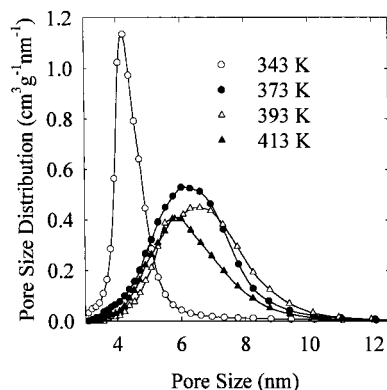


Figure 9. Pore-size distributions calculated using the BJH method for silicas prepared via postsynthesis restructuring of 3.5 nm MCM-41 material in aqueous emulsion of DMHA at different temperatures.

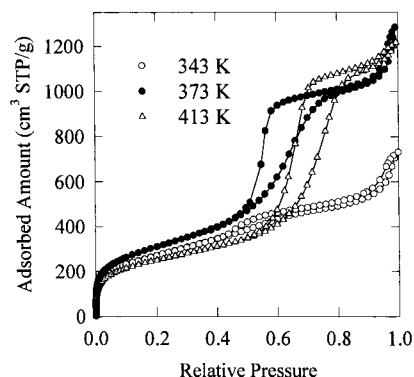


Figure 10. Nitrogen adsorption isotherms for silicas prepared via postsynthesis restructuring of 3.5 nm MCM-41 material in aqueous emulsion of dimethyldecylamine (DMDA) at 343, 373, and 413 K.

lowest temperature (i.e., 373 K). The porous structure of the material prepared at 393 K was also studied using transmission electron microscopy and found to be disordered.⁷ It is interesting to note here that a sample restructured for 3 days at 343 K exhibited an appreciable pore-size enlargement (from 3.5 to 4.2 nm) and a pore volume increase (from 0.8 to more than 1 cm³/g) without any significant loss of structural ordering. The nitrogen adsorption isotherm for this sample featured a quite narrow capillary condensation step. The pore size obtained from nitrogen adsorption data was in a good agreement with that estimated on the basis of the geometrical model of honeycomb structure,^{26,27} thus indicating retention of the hexagonal structure during the pore-size enlargement. However, the pore-size distribution exhibited a small but noticeable tail toward larger pore sizes. These results indicate that the pore-size increase with retention of the structural ordering can in fact be attained in some cases of restructuring with amines.

In contrast to the results of the direct synthesis described above, amines with shorter alkyl chains such as DMOA and DMDA were also found to be suitable for increasing the pore size of MCM-41 during postsynthesis restructuring. The effect of DMDA treatment was studied in detail. Long treatment times (3 days) were found to be suitable for the preparation of materials with significantly (2–3-fold) enlarged pores, large pore volumes, and monodisperse PSDs, when treatment temperatures of 373 K or more were used.⁷ The material obtained after 3 days of treatment at 373 K exhibited an adsorption isotherm, pore-size distribution, and pore volume similar to those of the samples synthesized using postsynthesis treatment in water–DMHA emulsion (3 days at 373–413 K) (see Figures 10 and 11). The materials restructured at 393, 403, and 413 K for 3

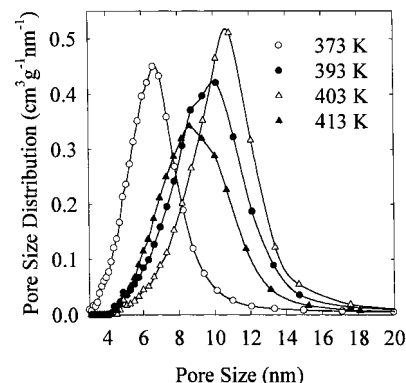


Figure 11. Pore-size distributions calculated using the BJH method for silicas prepared via postsynthesis restructuring of 3.5 nm MCM-41 material in aqueous emulsion of dimethyldecylamine (DMDA) at different temperatures.

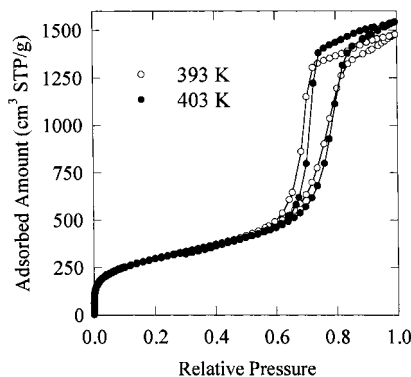


Figure 12. Nitrogen adsorption isotherms for silicas prepared via postsynthesis restructuring of 3.5 nm MCM-41 material in aqueous emulsion of dimethyldecylamine (DMDA) at 393 and 403 K.

days using DMDA were especially interesting due to their pore sizes in the range 9–11 nm and their extremely large pore volumes of about 2 cm³/g. As can be seen in Figures 10–12, the sample obtained at 403 K exhibited the highest adsorption capacity, the narrowest PSD, and the largest pore size. For this sample, the maximum of its PSD was located at about 11 nm and the primary mesopore volume as well as the total pore volume were extremely high (2.2 and 2.38 cm³/g, respectively). TEM revealed that the structure of the material obtained at 423 K was disordered.⁷ The porosity (defined as the pore volume divided by the sum of the pore volume and the volume of the pore walls) was estimated to be equal to 0.84, assuming that the density of the pore walls is 2.2 g/cm³. Despite the extremely high porosity of the samples obtained at 393 and 403 K, there was no evidence of structural collapse after 1 year of storage of the calcined form in ambient air. In contrast to the results of higher temperature treatments, MCM-41 sample restructured at 343 K had an extremely broad PSD, a low pore volume, and a detectable amount of micropores. This may indicate that, at such a low temperature, the silica framework was not flexible enough to undergo significant pore-size enlargement and thus the swelling action of the amine led to breakage of pore walls and caused extensive structural degradation. Alternatively, the structure of the sample might have collapsed during calcination.

The evolution of the porous structure for calcined samples obtained via restructuring at 393 K in the presence of DMDA was studied using nitrogen adsorption. It was found that the process leads an initial loss of the structural ordering, which manifested itself in broadening of the pore-size distribution and shift of its maximum toward larger pore sizes accompanied with a gradual development of significantly larger pores. The amount

TABLE 3: Structural Properties of Silicas Prepared Using Postsynthesis Restructuring in Aqueous Emulsions of Amines^a

amine	<i>t</i>	<i>T</i> (K)	<i>S</i> _{BET} (m ² /g)	<i>V</i> _t (cm ³ /g)	<i>V</i> _p (cm ³ /g)	<i>w</i> _{BJH} (nm)
DMHA	3 d	343	1160	1.56	1.03 ^b	4.21
DMHA	3 d	373	1170	1.92	1.6	6.2
DMHA	3 d	393	1040	1.70	1.5	6.6
DMHA	3 d	413	850	1.25	1.1	5.7
DMDA	3 d	343	970	1.09	0.45 ^{b,c}	3.2 ^d
DMDA	3 d	373	1120	1.92	1.5	6.6
DMDA	6 h	393	1050	1.21	1.0	4.3 ^d
DMDA	15 h	393	990	1.32	1.1	4.7; 8.8 ^{d,e}
DMDA	3 d	393	1080	2.28	2.1	10.1
DMDA	10 d	393	940	2.00	1.8	10.1
DMDA	3 d	403	1070	2.38	2.2	10.9
DMDA	3 d	413	900	1.86	1.7	8.6
DMOA	3 d	393	1110	1.39	1.3	7.8

^a DMHA, *N,N*-dimethylhexadecylamine; DMDA, *N,N*-dimethyldodecylamine; DMOA, *N,N*-dimethyloctylamine; *t*, time of the treatment in hours (h) or days (d); *T*, temperature of the treatment; *S*_{BET}, BET specific surface area; *V*_t, total pore volume; *V*_p, primary mesopore volume calculated from BJH incremental pore size distributions; *w*_{BJH}, BJH pore size. ^b α_s -plot method was used to evaluate *V*_p. ^c *V*_p includes micropore volume of about 0.03 cm³/g. ^d Very broad peak on the pore-size distribution. ^e Bimodal pore-size distribution.

of smaller pores gradually decreased, and after about 2 days of treatment, there was no evidence of their presence and only the enlarged pores were observed. The pore-size distribution of the latter was quite narrow and did not change appreciably during extended treatments for up to 10 days. The surface area initially dropped by 10–15% after the first several hours of treatment and then increased slightly (after 2–3 days), and subsequently, it decreased to a small extent during extended treatments (5–10 days). However, as shown in Table 3, these variations in surface area were of small magnitude ($\pm 7\%$). The pore volume was the highest after 3 days of restructuring. No evidence of microporosity was observed for any of these calcined materials. The conservation of the surface area and the lack of microporosity suggest that the structure of pore walls was most likely retained during the restructuring and there was no appreciable structural collapse during calcination. Moreover, if degradation of pore walls actually took place, it would be difficult to explain why the process did not ultimately lead to the collapse of the structure of the material, as was observed in the case of extensive hydrothermal restructuring in the mother liquor.⁶ However, it should be kept in mind that the porous structures formed during the postsynthesis treatments with amines appeared to be disordered, which is difficult to reconcile with the idea of retention of the original structure of pore walls. There are several additional clues, which suggest what kind of transformation actually took place. The pore-size increase after the restructuring with amines observed for the calcined materials was usually not gradual but involved the appearance of significantly enlarged pores at the expense of the smaller ones. Moreover, it was difficult to control the sizes of the resulting pores and the latter were often about 2 or 3 times larger (about 6.5–7 or 8.5–11 nm) than that of the parent material (about 3.5 nm). Other interesting information can be inferred from the consideration of the relation between the pore volume:surface area ratio and the pore size. Such a relation is characteristic of a particular pore geometry. For instance, in the case of cylindrical pores, one expects that $w = 4V/S$, where *w*, *V*, and *S* are the diameter, volume, and surface area of the pores, respectively. In our studies of MCM-41, *w* (calculated from the XRD spacing and pore volume²⁷ or, alternatively, the BJH method calibrated using the results of such calculations²¹) was

usually found to be equal to ca. 4.6V/S (this deviation from the value expected for cylindrical pores is likely to result from inaccuracy of the specific surface area evaluation, which may be due to the fact that the range of data points commonly used in the nitrogen BET procedure appears to be inappropriate for porous silicas²¹). It was interesting to notice that the relation between the pore volume:surface area ratio and the pore size (evaluated using the calibrated BJH method)²¹ for the materials which underwent long treatments with amines was similar to that for MCM-41 materials, such as the mother sample, which was subjected to the hydrothermal treatment. This suggests that the geometry of pores of the materials obtained after extended treatment in emulsions of amines is similar to that of MCM-41 silicas and may be close to cylindrical.

On the basis of all these observations, it is proposed that the pore-size enlargement may involve not only a gradual pore size increase, as was the case for high-temperature unit-cell enlargement processes without addition of amines, but also breakage of parts of the pore walls, which separate two or more of the adjacent pores. The newly created large pores may then adapt shapes similar to cylindrical. Since large pores would be formed via “opening” of the pore walls separating the original small pores, the surface area before and after the transformation would be similar. Such a process is relatively easy to envision for two pores but seems to be a little more involved for three or more pores. In the latter case, the process may actually involve two or more steps in which initially two pores transform into a single pore and subsequently the wall between the latter and the third pore may break down leading to further pore-size enlargement. On the basis of this model, it may be concluded that the adjacent enlarged pores may be connected to some extent with one another, since one cannot expect that the pore walls would break in such a way that only isolated doublets or triplets of pores would be formed. The process of breakage of pore walls and formation of enlarged pores may eventually stop due to increased framework condensation (as shown earlier using ²⁹Si MAS NMR).⁷ It is also important to note here that the weight loss during calcination of MCM-41 treated with DMDA at 393 K was quite independent of the restructuring time (from 6 h to 10 days). This would suggest that several hours of the treatment are enough to incorporate a large amount of amine into the structure of MCM-41 and further treatment does not lead to the increase of this amount. Thus, the volume occupied by the surfactant-amine phase in the siliceous framework of noncalcined materials should be similar for the samples prepared using both short and long treatment times. This finding is rather surprising, since pore volumes of calcined samples treated for short periods of time (e.g., 6 and 15 h) were much lower than those for the samples subjected for longer treatments of 2–10 days (see Table 3). Thus, there appears to be a significant difference in the volume of pore channels before and after calcination for materials prepared at short contact times, which can be explained if the former underwent extensive shrinkage or partial collapse during calcination. If the observed low pore volumes were due to partial structural collapse, it is important to keep in mind that the surface area of these samples is relatively high (only about 20% less than that of the nonrestructured MCM-41 and ca. 5–10% less than that of the sample prepared at treatment times of 3 days). Thus, the pores, which could possibly collapse, would have to exhibit large volumes and relatively small surface areas what requires their large size in comparison to other pores in the structure. In other words, these pores would have to be the ones which underwent the most extensive enlargement. This is not unlikely, since the

extreme pore-size enlargement may substantially weaken the framework. Moreover, the formation of pores of diameter significantly exceeding 10 nm (about 3 times that of the nonrestructured MCM-41) was strongly indicated for some DMHA-treated materials prepared for instance at 373 K. So, in the case of treatment with DMDA and other amines, the initial pore-size enlargement may be very nonuniform and the pores expanded too extensively may be prone to collapse during calcination. Longer treatments lead to increased pore-size uniformity, and framework condensation makes the framework more stable, so much so it does not collapse upon calcination and the resulting material can be stored under ambient air for at least 1 year without evidence of structural degradation despite its extremely large pore volume and surface area.

Comparison of Pore-Size Enlargement Processes Involving DMHA as an Expander and Reasons for Structural Differences between the Resulting Large-Pore Materials. As was already discussed, DMHA is crucial in several types of synthesis procedures that lead to large-pore materials with distinct structural features. The hydrothermal restructuring in the mother liquor and similar high-temperature procedures (see Table 1) involve a gradual pore-size enlargement from about 4 to 6.5 nm. The pore-size increase was explained as a result of swelling action of in-situ generated DMHA,^{7,10,12} and the micelle-expanding properties of DMHA were confirmed by successful synthesis of large-pore materials in a variety of conditions (see ref 7 and the current study). There is also a strong evidence that tetramethylammonium (TMA^+)^{11,12,28} or other small cations, such as tetraethylammonium (TEA^+) and Na^+ ,¹¹ play an important role in the pore-size enlargement in high-temperature conditions. It was shown that TMA^+ is more suitable than the other cations mentioned above,¹¹ which was additionally confirmed by the results of other studies, as discussed elsewhere.^{12,28} Although TMA^+ and, alternatively, other cations, such as TEA^+ and Na^+ , were shown to be incorporated into the micelles during the unit cell enlargement, it is unlikely that they are the actual swelling agents because of the following reasons. The known swelling agents (such as TMB, DMHA, and DMDA) work in a wide range of temperatures, so it is difficult to understand why the hypothetical swelling action of TMA^+ or alike would take place only at high temperatures (usually 423 K or more). Also, even though incorporation of sodium cations into the micelles is not likely to lead to an appreciable increase in their diameter, the unit-cell enlargement was shown¹¹ to take place in the presence of Na^+ . Finally, the unit-cell expansion can be induced by heating an as-synthesized CTMA^+ -templated MCM-41 in pure water at 423 K, thus demonstrating that incorporation of cations is not necessary for the pore-size enlargement.²⁸ So, the presence of small cations and, especially, TMA^+ in the synthesis gel provides favorable conditions for the unit-cell enlargement but is not necessary for the latter to take place.²⁸ This in turn supports the hypothesis that high-temperature decomposition of CTMA^+ and the consequent formation of DMHA is a crucial factor in the pore-size expansion under high-temperature conditions in the absence of swelling agents. It also needs to be noted here that treatment of as-synthesized MCM-41 material (the sample from the batch used in most of the experiments described in the current study) in a water solution of TMAOH (1.5 wt %) for 3 days at 393 K resulted in no unit-cell expansion and appearance of a lamellar phase, whereas, under similar conditions, DMHA, DMDA, and DMOA exhibit strong swelling action.

As was discussed above, there is strong evidence that in-situ generation of DMHA is the main cause of the pore-size

enlargement in high-temperature conditions. It is noteworthy that these processes preserve or even improve the hexagonal structural ordering and often lead to the preparation of high-quality MCM-41. In contrast, the pore-size enlargement using amines in direct synthesis and in postsynthesis treatment results in lowering or even loss of the structural ordering. These differences can be explained when one takes into consideration different mechanisms of these processes. In the case of the high-temperature approaches, the starting material exhibits good structural ordering characteristic of MCM-41 and the swelling agent is gradually generated via partial decomposition of the surfactant molecules and likely to be evenly distributed within the micelles. So, the increase in the diameter of micelles and the corresponding increase in the pore size of the silica matrix is gradual and essentially uniform throughout the material. In the case of the direct synthesis with amines (such as DMHA, TOA, or TDDA) as expanders, the amine is likely to influence the initial stages of formation of the silica-surfactant mesophase not only by increasing its interplanar spacing but also by lowering the structural ordering. For instance, in the case of DMHA, the quality of materials decreases as the amount of the amine increases. The amines which were found to act as expanders in the direct synthesis exhibit either a single long alkyl chain (that is hexadecyl) or three fairly long (octadecyl, dodecyl) alkyl chains. In contrast, the addition of less bulky trialkylamines (TMA, TEA) or shorter chain alkyldimethylamines (DMDA, DMOA) was found to merely disrupt the formation of the ordered material thus affording poorly ordered or disordered samples. This may be related to the more pronounced hydrophilic character of these amines. The fact that the long-chain amine (DMHA) exhibits better swelling properties than the bulky trialkylamines may possibly be related to the higher ability of the former to adapt conformations compatible with the arrangement of the surfactant molecules in the micelles, but further studies would be needed to explain these experimental findings.

In the case of the postsynthesis treatment with amines, the whole amount of amine is added at once rather than gradually generated as is the case of the high-temperature unit-cell enlargement without addition of amines. Thus, the process is likely to involve a rapid, significant, and highly nonuniform pore-size enlargement, which may be responsible for lowering or loss of periodicity and broadening of pore-size distribution during the process.

Perspectives of Future Work. Further studies are required to optimize the synthesis conditions and to explore the application of different amines in order to further improve the structural ordering and to extend the upper limit of pore sizes attainable using amines as expanders in the direct synthesis. It would also be interesting to establish conditions under which significant pore-size enlargement during the treatment with emulsions of amines or other organic additives can be achieved without loss of structural ordering. Moreover, studies would be desirable in the direction of improvement of the pore-size uniformity by adjusting temperature, relative amount of the amine, and the kind of amine used. Finally, it would be interesting to explore if amine treatments are suitable for the pore-size adjustment of (i) ordered mesoporous silicas other than MCM-41, (ii) framework-modified ordered mesoporous silicas, and (iii) non-siliceous ordered mesoporous materials.

Conclusion

The current study demonstrated that it is possible to use long-chain alkylamines as expanders to synthesize large-pore MCM-

41 under mild conditions. For instance, the pore-size adjustment in the range from 3.5 to 7.7 nm can be achieved by adding proper amounts of DMHA. The obtained large-pore materials exhibited large primary mesopore volumes (above 1 cm³/g), but the structural uniformity decreased as the pore size increased. Further adjustment of synthesis conditions may lead to improved ordering of these materials. Pore-size enlargement of as-synthesized MCM-41 materials was also induced by subjecting them to aqueous emulsions of amines at elevated temperatures. This novel approach for pore-size engineering afforded materials with narrow pore-size distributions, pore sizes up to 11 nm, mesopore volumes up to as much as 2.15 cm³/g, and usually disordered structures. There were no significant surface area changes for the calcined materials after the pore-size enlargement and no evidence of development of microporosity. Moreover, the large-pore materials did not undergo any appreciable degradation during extended treatments, in contrast to the hydrothermal restructuring of MCM-41 in the mother liquor, which ultimately leads to structural collapse. The pore structure of amine-treated materials was usually disordered, and the pore-size increase was often not gradual but involved the development of significantly enlarged pores at the expense of the original small ones. Thus, one cannot exclude the possibility that the walls between pores may actually break during the process in such a way that pairs or triplets of adjacent pores transform into single pores.

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