

THE EFFECTS OF PROCESSING PARAMETERS ON THE SYNTHESIS OF SILICEOUS MCM-41 FROM COLLOIDAL SILICAS

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Received July 15, 1997

Accepted November 26, 1997

Well-ordered as-synthesized siliceous MCM-41 mesoporous molecular sieves can be prepared from the sol of colloidal silica (Ludox HS-40 and AS-40) only under optimized conditions. Two processing parameters have a significant effect on the structure. First, the period of stirring the mixture of Ludox AS-40 or HS-40 and tetraethylammonium hydroxide should be extended to 22 h. Second, the following temperature regime should be used: the reaction mixture consisting of colloidal silica, tetraethylammonium hydroxide, hexadecyltrimethylammonium chloride and water is being first aged at ambient temperature for 20 h, then the temperature is gradually increased and finally the mixture is kept at 100 °C for 40 h. As-made MCM-41 prepared even by an optimized procedure contains after calcination some proportion of an amorphous phase. Extraction with water of the as-made material is a suitable procedure for the improvement of the phase purity as less well-ordered and amorphous particles are preferentially dissolved and thus removed. In this way, a substantial improvement in the quality of MCM-41 molecular sieves can be achieved.

Key words: Siliceous MCM-41 mesoporous molecular sieves; Synthesis optimization; Phase purity.

Recently, a number of valuable studies have been published dealing with the synthesis of MCM-41 mesoporous molecular sieves¹⁻²⁶. Klinowski *et al.* have studied in detail the phase purity of the as-made material and have shown that this material prepared under optimized conditions contains a small proportion of lamellar and amorphous phases¹⁷. According to these authors the properties of the product depend on the source of silica (fumed or fused silica) and on other processing parameters such as the gel ageing time, the temperature and the duration of the synthesis.

The present study deals with the investigation of the effects of processing parameters on the quality of siliceous MCM-41 molecular sieves, colloidal silicas, namely Ludox AS-40 and HS-40 (Du Pont), being chosen as silica sources. The main aim of this study is to find reaction conditions and treatments of the as-made material which enable to minimize the content of undesirable phases in the final product.

EXPERIMENTAL

Chemicals

Tetraethylammonium hydroxide (TEAOH, 20 wt.% water solution) and hexadecyltrimethylammonium chloride (25 wt.% water solution) were obtained from Aldrich. Colloidal silica Ludox HS-40 (Du Pont) containing 39.77 wt.% of SiO_2 was stabilized by Na_2O ($\text{SiO}_2/\text{Na}_2\text{O} = 90$). The particle diameter and surface area were 12 nm and $217 \text{ m}^2/\text{g}$, respectively. Ludox AS-40 with 40.81 wt.% of SiO_2 was stabilized by NH_3 and contained 0.16 wt.% of NH_3 and 0.08 wt.% of Na_2O occluded within particles. The particle diameter and surface area were 21 nm and $140 \text{ m}^2/\text{g}$, respectively.

Synthesis

To show the effect of individual synthesis parameters about 50 samples were prepared. First, the composition of the reaction mixture was optimized. For this purpose a series of samples was prepared according to the following recipe. Ludox HS-40 or AS-40 (18.5 g) was mixed with 0–24.4 g of distilled water and 9.25–27.75 g of water solution of TEAOH in a beaker and stirred with a magnetic stirrer for 3 min. Then 12.5–50 g of water solution of HDTMACl was added with a linear pump at a flow rate of 5 ml/min under stirring. After the total amount of HDTMACl had been added, the mixture was stirred for 6 min. Then it was charged into a 250-ml polypropylene bottle and kept at $100 \text{ }^\circ\text{C}$ for 100 h. The material formed was filtered, washed with distilled water and extracted with water and ethanol in a Soxhlet apparatus for 4 h each. During the Soxhlet extraction, water or ethanol were replaced by the fresh solvents once or twice. Calcination was carried out in air at $600 \text{ }^\circ\text{C}$ for 20 h (a heating rate $3 \text{ }^\circ\text{C}/\text{min}$).

In order to determine the influence of processing parameters other than the composition of the reaction mixture, another series of samples was synthesized according to the following procedure. Ludox HS-40 or AS-40 (18.5 g) was mixed with 15 g of distilled water and 18.5 g of water solution of TEAOH in a beaker and stirred for 22 h with a magnetic stirrer. Then 25 g of water solution of HDTMACl was added with a linear pump at a flow rate of 5 ml/min. After 15 min of stirring, the mixture was charged into a 250-ml polypropylene bottle and aged at room temperature for 20–340 h without stirring. Afterwards it was put into a heating box and kept at $100 \text{ }^\circ\text{C}$ for 40 h, this temperature being attained at a heating rate of $10 \text{ }^\circ\text{C}/\text{h}$. Then the material formed was filtered, washed with distilled water and extracted by the following procedures: (i) by a Soxhlet extraction with ethanol for 8 h, (ii) by a Soxhlet extraction with water and ethanol for 4 h each, (iii) by three times boiling 5 g of as-synthesized MCM-41 in 0.5 l of 0.1 M ethanolic solution of NH_4NO_3 under a reflux condenser for 1 h followed by a Soxhlet extraction with ethanol for 4 h. During the Soxhlet extraction, water or ethanol were replaced by the fresh solvents once or twice. The weight loss due to the extraction was always determined by subtracting the weight of the extracted sample dried at $60 \text{ }^\circ\text{C}$ from that of the starting material. Calcination was carried out in air at $600 \text{ }^\circ\text{C}$ (heating rate $3 \text{ }^\circ\text{C}/\text{min}$) for 20 h. Several samples were first calcined in flowing nitrogen at $400 \text{ }^\circ\text{C}$ ($3 \text{ }^\circ\text{C}/\text{min}$) for 5 h; then nitrogen was replaced by air and temperature increased to $600 \text{ }^\circ\text{C}$ ($3 \text{ }^\circ\text{C}/\text{min}$), the samples being kept at this temperature for another 15 h.

Characterization

Powder X-ray diffraction data were obtained on a Seifert 3000 P diffractometer in the Bragg–Brentano geometry arrangement using $\text{CoK}\alpha$ radiation with a graphite monochromator and a scintillation detector.

The adsorption isotherms of nitrogen at $-196\text{ }^{\circ}\text{C}$ were measured with an Accusorb 2100E instrument (Micromeritics). Each sample was degassed at $350\text{ }^{\circ}\text{C}$ for at least 20 h until a pressure of 10^{-4} Pa was attained.

Thermal analysis was carried out in flowing synthetic air using a Netzsch STA 409 Simultaneous Thermal Analyzer. The sample temperature was increased linearly from ambient to $800\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

^{29}Si MAS NMR experiments were performed on a Bruker ASX400 spectrometer operated at 79.49 MHz. Two different pulse sequences were applied to every sample: (i) single pulse excitation of $5\text{ }\mu\text{s}$ and high power decoupling of protons during data acquisition (HPDEC), and (ii) proton to silicon cross-polarization and high power decoupling during data acquisition (CPMAS) with $\pi/2 = 5\text{ }\mu\text{s}$. Samples were rotated under magic angle at 5 000 Hz (HPDEC) and 3 500 Hz (CPMAS). Recycle delays during data acquisition were 60 s (HPDEC) and 2 s (CPMAS). Chemical shifts of the ^{29}Si NMR signals are given in ppm with respect to tetramethyl silane.

RESULTS

Quality of Samples Prepared

As shown in Fig. 1, the isotherms of materials synthesized can be classified according to their shape. The type S1 isotherm is observed on well-ordered MCM-41 materials, while the type S2 isotherm on less well-ordered ones, characterized by a less steep increase in adsorption. With both these types, a plateau at relative pressures of 0.4 to 0.7 follows the steep increase in adsorption. The small slope of this plateau is caused by the multilayer coverage of the small external surface (equalling the cumulative surface area of all pores not belonging to the honeycomb structure). With the type S3 isotherm, however, the adsorption continues to grow even at relative pressures greater than 0.4. Consequently, this material is characterized by a relatively large external surface area, which clearly points to structure imperfections.

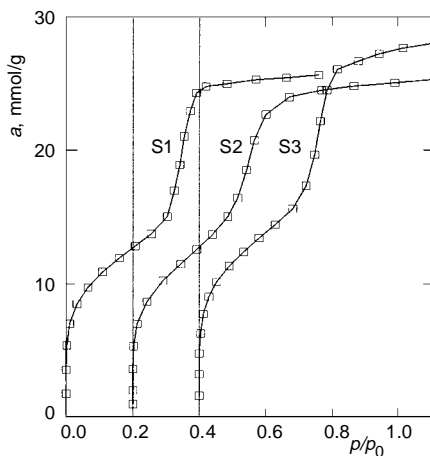


FIG. 1

Adsorption isotherms of nitrogen at $-196\text{ }^{\circ}\text{C}$ of the type S1, S2 and S3. Curves S2 and S3 are offset by $p/p_0 = 0.2$ and 0.4 , respectively

This classification of isotherms is supported by the XRD data. The X-ray diffractogram of a material with the type S1 isotherm is characterized by four well-developed reflections (Fig. 2). With a sample characterized by the type S2 isotherm, (110), (200) and (210) reflections are less well-resolved. Samples with the type S3 isotherm exhibit only two broad reflections.

The pore volume V_p , the external surface area S_{ext} and surface area of pore walls S_w have been determined for all samples by means of comparison plots²⁷. The pore diameter D_p and pore wall thickness δ_{ADS} have been calculated according to the geometrical model of honeycomb structure from adsorption data only for the type S1 materials because only these sieves fulfil the requirements of this model^{28,29}. Alternatively, the pore wall thickness δ_{XRD} has been calculated from the lattice constant a_0 determined by XRD and the pore diameter D_p obtained from adsorption data^{28,29}.

Synthesis from Ludox HS-40

Table I shows several selected samples used for the optimization of the composition of the reaction mixture and their quality characterized by the type of nitrogen isotherm. Samples are described by a combination of the designation of the corresponding series (*e.g.*, A1) and symbols of their treatment (*e* and *w* stand for extraction with ethanol and water, respectively, and *c* for calcination). From data obtained the following conclusions can be drawn. While an increase in the content of TEAOH did not influence the structure of MCM-41 (see sample A3-wec synthesized with a 1.5 times larger amount of TEAOH), its decrease had a markedly unfavourable influence (see sample A2-wec synthesized with half an amount of TEAOH). The variation in the content of HDTMACl had a similar effect (see samples A4-wec and A5-wec). This optimization resulted in the composition of the reaction mixture of sample A1-wec. Its structure

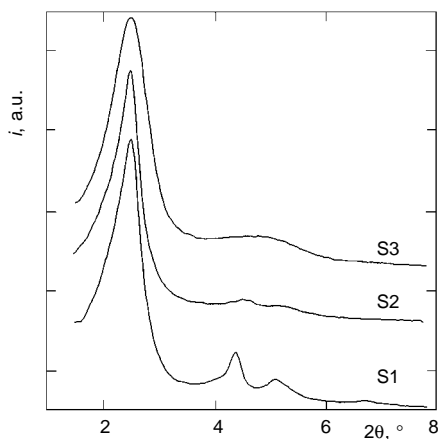


FIG. 2
X-Ray diffractograms of samples with isotherms of the type S1, S2 and S3

parameters (Table II) are typical for a MCM-41 molecular sieve, but the nitrogen isotherm is only of the type S2.

Considering that even the best sample prepared according to the described procedure does not achieve the highest quality, the treatment of the reaction mixture with optimum composition was varied (see samples B1-we to B3-we in Table II). It was found that two processing parameters can significantly contribute to an improvement in the quality of the structure. First, the period of stirring of the mixture of Ludox and TEAOH should be extended to 22 h, *i.e.* overnight. An improvement in the quality of the structure was achieved with a period of stirring of 12 h already but the stirring overnight is most convenient for practical reasons. Second, the following temperature regime should be used: the reaction mixture is first aged at ambient temperature for 20 h, then the temperature is being gradually increased and finally the mixture is kept at 100 °C for 40 h. The lengthening of the reaction time at 100 °C had no favourable influence.

TABLE I

Variation of the composition of the reaction mixture expressed as molar ratio of components

Sample	SiO ₂ ^a	TEAOH	HDTMACl	H ₂ O	Type ^b
A1-wec	1	0.21	0.16	27	S2
A2-wec	1	0.11	0.16	27	S3
A3-wec	1	0.32	0.16	27	S2
A4-wec	1	0.21	0.08	27	S3
A5-wec	1	0.21	0.32	28.6	S2

^a Ludox HS-40. ^b Type of nitrogen isotherm.

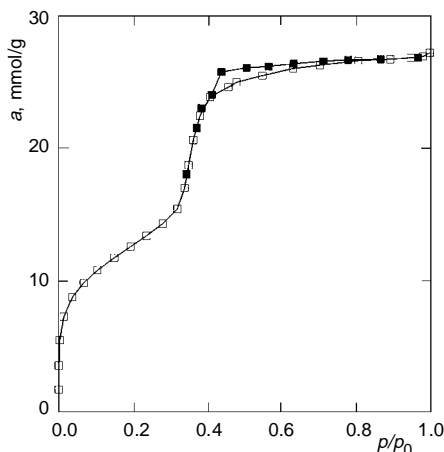


FIG. 3

Adsorption isotherm of nitrogen at -196 °C on sample B1-ec. Solid points denote desorption

On the contrary, a too long reaction time may cause the formation of undesirable phases¹⁷. These experiments led to a significant improvement in the quality of the structure, which can be documented by sample B1-wec, which is characterized not only by the structure parameters typical for a high-quality MCM-41 molecular sieve but also by the type S1 isotherm (Table III). The values of the pore wall thickness obtained

TABLE II
Synthesis conditions

Sample	PS1 ^a h	PS2 ^b h	PA1 ^c h	HR ^d °C/h	PA2 ^e h
Syntheses from Ludox HS-40					
A1-we	0.05	0.10	0	suddenly	100
B1-we	22	0.25	20	10	40
B2-we	22	0.25	340	–	–
B3-we	22	0.25	340	10	40
B1-e	22	0.25	20	10	40
Synthesis from Ludox AS-40					
C1-we	22	0.25	20	10	40

^a Period of stirring the Ludox HS-40 (AS-40)–TEAOH mixture; ^b period of stirring the Ludox HS-40 (AS-40)–TEAOH–HDTMACl mixture; ^c period of ageing the reaction mixture at ambient temperature; ^d heating rate of the reaction mixture; ^e period of ageing the reaction mixture at 100 °C.

TABLE III
Structure parameters

Sample	Type ^a	S_w m ² /g	S_{ext} m ² /g	V_p cm ³ /g	D_p nm	δ_{ADS} nm	a_0 nm	δ_{XRD} nm
Syntheses from Ludox HS-40								
A1-wec	S2	1 022.6	17.4	0.843				
B1-wec	S1	997.2	23.4	0.864	3.64	0.81	4.6	1.14
B2-wec	S3	679.5	52.7	0.560				
B3-wec	S3	973.4	141.6	0.845				
B1-ec	S2	842.1	270.3	0.790				
Synthesis from Ludox AS-40								
C1-wec	S1	923.6	26.6	0.777	3.53	0.87	4.6	1.25

^a Type of nitrogen isotherm.

exclusively from adsorption data (δ_{ADS}) and by combining XRD and adsorption data (δ_{XRD}) are within the limits most often published in the literature for high-quality MCM-41 materials, which can be regarded as a proof of the consistency of structure parameters²⁹.

No favourable influence was found when the reaction mixture was aged at ambient temperature for a prolonged time (such as 2 weeks with B2-wec), when only a part of the colloidal silica in the reaction mixture was transformed to MCM-41. The complete transformation was achieved at 100 °C (B3-wec), but only a sample with the type S3 isotherm was obtained.

We have found that special attention should be given to the extraction of as-synthesized samples. Its influence will be demonstrated on sample B1-ec (Table II). This sample was prepared from the same as-made material as sample B1-wec, but the extraction with water was omitted. With sample B1-ec a less steep increase in adsorption at $p/p_0 = 0.3$ – 0.4 was observed; both the volume and surface area of the MCM-41 mesopores are smaller (Table III). Its isotherm is further characterized by a small hysteresis loop due to the capillary condensation in mesopores larger than 4 nm (Fig. 3). For this reason, sample B1-ec exhibits by a larger external surface (Table III). Thus, the extraction with water had a surprising effect: a well-ordered structure was observed after calcination (Fig. 4, Table III). All other samples behaved analogously, *i.e.* the extraction with water always substantially improved the regularity of the porous structure.

The weight loss of sample B1 due to the extraction with ethanol (sample B1-e) equalled 4 wt.% only, while that due to the extraction with water for 4 h followed by the extraction with ethanol (sample B1-we) was 17 wt.%. It follows that at elevated temperature of ≈ 90 °C material B1 redissolves and a solution containing silicate and surfactant components is transferred into the boiling flask.

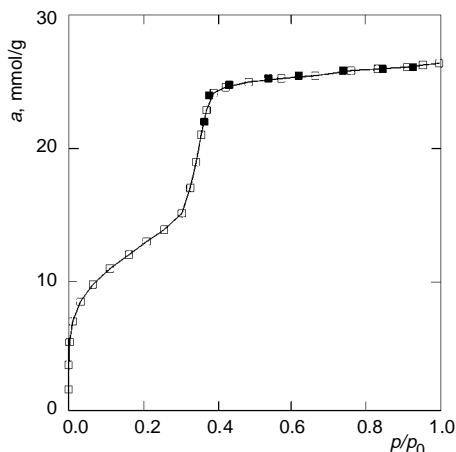


FIG. 4

Adsorption isotherm of nitrogen at -196 °C on sample B1-wec. Solid points denote desorption

The extraction of organic matter from as-synthesized samples using alcoholic solution of NH_4NO_3 was efficient (see results of thermoanalysis). This procedure, however, did not lead to an analogous improvement in quality as the extraction with water. The samples obtained had a somewhat smaller surface area and pore volume.

Calcination atmospheres other than air (nitrogen) were also used but no favourable effect was found. The structure of samples calcined in nitrogen was practically identical with that of samples calcined in air.

Synthesis from Ludox AS-40

In parallel with syntheses from Ludox HS-40, analogous ones using Ludox AS-40 as silica source were carried out. It can be concluded that different properties of silica sources used do not have a decisive influence on the quality of MCM-41 obtained. Generally the synthesis from Ludox AS-40 is slower than that from Ludox HS-40. Sample C1-wec prepared from Ludox AS-40 analogously to sample B1-wec (Table II) has a well-ordered MCM-41 structure (Table III).

Thermal Analysis

The TGA pattern of as-made material B1 was similar to those published in the literature^{2,7,16}. After the extraction with ethanol only (sample B1-e) and water and ethanol (sample B1-we) the content of surfactant was practically identical, equalling ca 35%. As after the extraction with water the surfactant/silica ratio remains unchanged, the weight loss during this treatment is caused by the simultaneous redissolution of both inorganic and organic components of the as-made material.

The extraction with an ethanolic solution of NH_4NO_3 followed by a Soxhlet extraction with ethanol decreased the content of surfactant to ca 10%.

²⁹Si MAS NMR Measurements

The ²⁹Si MAS NMR measurements were performed on samples B1, B1-e, B1-we and B1-wec. The spectra of all samples consist of three resonances at about -90, -100 and -110 ppm. The first pulse sequence applied (HPDEC) enables a quantitative analysis of the obtained signals and the second one (CPMAS) is sensitive to the ²⁹Si-¹H dipolar coupling, which drastically depends on the respective internuclear distance. Numerical deconvolution was done with a set of three gaussian lines at the positions mentioned. The gaussian shape of all signals is indicative of a distribution of structural environments due to the locally amorphous structure of pore walls. Integral intensities of the signals are given in per cent in Table IV.

DISCUSSION

Preparation of As-Synthesized Materials

This part of discussion uses the detailed analysis of the dissolution of colloidal silica due to its interaction with organic bases presented in Iler's excellent book³⁰. Colloidal silica interacts with TEAOH and is dissolved, forming the silicate salt. Dissolution of colloidal silica is catalyzed by OH⁻ ions and its rate is proportional to the surface area of silica. If colloidal silica with a smaller surface area is used (Ludox AS-40), MCM-41 structure forms more slowly than from a more dispersed silica (Ludox HS-40). A sufficient amount of the soluble silicate in the reaction mixture is obviously one of the necessary conditions for the formation of a well-developed structure. Therefore the low quality of sample A2-wec synthesized with half an amount of TEAOH is caused by an insufficient concentration of soluble silicate.

Immediately after the addition of HDTMACl, oligomeric silicate anions replace Cl⁻ and OH⁻ anions to form inorganic (silicate)-organic (surfactant) aggregates. Multidentate interactions of oligomeric silicate anions with the surfactant cations have several implications. In particular, the screening of the electrostatic double-layer repulsion among aggregates induces self-assembly of the hexagonal silicatropic liquid crystal mesophase⁵.

With increasing time and temperature, the silicate part of the mesophase undergoes condensation. Among various temperature regimes tested for the treatment of the reaction mixture, the procedure shown with sample B1-wec has come best. In particular a slow increase in temperature of the reaction mixture (when the temperature can be

TABLE IV
²⁹Si MAS NMR data

Sample	Pulse sequence	Integral intensity, %			Q ⁴ /(Q ² + Q ³)
		-90 ppm	-100 ppm	-110 ppm	
B1	HPDEC	5.6	40.2	54.2	1.18
	CPMAS	4.9	52.1	43.0	0.75
B1-e	HPDEC	7.2	40.8	52.0	1.08
	CPMAS	6.2	52.4	41.4	0.71
B1-we	HPDEC	5.5	44.7	49.8	0.99
	CPMAS	6.5	52.0	41.5	0.71
B1-wec	HPDEC	3.7	33.6	62.7	1.68
	CPMAS	10.8	51.1	38.1	0.62

expected to increase uniformly in the whole volume) positively influences the reproducibility of the synthesis.

Extraction and Calcination

Although the samples extracted with ethanol or with water and ethanol contain practically the same amounts of the surfactant, they differ in quality (compare sample B1-ec and B1-wec). This difference is clearly caused by the influence of the extraction with water. Two possible mechanisms of its action can be offered: (i) The polymerization of the silicate is completed during the extraction and (ii) water removes the less well-ordered and amorphous particles from the as-synthesized material.

According to the literature^{13,17-19}, the observed three lines in ²⁹Si MAS NMR spectra at about -90, -100 and -110 ppm correspond to Q², Q³ and Q⁴ silicate species, respectively (Table IV). These Qⁿ species are defined as Si(OSi)_n(OH)_{4-n}, the value of *n* being a measure of the degree of polymerization of silicate. Consequently, the degree of cross-linking of silicate can be suitably characterized by the ratio Q⁴/(Q² + Q³) determined by the HPDEC method. In accordance with literature¹³, the extraction with ethanol leads to a slight decrease in the cross-linking for electrostatically templated MCM-41 samples. Extraction with water further decreases the ratio Q⁴/(Q² + Q³). Therefore any stabilization of pore walls due to a higher cross-linking owing to the extraction with water can be ruled out. A significant increase in the cross-linking occurs, however, after calcination when the ratio Q⁴/(Q² + Q³) increases by ≈50%. Due to the ²⁹Si-¹H cross-polarization, the ratio Q⁴/(Q² + Q³) determined by the CPMAS method of all samples decreases to ≈0.7 in comparison with this ratio determined by the HPDEC method. Clearly the surfactant template molecules present in uncalcined samples offer a source of protons. As relative intensities of all three bands in CPMAS spectra of extracted samples do not practically depend on the extraction treatment and do not differ from those of the as-made material, the interaction between the silicon atoms in the pore walls and the surfactant molecules can be concluded to be unaffected. A marked increase in the relative intensity of the Q² and Q³ lines in CPMAS spectrum of sample B1-wec indicates that part of silicon atoms participates in silanol groups.

It was found that the weight loss observed in the extraction with water was much larger than that due to ethanol. This is an obvious consequence of the dissolution of the as-synthesized material in the extraction with water. The less well-organized particles (or particles with other than hexagonal structure) may be assumed to dissolve first, as electrostatic interactions between the silicate and cationic head-groups are weaker than in the case of well-organized particles with the honeycomb structure. Therefore, the mechanism (ii) is the main reason for the favourable effect of the water extraction.

It is possible to draw the conclusion, that even the best quality as-made MCM-41 prepared from colloidal silica by an optimized procedure contains some proportion of additional phases with other than hexagonal structure. This conclusion is in accordance

with a recent study by Klinowski *et al.*¹⁷, who have optimized the synthesis of siliceous MCM-41 from fumed silica or Cab-O-Sil M-5 fused silica. These authors have shown that the products of their synthesis always contain some amount of lamellar and amorphous phases in addition to the desired MCM-41 product. However, the present communication shows that the extraction with water is a suitable method for the improvement of the phase purity.

The financial support of the Volkswagen Foundation (contract No. I/72134) is gratefully acknowledged.

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