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Effects of temperature on the structure of mesoporous silica materials templated with cationic surfactants in a nonhydrothermal short-term synthesis route

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ARTICLE INFO	A B S T R A C T
Keywords: Sol-gel processes Porous materials Temperature Krafft point MCM-41	This paper reports the influence of synthesis temperature on the structure of mesoporous silica materials tem- plated with ionic surfactant. The results obtained allow for the prediction of optimal temperature value to be used in nonhydrothermal short-term synthesis. The model materials were mesoporous silicates of MCM-41 type. The samples were prepared under alkaline conditions using tetraethyl orthosilicate as a silica source and cetyl- trimethylammonium bromide or octadecyltrimethylammonium bromide as templates. An increase in synthesis temperature led to a rougher surface and decrease in the long-range ordering of the materials obtained, while a slight temperature decrease produced additional porosity. The reasons for these structural disturbances were briefly explained. The best material structure was obtained by synthesis at a temperature slightly higher than the Krafft temperature of surfactant of the porosity template.

1. Introduction

Since discovering new materials of M41S type in 1992 [1,2], their preparation and properties are still under investigation. MCM-41 silica, the most popular member of this family, is known as a cationic surfactant templated mesoporous material with hexagonally arranged cylindrical pores of uniform size and large surface area. Its structure typically is characterised using transmission electron microscopy (TEM), X-ray diffractometry (XRD) and low-temperature nitrogen adsorption methods [3,4]. Pore dimensions of this material can be adjusted from 2 nm to 11 nm by changing the chain length of surfactants, by solubilisation, or adding auxiliary agents [2,5,6]. Due to their properties, mesoporous materials of MCM-41 type are used widely in many applications, such as catalyst supports [3,7,8], sensors [9,10], adsorbents [11,12] and drug carriers [13–15].

Many attempts to understand the formation of the unique structures and properties of M41S type silicates have occurred. First, the synthesis of these materials was explained using the liquid crystal template mechanism, where an organic surfactant forms liquid crystal micelles and a silica precursor polymerises on the template [2]. Further research led to another model, a cooperative mechanism in which an inorganic precursor and a surfactant participate simultaneously in the formation of silica mesophase [16]. Until now, many synthesis procedures of MCM-41 silicas have been introduced. Most were carried out at a high temperature with hydrothermal treatment [17–19]. Hydrothermal ageing has a high impact on the structure and physical properties of mesoporous silica [17]. However, various types of mesoporous silica materials have also been synthesised at room temperature recently [20,21]. It offers the possibility of introducing thermally unstable compounds, e.g., biologically active substances, into them at the synthesis stage. This way, the time and costs of material production are also significantly reduced. But for materials templated by ionic surfactants, the same preparation routes at room temperature often lead to slightly different products. The samples obtained show varying degrees of structure ordering, as detected by the XRD method. The nitrogen adsorption isotherms for synthesised materials exhibit various shapes and sometimes possess more than one hysteresis loop. It is due to imprecise selection and description of synthesis conditions. The most frequently omitted parameter is the synthesis temperature. 'Room temperature' has no precise scientific definition but is usually assumed to be in the range of 20-25 °C. This term is also sometimes equated to the ambient temperature that is the actual recorded temperature of the surrounding area.

This paper investigated the effect of small changes in the synthesis temperature on the structural parameters of mesoporous silica samples

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Received 16 February 2021; Received in revised form 29 March 2021; Accepted 9 April 2021 Available online 15 April 2021 0022-4596/© 2021 Elsevier Inc. All rights reserved. prepared at low temperatures using cationic surfactants. Cetyltrimethylammonium bromide and octadecyltrimethylammonium bromide, as the most popular ionic templates, were studied.

2. Materials and methods

Cetyltrimethylammonium bromide (CTAB), octadecyltrimethylammonium bromide (OTAB), tetraethyl orthosilicate (TEOS) and ammonia (25%) were purchased from Sigma-Aldrich and used as received.

All samples were synthesised in alkaline conditions. The methodology used here was as close as possible to most procedures reported in the literature. The following molar composition was chosen for the reaction mixtures: 1 TEOS : 0.14 CTAB (or OTAB) : 1.4 ammonia : 138.8 H₂O.

Surfactant dissolution with water took place at 40 °C, and the mixture was then cooled or heated to 20, 30, 40, 50 or 70 °C. After the addition of ammonia, TEOS was dropped in over 30 min with continuous stirring. The synthesis mixture was aged for 1 h and then filtered, washed with deionised water and dried at 90 °C. Calcination was conducted in air at a heating rate of 1 °C/min and then maintained at 500 °C for 3 h.

The yields of the synthesis reactions of the materials obtained at 30, 40 and 50 $^\circ C$ were about 90%, at 70 $^\circ C$ 85% and 20 $^\circ C$ 83%.

Samples derived with the surfactants cetyltrimethylammonium bromide (CTAB) and octadecyltrimethylammonium bromide (OTAB) were designated S16 and S18, respectively. The number at the end of the sample name (20, 30, 40, 50 or 70) indicates the temperature at which the material was synthesised. The uncalcined samples were marked with the letters AS (as-synthesised).

The transmission electron microscope (TEM) Talos F200X (Thermo ScientificTM) was used to obtain TEM images. The sample for the TEM observations was prepped by dropping the ethanol particle dispersion, created by an ultrasonic technique, on a carbon film supported on a 300-mesh copper grid.

The atomic force microscopy (AFM) measurements were taken using a multimode scanning microscope NanoScope V (Digital Instruments, USA) in AFM tapping mode.

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded at room temperature on a Nicolet 6700 spectrometer (Thermo ScientificTM), using the smart iTR diamond ATR method in the range of 600–4000 cm⁻¹ at 4 cm⁻¹ resolution.

X-ray diffraction (XRD) measurements were performed using an HZG-4 diffractometer (Carl Zeiss Jena, Germany) applying monochromatic Cu K_{α} radiation.

Nitrogen adsorption/desorption isotherms were measured at -196 $^{\circ}$ C on an ASAP 2010 volumetric adsorption analyser (Micromeritics Instrument Corp.).

3. Calculation

The pore size distribution was obtained from the isotherm's desorption branch using the Barrett-Joyner-Halenda (BJH) method. The specific surface area (S_{BET}) of the investigated samples was evaluated using the standard BET method for the adsorption data in a relative pressure p/p_0 range from 0.04 to 0.25. The total pore volume (V_p) was estimated from single point adsorption at the relative pressure of 0.98. The average primary mesopore diameter (w_d) was calculated based on XRD and nitrogen adsorption data according to the equation: $w_d = cd_{100}[\rho V_{meso}/(1+\rho V_{meso})]^{1/2}$, where c = 1.213 is a constant for hexagonal pore geometry, d_{100} is basal spacing calculated from XRD measurements [5], $\rho = 1.6$ g/cm³ is the density of MCM-41 material walls [22] and V_{meso} is primary mesopore volume obtained from α_s method on the base of nitrogen adsorption isotherm [5]. The reference sample was Lichrospher Si-1000 (Merck) macroporous silica with a surface area of 38 m²/g. The thickness



Fig. 1. TEM images of samples: S16-20 (a), S16-30 (b) and S16-70 (c).



Fig. 2. X-ray diffraction patterns of the as-synthesised (a) and calcined (b,c) samples prepared using CTAB (a,b) and OTAB (c) as templates.

of the pore wall (*t*) was estimated using the equation: $t = a_0 - w_d$, where: $a_0 = 2d_{100}/(3)^{1/2}$ is a pore centre distance [5].

4. Results and discussion

Octadecyltrimethylammonium bromide and cetyltrimethylammonium bromide, as the surfactants most commonly used in the synthesis of mesoporous materials, were selected for the study. Their molecules are very similar, differing slightly in the length of the alkyl chain. The composition of the reaction mixture was analogous to those typically used to synthesise MCM-41 samples. The molar ratio of silica precursor to surfactant and the surfactant concentration in the starting solution was important. It is well known that surfactant molecules (monomers) in aqueous solution show a distinct tendency to arrange themselves into organised, thermodynamically stable molecular aggregates known as micelles. Those aggregate structures form over a narrow range of surfactant concentration called the critical micelle concentration (CMC). The CMC values for CTAB and OTAB are 0.9 mmol/L [23] and 0.3 mmol/L [24], respectively. The concentration of surfactants in the reaction systems used here significantly exceeds these values. It is also higher than the second critical micelle concentration (CMC2), above which cylindrical micelles form porosity templates. The CMC2 values for both surfactants tested are around 3 mmol/L [25]. A temperature range of 20-50 °C was used in the study. However, for the CTAB surfactant, an even higher synthesis temperature (70 °C) was examined to more clearly capture the structural differences of the materials obtained at higher temperatures.

These differences are already apparent in Fig. 1, presenting TEM images of samples obtained with CTAB at 20, 30 and 70 $^{\circ}C.$ Image 1a

(taken along the [110] direction) shows the arrangement of cylindrical pore channels in a sample prepared at 70 °C. It is worth noting that this sample flaked easily along these channels when prepped for microscopic testing. The visible pores are parallel and of uniform diameter. Besides, inclusions of small crystallites in the form of dark spots are present. The remaining images were taken along the [100] direction. They show typical cross-sectional views of granules formed by many fine particles. In Fig. 1b, the configuration of aggregates allows for the observation of nanopores, while in Fig. 1c, they are tightly-clustered and overlap, making the pores hard to see.

The organisation of pore systems in the materials obtained was also characterised by X-ray diffraction. Diffractograms of samples prepared with the surfactants CTAB and OTAB are collected in Fig. 2. For samples that precipitated at lower temperatures, reflections characteristic for an ordered hexagonal array of pores are visible: (100), (110) and (200). With an increase in the synthesis temperature, the first reflection broadens and decreases, which comes with broadening and then overlapping the second and third reflections. It indicates that large-scale ordering becomes poorer. It is a well-known and already studied phenomenon. Likewise, it correlates with the characteristic behaviour of ionic surfactant micelles, in which higher temperatures reduce the number of micelle aggregation [26,27]. Fig. 2a shows the diffractograms of uncalcined samples obtained with CTAB. Here, reflections characteristic of the hexagonal structure are also visible, although slightly shifted towards lower values of 2 theta when compared with the corresponding calcined samples. It indicates that the permanent material structure is formed at the silica precipitation stage. When calcined, it shrinks only slightly due to condensation of the silanol groups during heat treatment.



Fig. 3. FTIR spectra of as-synthesised (a) and calcined (b) samples obtained with CTAB.



Fig. 4. Two-dimensional (a,d) and three-dimensional (b,e) images of surface and cross-section profiles (c,f) for samples S16-20 (a-c) and S16-70 (d-f).

The condensation of silanol groups during calcination was confirmed by FTIR spectroscopy. Fig. 3 shows the FTIR spectra of as-synthesised and calcined samples obtained using CTAB. The spectra of non-calcined materials (Fig. 3a) show bands characteristic of the organic surfactant present in the silica pores. The bands with frequencies at 2850 cm⁻¹, 2920 cm⁻¹ and 1490 cm⁻¹ are characteristic of the surfactant alkyl chain and correspond to the stretching of the C-H bonds in the CH₂ and CH₃ groups. The vibrational band at 984 cm⁻¹ refers to the asymmetric stretching of the CH3-N bond. All samples show bands characteristic of symmetric and asymmetric stretching vibrations of the Si-O-Si groups, with frequencies in the 808 cm⁻¹, 1080 cm⁻¹ and 1240 cm⁻¹ regions. A band characteristic of the Si-OH silanol groups at 950 cm⁻¹ is also visible. Due to adsorbed water presence, a low intensity band attributed to vibration and stretching of the O-H bond at 1640 cm⁻¹ is observed [28]. The calcination process causes an increase in the intensity of the bands at 1060 cm⁻¹ wavelength and a shift of their maxima by 20 units towards higher values while slightly decreasing the band intensity at 1240 cm⁻¹. It is accompanied by the appearance of a band at 1180 cm⁻¹ corresponding

to asymmetrical Si-O stretching vibrations [29]. Comparing the ratio of the sum of signals from Si-O-Si groups to those from Si-OH groups indicates the formation of siloxane groups at the cost of silanol groups during the calcination process. The surface structure of synthesised materials was examined using the AFM technique. Fig. 4 shows two- and three-dimensional images of surface and cross-section profiles for S16 samples obtained at two distant temperatures: 20 and 70 °C. The roughness coefficients (Ra) calculated, using the standard software used for AFM measurements, are 13 nm and 17 nm for samples S16-20 and S16-70, respectively. In calculating the roughness coefficients, sample height was adjusted to account for the curvature of the material particles. The S16-20 sample has a significantly smoother surface compared to that of S16-70. The silicate synthesised at 70 $^\circ C$ exhibits high roughness as if it comprised permanently adhered fine particles. During the synthesis of gels in an alkaline medium, hydrolysis of the alkoxide groups is the rate-limiting step in the reaction. When the first alkoxide group hydrolyses, the remaining groups hydrolyse rapidly, and small nuclei form from fully hydrolysed components. Alkaline media promote dissociation



Fig. 5. Nitrogen adsorption/desorption isotherms (a,c) and pore size distributions (b,d) for the samples prepared using CTAB (a,b) and OTAB (c,d) as a templates. (Several isotherms have been shifted along the Y-axis.)

Table 1	Та	ble	1
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Structural parameters of investigated MCM-41 samples prepared using CTAB (S16) and OTAB (S18) as templates obtained from XRD and nitrogen adsorption data.

Sample	Synt. temp. (°C)	S _{BET} (m ² /g)	<i>V_p</i> (cm ³ / g)	D _{meso} ^a (nm)	<i>w_d</i> (nm)	t (nm)
S16-20	20	1114	0.83	2.30	3.29	0.96
S16-30	30	1117	0.98	2.48	3.47	0.97
S16-50	50	1132	1.14	2.70	3.80	1.06
S16-70	70	1169	2.35	2.64	3.82	1.09
S18-20	20	1064	0.94	3.11	4.76	1.39
S18-40	40	1079	1.91	3.02	4.43	1.30
S18-50	50	1047	1.93	2.86	3.82	1.13

^a Pore diameter obtained from maximum of PSD peak.

of silanol surface groups, increasing surface charge density and stabilising colloidal suspensions. At low temperature, silicate condensation is slow, and ion-pair interactions determine the assembly. At higher temperatures (>50 °C), the kinetics of condensation dominate and both thermodynamics and kinetics favouring cooperative bonding initiated by silica decrease. Thus, at 70 °C, TEOS condenses rapidly to form small primary particles that stick together.

The structure parameters of samples templated with CTAB and OTAB surfactants were studied using the low-temperature nitrogen adsorption method. The nitrogen adsorption/desorption isotherms for investigated samples and corresponding pore size distributions obtained from the desorption branch of isotherms are shown in Fig. 5. All the isotherms are of type IV according to International Union of Pure and Applied

Chemistry (IUPAC) classification [30]. They possess hysteresis loops of type H1 characteristic for mesoporous materials with cylindrical channels. At a relative pressure of about 0.3, there is a sharp increase in the amount of nitrogen adsorbed. This steep nitrogen uptake is due to the filling of the primary mesopores. A second hysteresis loop appears at the relative pressure of about 0.9 for samples prepared at higher temperatures, which coincides with a decrease in the size of the primary silica granules and is caused by small voids between them. These tiny granules are seen in the TEM images in Fig. 1. For sample S16-20, there is no second hysteresis loop on the isotherm at $p/p_0 = 0.9$. The inter-grain space here is larger than the mesopore dimensions, and capillary condensation does not occur.

As shown in Fig. 5b,d and in Table 1, an increase in the synthesis temperature of S16 samples results in a slight shift of the pore diameter towards higher values and simultaneously a thickening of the pore walls. The opposite tendency is observed for samples S18 prepared with OTAB as a template. However, in both cases, the temperature of 20 °C leads to the forming of additional pores. The second peak appears slightly in the PSD for sample S16-20 at a diameter of about 3.7 nm. It is more visible on the inset in Fig. 5b. In the pore size distribution of sample S18-20, this second peak is clearly distinguishable (Fig. 5d). The isotherm of this sample has an additional narrow horizontal hysteresis loop (Fig. 5c), characteristic of slit pores [30]. The only difference between the two synthesis systems studied is the surfactant used as a template. Thus, the aqueous surfactant solution properties are the cause for differences found in the structural parameters of samples obtained at the same temperature.

These correspond with the mechanism of liquid crystal templating, in which the behaviour of a surfactant determines the structure of the final



Concentration

Fig. 6. Schematic representation of the solubility curve for the ionic surfactants.

product obtained. Ionic surfactants exhibit an unusual phenomenon in that their solubilities increase rapidly above certain temperatures, called the Krafft point (or Krafft temperature). Below the Krafft temperature (T_K) , the surfactant solubility is insufficient for micelles to form — see Fig. 6. As the temperature rises, the solubility slowly increases until reaching the Krafft temperature. The surfactant molecules now group as micelles, so a large increase in solubility is observed. When the micelle solution is cooled down to cross the solubility limit, the surfactants 'freeze' and no longer form stable micelles. They convert into crystals or bilayers. Thus, small changes in the synthesis temperature cause measurable changes in the structure of the materials obtained. The Krafft temperatures are about 25 °C for CTAB and 36 °C for OTAB [31]. Therefore, the additional porosity observed for samples prepared at 20 °C can be a consequence of the existence of incompletely dissolved (or rather re-precipitated) parts of the surfactant. Another reason may be the formation of a lamellar phase under synthesis conditions. This lamellar phase and the undissolved surfactant parts disintegrate during calcination and cause additional free spaces in the silica structure. Additional confirmation of the creation of a lamellar phase is provided by the mentioned behaviour of samples obtained at 20 °C during preparation for TEM measurements. The material particles fractured mainly along the pore channels, and images were only obtainable along the [110] direction. It suggests that the crushing of the particles took place in the areas where the lamellar phase existed. Also, the presence of fissure pores detected by the nitrogen adsorption method in samples obtained at 20 °C confirms the formation of a lamellar phase at this temperature, which after calcination gives free flat spaces. Furthermore, additional inclusions in the silica network, in the form of dark dots, are visible in Fig. 1a. These may be surfactant crystallites tightly surrounded by silica and not burned off during the calcination process.

5. Conclusions

The synthesis temperature of mesoporous silica materials templated with ionic surfactants plays a crucial role in their preparation. The increase in temperature during the nonhydrothermal, short-term production of MCM-41 samples leads to a decrease in the ordering of their structure and causes an increase in the sample surface roughness. On the other hand, a too low synthesis temperature results in local structural disorder (in the form of crystallites or lamellar phase) created at the template framework formation stage, leading to generating additional pores during calcination. The best structure with a smooth surface, homogeneous pores and long-range ordering forms when the silica material is precipitated at a temperature slightly higher than the Krafft point of the surfactant used as a porosity template. It is particularly important for short-time synthesis at low temperature, where no further remodelling of the silica network is possible.

CRediT authorship contribution statement

Anna Borówka: Conceptualization, Resources, Writing – original draft, Visualization, Writing – review & editing. Krzysztof Skrzypiec: Data curation, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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