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Thermogravimetric monitoring of the MCM-41 synthesis

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Abstract

MCM-41 materials were synthesized using cetyltetramethylammonium bromide (CTMABr) as the template and two types of silicas: regular silica-gel and colloidal fumed silica. The synthesis was made under hydrothermal conditions at 100°C by adjusting the pH of the hydrogel to 10. A small amount of the sample was taken after each pH adjustment and analyzed by high-resolution thermogravimetry in order to determine the temperature ranges related to water desorption, surfactant decomposition and silanol condensation for the mesostructures studied, as well as to estimate their overall quality. The BET specific surface area and pore size distribution for calcined MCM-41 materials were evaluated from nitrogen adsorption isotherms. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrothermal synthesis; MCM-41; pH adjustment; Thermogravimetry

1. Introduction

In the early 1990's a new class of ordered mesoporous materials were synthesized via self-assembly of silica and surfactant species [1,2]. The negatively charged silica species interact with surfactant cations under hydrothermal conditions forming the self-assembled mesostructured composite, which after surfactant removal via calcination and/or extraction gives an ordered mesoporous material (see Fig. 1). The aforementioned class of materials is known as the M41S family and includes such structures as MCM-41 (hexagonal phase) and MCM-48 (cubic phase). The most popular phase, MCM-41, consists of hexagonally ordered channels having amorphous silica walls.

The formula of the surfactants used to synthesize mesoporous materials can be represented by: $(C_nH_{2n+1})(CH_3)_3N^+X^-$, where n is usually greater than 10, and $X = Cl$, Br or OH. One of the most important aspects in varying the surfactant chain size (n value) is the possibility to tailor the pore width [2–4]. Hexadecyltrimethylammonium bromide is most often used for the synthesis of MCM-41 and MCM-48 mesophases. The self-assembly process is usually carried out at a temperature between 80 and 120°C, although higher temperature and room temperature synthesis also have been reported [5–8]. The pH conditions can vary from acidic [5] to neutral [5,7] and basic [8].

It was shown recently that a high quality MCM-41 could be synthesized by adjusting pH during the hydrothermal synthesis [9,10]. However, not much attention has been given to the MCM-41 formation during the pH-adjusted hydrothermal synthesis. Since our previous studies [11,12] showed that the high-resolution thermogravimetric analysis (TGA) of

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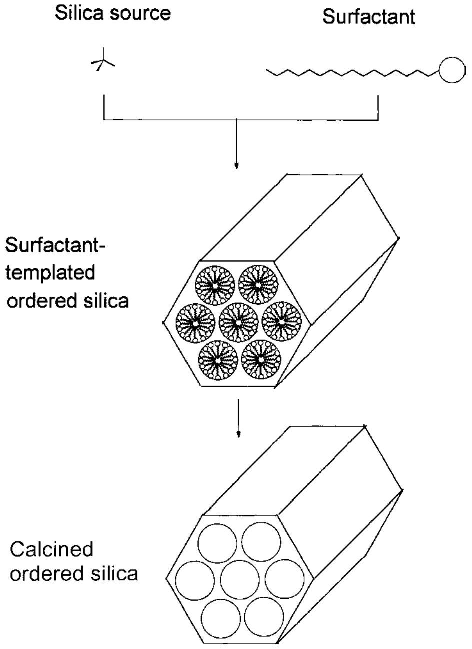

Fig. 1. Synthesis scheme for MCM-41 materials.

mesostructured samples provides valuable information about the resulting materials, we employed this technique to monitor the pH-adjusted synthesis of MCM-41. This was done by collecting the MCM-41 samples after each pH adjustment step and analyzing them by TGA. In addition, nitrogen adsorption isotherms were measured for calcined samples in order to determine the surface and structural properties of the resulting materials.

2. Experimental

2.1. Hydrothermal synthesis

The chemicals used to synthesize MCM-41 were regular silica (Aldrich Chemical, Co.), fumed silica M-5 (Cab-O-Sil), both of analytical grade, sodium silicate solution containing 27% SiO_2 and 14% NaOH (Aldrich Chemical, Co.), cethyltrimetrylammonium bromide, $C_{16}H_{33}(CH_3)_3NBr$ (Aldrich Chemical, Co.), and distilled water. The pH adjustment was done with 1% acetic acid in ethanol solution [10]. The chemical reactants were mixed in order to obtain gels with the following molar composition: $4SiO_2$:1-Na_2O:1$C_{16}H_{33}(CH_3)_3NBr$:200H_2O.

The reaction mixture was prepared as follows: 0.567 g of silica, 2.8 ml of the sodium silicate solution and 10 ml of water were placed into a 100 ml teflon beaker and stirred at 60–70°C for 2 h in order to obtain a clear solution. A solution prepared from 2.214 g of cethyltrimethylammonim bromide and 12 ml of distilled water was added to the aforementioned mixture and aged for 1 h at room temperature. The amounts of reactants listed above were estimated in order to synthesize about 2 g of calcined samples.

Two hydrogels prepared by using different silicas (regular and fumed) were placed into 45 ml teflon-lined autoclaves and heated at 100°C for 3 days. Their pH was measured each day and adjusted to 9.5–10. Before each pH adjustment, a small sample was collected, dried at room temperature and analyzed by using high-resolution thermogravimetry. The final samples were washed with 25 ml of 2% HCl:EtOH solution and subsequently calcined at 550°C for 1 h in nitrogen and an additional hour in air. The calcination temperature was reached at a heating rate of 2.5°C/min.

2.2. Thermogravimetric analysis

Thermogravimetric analysis was carried out using a high-resolution thermogravimetric analyzer (TGA 2950 model) from TA Instruments, Inc. (New Castle, DE). The TGA data were collected in nitrogen (60 ml/min nitrogen flow) from room temperature to 1000°C using the maximum heating rate of 5°C/min. The resolution and sensitivity parameters of the instrument were set at 4 and 6, respectively.

2.3. Adsorption measurements

Nitrogen adsorption measurements were carried out at –196°C using a volumetric adsorption analyzer (ASAP 2010 model) from Micromeritics (Norcross, GA, USA). Each sample (ca. 0.1 g) was degassed at 200°C for 2 h in the degas port of the instrument. The measurements were carried out over a relative pressure ranging from ca. 10^{-6} to 0.995. The specific surface area was determined according to the standard Brunauer–Emmett–Teller (BET) method [13]. The pore size distribution was obtained by the Barrett–

Joyner–Halena (BJH) method [14] with the corrected Kelvin equation [15].

3. Results and discussion

Two MCM-41 samples were synthesized using different silicas. One of them, MCM-41(A), was prepared form Aldrich silica-gel (60–200 mesh, 150 Å), whereas another, MCM-41(B), was synthesized from Cab-O-Sil fumed silica. In both cases, the pH adjustment was done during hydrothermal synthesis according to the procedure reported elsewhere [10]. The pH-adjusted synthesis was monitored by high-resolution TGA in order to obtain information at different stages of the MCM-41 formation.

The initial pH values of both hydrogels were extremely basic (pH = 14). After one day, these values decreased to around 11–12. This suggests that the hydroxyl concentration in the synthesized gels decreased during hydrothermal process due to the self-assembly of silica species. In order to control the self-assembly process, the pH was successively adjusted and maintained about 9.5–10 during the synthesis [16]. The pH was checked each day, and three and two adjustments were required for the MCM-41(A) and MCM-41(B) samples, respectively. Although both silicas were good starting materials, the hydrothermal process seemed to be slower when regular silica-gel was used instead of fumed silica. The fumed silica was previously used in the hydrothermal synthesis at 150°C for 48 h [17]. However, by adjusting pH of the gel to ca. 9.5–10, this synthesis can be carried out at even lower temperature, i.e. about 100°C.

It was previously reported that thermogravimetric analysis of MCM-41 materials in nitrogen atmosphere show three or more weight losses [18,19]. However, the high-resolution TGA curves for the samples collected after each pH adjustment show four weight losses (see Figs. 2 and 3 for MCM-41(A) and MCM-41(B), respectively). The weight loss steps are located in the following temperature ranges: i) from 25 to 170°C (thermodesorption of physically adsorbed water); ii) from 170 to 270°C (surfactant decomposition); iii) from 270 to 530°C (residual surfactant decomposition and silanol condensation), and iv) from 530 to 740°C (residual silanol condensation).

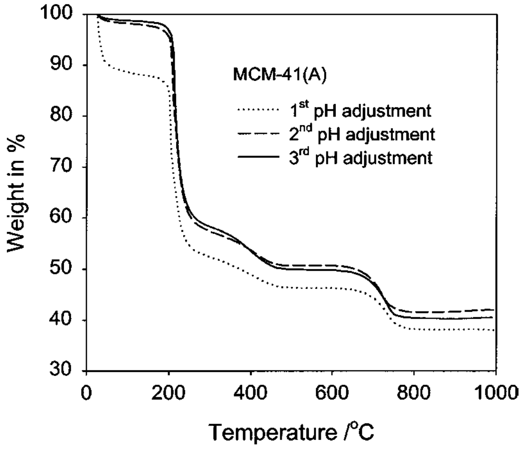

Fig. 2. TGA curves for unwashed MCM-41(A) samples synthesized with pH adjustment using regular silica-gel.

For the MCM-41(A) sample, after the first pH adjustment, about 13% of water was desorbed, i.e. about three times more in comparison to the amount desorbed from MCM-41(B). After the second pH adjustment, these amounts were practically constant, i.e. about 2%. As regards surfactant decomposition, after the second and third pH adjustments, about 40% weight loss was measured, which was greater than the corresponding weight loss for the sample after the first pH adjustment. This indicates that the amount of self-assembled CTMA$^+$ cations with silica species during

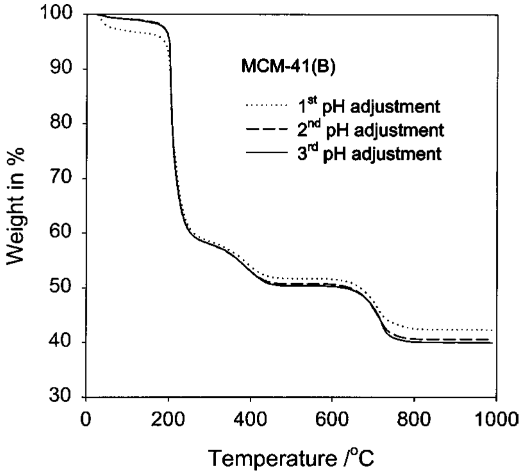

Fig. 3. TGA curves for unwashed MCM-41(B) samples synthesized with pH adjustment using fumed silica.

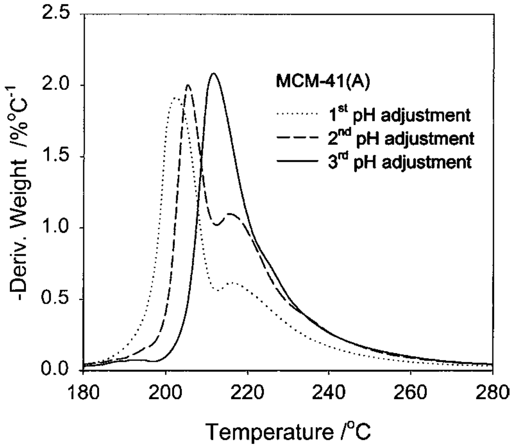

Fig. 4. DTG curves for unwashed MCM-41(A) samples corresponding to the TGA curves shown in Fig. 2.

the second and third day of the synthesis is greater in comparison to the amount self-assembled during the first day, which is in agreement with the earlier data for MCM-41 materials [18]. For both samples, the silanol condensation is analogous and accounts for ca. 8% of the total weight loss.

The silica reactivity is reflected by the shift of the surfactant removal step towards higher temperatures, which is clearly visible on the DTG curves for MCM-41(A) and MCM-41(B) shown in Figs. 4 and 5, respectively. For the MCM-41(A) samples taken after successive pH adjustments, the temperature corresponding to the maximum decomposition rate of the surfactant was shifted from 202 to 206°C and next to 212°C (see Fig. 4). Also, a shoulder on the DTG curve at ca. 218°C was observed for the samples after the first and second adjustments, and disappeared after the final pH adjustment. The MCM-41(B) exhibits a similar behavior with temperatures shifting from 202 to 203°C and next to 205°C. In this case, the shoulder on the DTG curve was also observed at the similar temperature as for MCM-41(A), but only for the sample after the first pH adjustment (see Fig. 5).

The final samples after washing with HCl:EtOH solution and drying, were again analyzed by high-resolution TGA over the temperature range from 25 to 1000°C. The TGA and DTG curves are shown in Figs. 6 and 7, respectively. As can be seen from the TGA curve, about 50% of the surfactant was removed after washing with the 2% HCl:EtOH solution. The main advantage of the surfactant removal by washing is the reduction of time required for calcination. It was observed for the MCM-41(A) sample that a small amount of physically adsorbed water was present, which was desorbed at the temperature range from 60 to 170°C with the maximum desorption rate at ca. 100°C (see Fig. 7). For both materials, the maximum rate of the surfactant removal appeared at tempera-

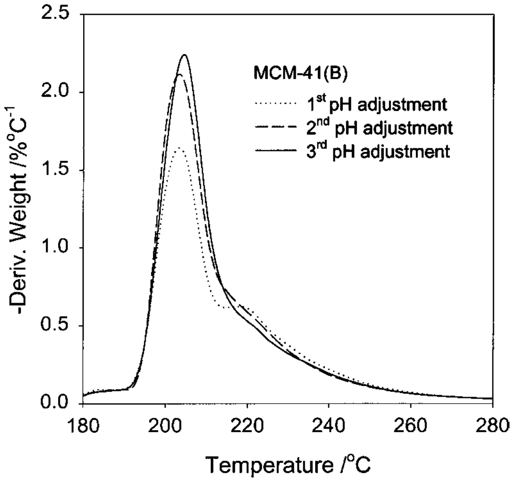

Fig. 5. DTG curves for unwashed MCM-41(B) samples corresponding to the TGA curves shown in Fig. 3.

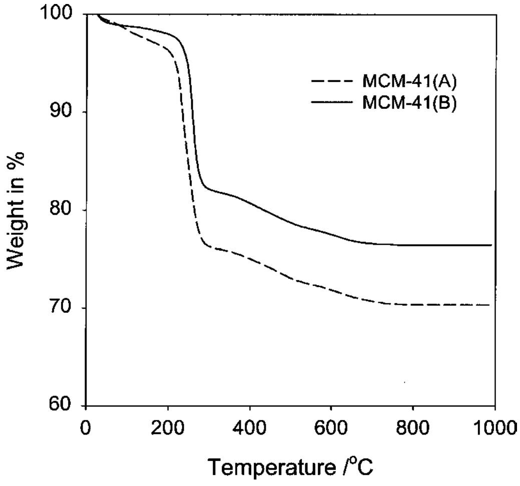

Fig. 6. TGA curves for the MCM-41(A) and MCM-41(B) samples after washing with 2% HCl:EtOH solution.

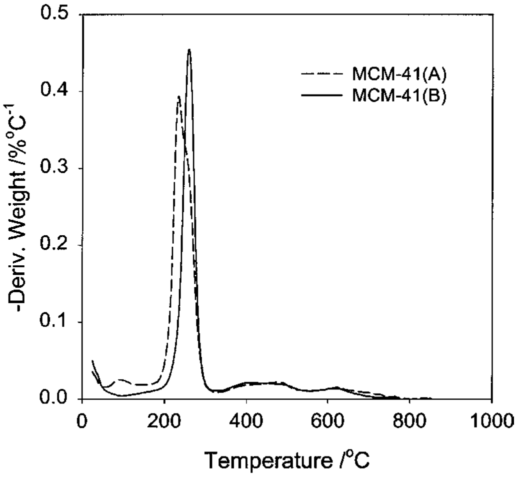

Fig. 7. DTG curves for the MCM-41(A) and MCM-41(B) samples after washing with 2% HCl:EtOH solution.

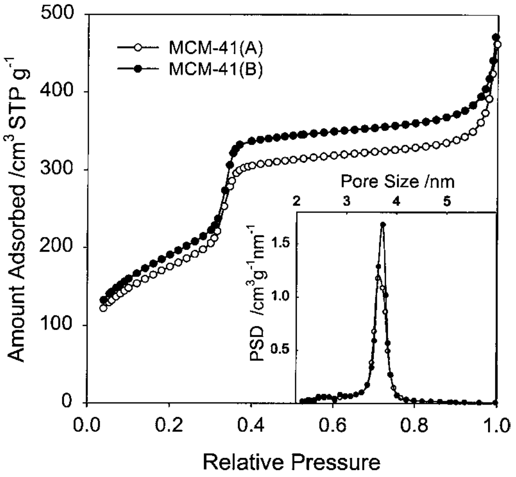

Fig. 8. Nitrogen adsorption isotherms and the corresponding pore size distributions (PSD) for calcined MCM-41(A) and MCM-41(B) samples.

tures higher than those observed for unwashed samples, which indicates that the remaining surfactant cations interact more strongly with silanol groups. The number of silanol groups in the samples, determined in the temperature range from 340 to 800°C, was equal to 4.8 mmol/g and 4.2 mmol/g for MCM-41(A) and MCM-41(B), respectively. Landmesser et al. [16] reported 4.4 mmol/g of silanol groups in the temperature range from 500 to 800°C.

The current study of the self-assembly of silica and surfactant species under controlled pH conditions indicates that pH plays an important role in this process. It was reported elsewhere [20] that in the pH range from 10 to 12 some phase transformations from hexagonal, via cubic to lamellar mesostructures can occur with increasing silica/surfactant ratio. At pH = 12 the lamellar phase is mostly formed [21]. However, at pH = 10, as reported by Ryoo et al. [10], high quality MCM-41 mesostructures are obtained.

Shown in Fig. 8 are nitrogen adsorption isotherms for both MCM-41 samples studied. A sharp step at the relative pressure range between 0.3 and 0.4 reflects nitrogen condensation in primary mesopores and is characteristic for mesostructured materials having uniform pores [15]. An increase in the amount adsorbed at the relative pressures greater than 0.4, especially visible for MCM-41(B), indicates the existence of secondary mesopores. The specific surface area, pore volume and pore sizes of the samples studied are given in the Table 1. Additional analysis included the determination of the pore size distribution according to the procedure developed by Kruk et al. [15]. As can be seen in the inset of Fig. 8 these distributions are quite narrow and similar for both samples. This confirms that the MCM-41 samples of similar properties can be synthesized from different silicas at relatively low temperature.

Table 1
Adsorption parameters for the MCM-41 samples studied[a]

Sample	Surface area, S (m^2/g)	Volume of primary mesopores, V_{me} (cm^3/g)	Total pore volume, V_t (cm^3/g)	Pore width, w (nm)
MCM-41(A)	639	0.46	0.66	3.6
MCM-41(B)	694	0.48	0.68	3.7

[a] S_{BET} — BET specific surface area and w — maximum of the pore size distribution.

4. Conclusions

The TGA study of the samples taken at different stages of the MCM-41 formation showed that the self-assembly of silica and surfactant species at 100°C and pH adjusted to about 9.5–10 seems to be dependent on the silica source. The synthesis of MCM-41 from fumed silica is more sensitive to the pH adjustment than that employing a regular silica gel. Also, it appears that high-resolution TGA is an effective technique to monitor the synthesis of the MCM-41 formation as well as to estimate the quality of the resulting materials. The nitrogen adsorption study showed that the two materials obtained have nearly the same physical and chemical properties.

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