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Preparation of spherical MCM-41 molecular sieve at room temperature: Influence of the synthesis conditions in the structural properties

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Abstract

A rapid and facile synthesis route to obtain mesoporous MCM-41 silica at room temperature under basic conditions using as template cetyltrimethylammonium bromide (CTAB) is reported. The synthesis variables such as reaction time, molar ratios of CTAB/TEOS and H_2O/ethanol in the initial gel composition were studied. Samples were characterized by X-ray diffraction, nitrogen adsorption–desorption analyses, scanning electron microscopy and transmission electron microscopy. It was found that reaction conditions affect the quality of the MCM-41 silica. This silica can be prepared at short periods of time, and it exhibited a uniform size and spherical morphology.

Keywords: MCM-41 silica; Room temperature synthesis; Mesoporous materials

1. Introduction

The synthesis of a new family of mesoporous molecular sieves with regular and constant pore diameters from 2 to 10 nm, designated as M41S, was reported in 1992 by the scientists at Mobil Oil Corporation [1,2]. These materials were prepared by hydrothermal transformation of basic silicate or aluminosilicate gels in the presence of quaternary ammonium surfactants with different alkyl chain lengths. Particularly, most of this research has been concentrated on MCM-41 silica because of its hexagonal arrangement of unidimensional mesopores with uniform and controllable pore diameter [3,4]. These mesoporous materials possessing high specific pore volumes, high specific surface areas and narrow adjustable pore size distribution can be synthesized by controlling some reaction conditions, such as, temperature, pH, surfactant/silica molar ratio, etc.

Generally, mesoporous MCM-41 molecular sieves have been synthesized by hydrothermal method in strong base medium [5,6]. But this method has some shortcomings, such as, high temperatures (60–150 °C), long reaction time (1–6 day), crystal-transforming phenomenon, etc. On the other hand, the advantages of using room-temperature in the synthesis of mesoporous sieves are: (1) no long reaction time are required, (2) the use of expensive autoclaves is not need (3) power saving, and (4) good reproducibility. In this route, usually alkoxysilanes have been used as silica source which are added to an aqueous solution of a cationic surfactant [7–9]. During hydrolysis progress, these alkoxisilanes generates alcohol and a nonlinear network of Si–O–Si via formation of intermediate alkoxy derivatives of silicic acid and polysilicates.

For many applications, such as, catalysis [10], sorption [11], separation [12], drug delivery [13,14], it would be more desirable to have an economically feasible method to prepare silica MCM-41 in a short synthesis time. Attempts have been made to synthesize MCM-41 at room temperature [9,15–17]. Voegtlin et al. [15] have prepared highly ordered MCM-41 at room temperature in 1 h, however, stability above 600 °C has not been given. Kumar et al. [18] have synthesized MCM-41

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analog at room temperature using hexadecylamine as templating agent showed improved stability. Nevertheless, most of the approaches suffer process difficulties in large scale preparation as the synthesis involves longer crystallization time at higher temperatures (100–150 °C). MCM-41 was synthesized by Mody et al. [9] at room temperature, but 1.0 N acid sulfuric or hydrochloric acid or acetic acid was used in their experiment. Moreover, the material showed a flaky morphology with severe overlapping. Vetrivel et al. [19] reported the preparation of MCM-41 at room temperature in short periods of time with the aid of ultrasonic irradiation. Nevertheless, mesoporous materials were not stable towards acidic solvents. More recently, Ma et al. [20] prepared mesoporous silica nanoparticles of MCM-41 with diameters between 200 and 400 nm under assistance of *n*-hexane by using TEOS as silica source. X-ray diffraction (XRD) and FE-SEM micrographs showed that the mesopore structure is not ordered.

Thus, the aim of this work was to prepare ordered and thermally stable mesoporous MCM-41 silica at room temperature and investigate systematically the effects of the synthesis time, CTAB/TEOS and H_2O/ethanol molar ratios for developing a simple, fast and reproducible method without necessity of additives. The obtained materials were characterized by XRD, SEM, TEM and nitrogen adsorption–desorption isotherms.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate, TEOS (98%, Aldrich) was selected as a source of silica and cetyltrimethylammonium bromide, CTAB (98%, Aldrich) was used as the structure directing agent. Deionized water was obtained from a system of two ionic interchange columns, Cole–Parmer Instruments, ethanol (99.8%) and aqueous ammonia solution, NH_4OH (29%) from Fermont were used to carried out the synthesis of mesoporous silica.

2.2. Preparation of mesoporous MCM-41 silica at room temperature

In a typical synthesis of mesoporous MCM-41 molecular sieve, 0.5 g CTAB were added to 96 mL of deionized H_2O under stirring. After the solution turned clear, 34 mL of ethanol was added and then 10 mL of aqueous ammonia solution was added to the system and it was allowed to mix for 5 min. After that, 2.0 mL of TEOS was poured into the solution immediately under stirring. Stirring was continued for 3 h at room temperature. The solid product was recovered by filtration and dried at room temperature overnight. The CTAB was removed from the composite material by calcining the sample at 540 °C for 9 h.

2.3. Characterization

The powder XRD patterns were recorded on SIEMENS D5000 diffractometer using CuK_α radiation. The diffraction data were recorded in the 2θ range of 2–10°. The morphology of the samples was examined using scanning electron microscope (JEOL JSM-7401F) operated at 5.0 kV. Transmission electron microscopy (TEM) was performed using a HRTEM Titan operated at 300 kV. N_2 adsorption–desorption isotherms were obtained on Quantachrome AS1Win equipment at −196 °C. Before the experiments, the samples were degassed under vacuum at 300 °C for 10 h. The specific surface area of the sample was calculated using BET method. The pore size distribution was calculated using desorption branches of nitrogen isotherms and Density Functional Theory (DFT) method.

3. Results and discussion

In order to investigate the influence of various synthesis parameters on the formation of the MCM-41 materials, different syntheses were conducted at room temperature by varying only one parameter.

3.1. Influence of reaction time

Mesoporous MCM-41 silica was prepared under magnetic stirring at different intervals of time between 1 and 7.5 h to explore the optimum synthesis conditions to obtain MCM-41 silica with high ordered mesostructure and particle morphology. The powder X-ray diffraction (XRD) patterns are showed in Fig. 1. All the samples showed three characteristic diffraction peaks, which correspond to the planes (100), (110), (200) of the hexagonal-ordered silica MCM-41. The XRD peak positions shifted to higher 2θ values as the synthesis time was increased (see Table 1). The shifting of the peaks to higher 2θ values might be associated with smaller mesopore size or thicker pore wall [17]. After the addition of TEOS, facilitation of

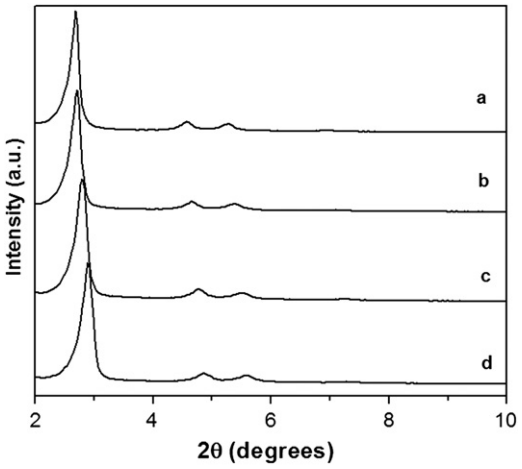

Fig. 1. XRD patterns of calcined MCM-41 synthesized at different reaction times: (a) 1 h, (b) 3 h, (c) 5 h and (d) 7.5 h.

Table 1
The 2θ and d100-spacing values for MCM-41 silica synthesized at different studied parameters.

Reaction time (h)	2θ (100)	2θ (110)	2θ (200)	d_{100} (nm)	Unit cell parameter a_0 (nm)
1	2.68	4.57	5.29	3.29	3.79
3	2.71	4.66	5.38	3.26	3.76
5	2.80	4.75	5.50	3.15	3.63
7.5	2.89	4.87	5.59	3.05	3.52
CTAB/TEOS molar ratio					
0.1	2.65	4.48	5.17	3.33	3.84
0.13	2.71	4.60	5.32	3.26	3.76
0.16	2.71	4.66	5.35	3.26	3.76
0.19	2.80	4.81	5.53	3.15	3.63
H_2O/ethanol molar ratio					
10	2.77	4.78	5.50	3.18	3.67
21	2.68	4.57	5.29	3.29	3.79
66	2.62	4.48	5.17	3.36	3.87
Calcination temperature (°C)					
540	2.56	4.36	5.05	3.44	3.97
650	2.62	4.54	5.23	3.36	3.87
750	2.77	4.75	5.44	3.18	3.67
850	3.01	ND	ND	2.93	3.38

hydrolysis and condensation of the silica source with longer stirring results in more stable and higher-ordered structure MCM-41 silica. This behavior has been previosuly reported by other authors [9–21]. Also, the XRD results revealed that the formation of mesoporous MCM-41 silica could be achieved in a short period of time (1 h) under alkaline conditions. The d_{100}-spacing values for calcined mesoporous MCM-41 silica decreased with aging time increases. According to the literature, a longer agitation time is required to promote silica condensation and it could prevent greater shrinkage of the mesostructure during calcination process [21]. Besides, using d_{100}-spacing values the unit cell parameter (the center-to-center pore distance) (a_0) can be calculated according with the next equation:

$$a_0 = 2d_{100}/(3)^{1/2} \quad (1)$$

From Table 1, it can be seen that the a_0 value decreased when reaction time increased, that is, longer reaction time made the pore size decrease.

3.2. Influence of CTAB/TEOS molar ratio

The dependence of the concentration of CTAB on the phase quality was also investigated. The CTAB/TEOS molar ratio in the initial gel was varied in the range of 0.1–0.19 keeping fixed molar ratios of H_2O/ethanol and H_2O/NH_4OH as 7.2 and 56.7, respectively and reaction time of 3 h. The powder XRD patterns of synthesized MCM-41 silica obtained by varying CTAB/TEOS molar ratios are shown in Fig. 2. From this figure, it can be seen that a MCM-41 mesophase was obtained in all the samples. Table 1 shows the 2θ and d-spacing of the plane

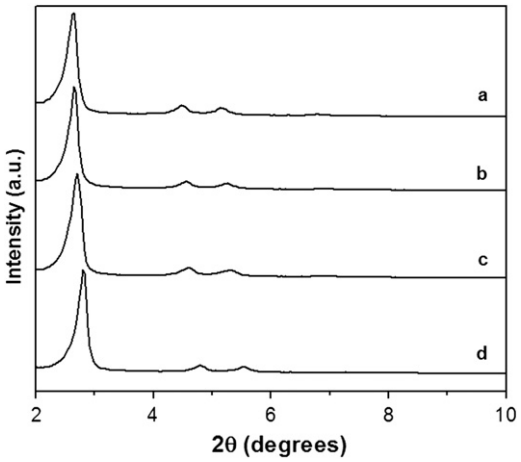

Fig. 2. XRD patterns of calcined MCM-41 synthesized at different CTAB/TEOS molar ratios: (a) 0.1, (b) 0.13, (c) 0.16 and (d) 0.19.

100 values for these samples. An increase in the surfactant concentration resulted in the shifting though to the higher 2θ value. Such behavior may be attributed to prohibition from unit cell growth and decreased polymerization of silica by an excess of surfactant (see Table 1). On the other hand, as the amount of TEOS is increased, a shift at lower 2θ values was observed. This behavior was attributed to thicker pore wall. The low CTAB/TEOS molar ratio could provide a several advantages compared with high CTAB/TEOS molar ratio in terms of synthesizing the mesoporous silica, for example, improvement of the stability of the entire mesostructure, increased framework thickness and requirement of a smaller amount of surfactant.

3.3. Influence of H_2O/ethanol ratio

The powder XRD patterns of the samples obtained by varying H_2O/ethanol molar ratio and keeping fixed CTAB/TEOS molar ratio of 0.16, NH_4OH content of 0.094 mol and reaction time of 3 h are illustrated in Fig. 3. It can be clearly seen from this figure that the formation of ordered MCM-41 phase even at H_2O/ethanol molar ratio of 66. In addition, it is interesting to note that, the characteristics peaks were found to shift towards lower 2θ values (see Table 1) when the H_2O/ethanol molar ratio in the starting gel was increased. The shifting of the peak to lower 2θ values might be associated with well grown unit cell [17]. Also, we can observe that as amount of ethanol is increased, d_{100}-spacing values decreased. This means that particles with hexagonal close packed pores arranged in a radial formation are formed at high ethanol concentration. This is the result of a combination of (i) a decreased of packing due to less tightly packed micelles and (ii) a very slow equilibrium toward the hydrolysis of TEOS due to solvating effects of the alcohol that influence the micelle formation, resulting in a slow growth of micelles on the surface of the center of the particles [22].

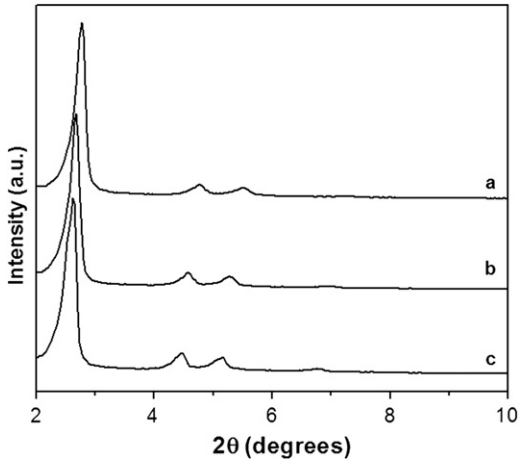

Fig. 3. XRD patterns of calcined MCM-41 prepared at different H_2O/ethanol molar ratios: (a) 10, (b) 21 and (c) 66.

3.4. Nitrogen adsorption–desorption studies

The nitrogen adsorption–desorption isotherms and pore size distribution for some samples of MCM-41 synthesized at different CTAB/TEOS molar ratios are depicted in Fig. 4a while Fig. 4b illustrates the pore size distribution curves obtained from DFT method. Both samples showed nitrogen adsorption – desorption isotherms typically of type IV. Samples exhibited pronounced steep condensation step for relative pressures 0.2–0.4 arising from condensation of nitrogen inside the primary mesopores and indicating good structural order of MCM-41. The condensation is steep particularly for MCM-41 prepared from CTAB/TEOS molar ratio of 0.16 as compared to MCM-41 silica synthesized from CTAB/TEOS molar ratio of 0.1. Thus, the quality of the product was found to affect the steepness of the condensation steep. The specific pore volume, BET surface area, average pore diameter and estimated pore wall thickness deduced from the nitrogen sorption isotherms for these samples are summarized in Table 2. High specific surface area values are obtained for both samples (higher than 1000 m^2/g). Also, MCM-41 mesoporous molecular sieves exhibited narrow pore size distribution (pore sizes from 1 to 3 nm). The wall thickness values were calculated by following Eq. 2:

$$W_t = a - \text{Pore diameter} \quad (2)$$

The estimated wall thickness values were in the range from 1.66 to 1.74 nm and they are agreeing with previous reports. [8,9–19]. All, these properties make them an attractive molecular sieve for application, such as, catalysis, sorption of organic molecules, chromatographic separations, as well as host for quantum confinement of guest molecules [23].

3.5. Thermal stability

In order to know the thermal stability of the MCM-41 synthesized with a CTAB/TEOS molar ratio of 0.16, this

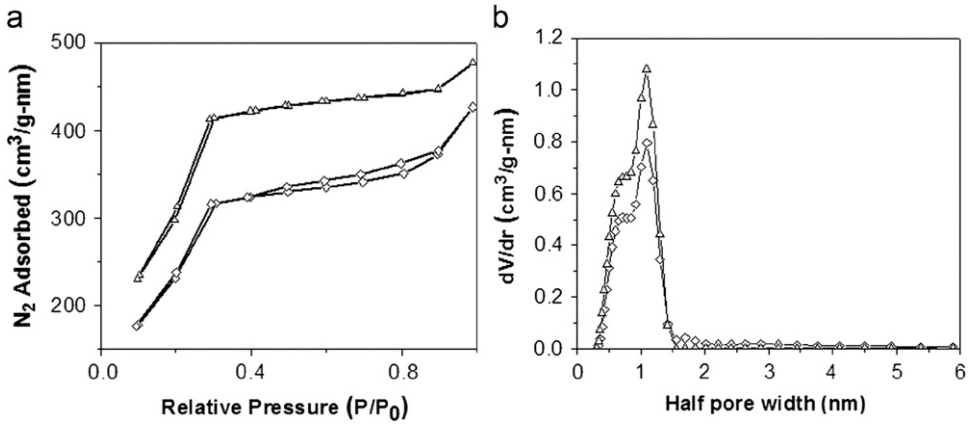

Fig. 4. Nitrogen adsorption–desorption isotherms (a) and pore size distribution (b) for MCM-41 synthesized at different CTAB/TEOS molar ratios: (△) 0.16 and (△) 0.1.

Table 2
Comparison of some parameters for MCM-41 silicas obtained at room temperature and different CTAB/TEOS molar ratios.

CTAB/TEOS ratio	Total pore volume (cm^3/g)	BET surface area (m^2/g)	DFT average pore diameter (nm)	Estimated wall thickness (nm)
0.16	0.653	1460	2.1	1.66
0.1	0.550	1094	2.1	1.74

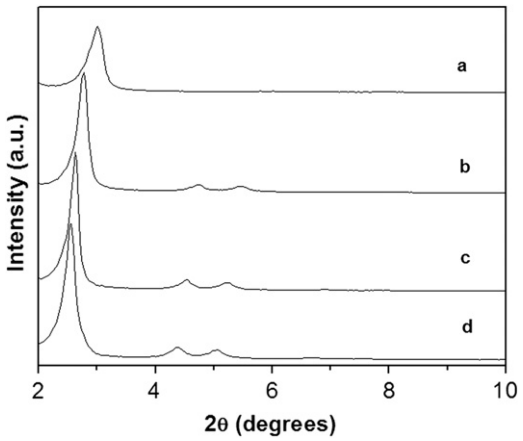

Fig. 5. XRD diffractograms of the MCM-41 (CTAB/TEOS molar ratio 0.16) after subjecting to thermal treatments: (a) 850 °C, (b) 750 °C, (c) 650 °C and (d) calcined sample at 540 °C.

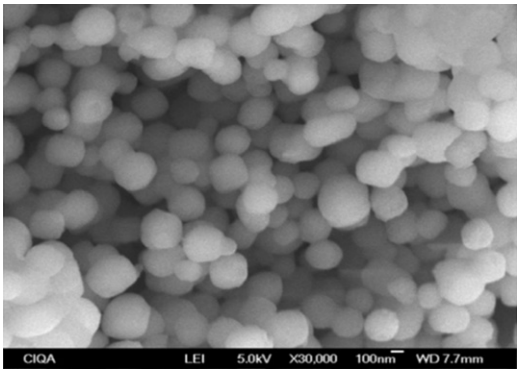

Fig. 6. Scanning electron micrographs of the MCM-41 (CTAB/TEOS molar ratio 0.16).

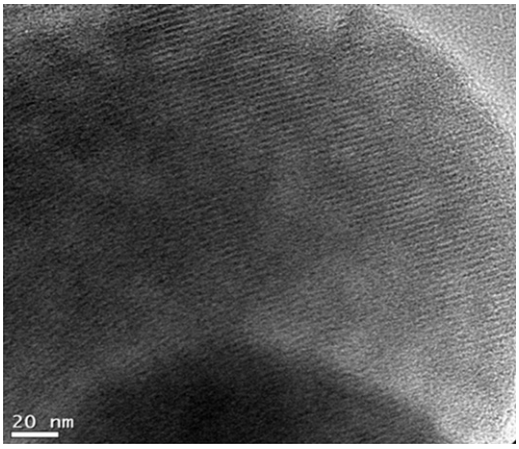

Fig. 7. Transmission electron micrographs of the MCM-41 (CTAB/TEOS molar ratio 0.16).

material was treated at different temperatures by following calcinations process. The heating rate was 2 °C/min and sample was kept during 6 h at the corresponding temperature. From Fig. 5, it can be seen that when MCM-41 was heat treated at 650 and 750 °C, no significance changes were observed in the XRD patterns. Only, a slight shift to higher 2θ values is observed in both cases (see Table 1). However, at temperature of 850 °C, the intensity of the peak (plane 100) not only decreased but also shifted to higher 2θ value and the peaks of the plane 200 and 210 disappeared under this condition. It means that at higher temperatures the pore structures collapses. This result is confirmed by the *d*-spacing and unit cell parameter values. The unit cell parameter of the MCM-41 calcined at 750 °C decreases about 7.5% with respect to the sample calcined at 540 °C (Table 1). Therefore, MCM-41 prepared at room temperature presented an acceptable thermal stability until 750 °C.

3.6. Morphology studies

The SEM micrograph of the mesoporous MCM-41 sieves is shown in Fig. 6. It can be observed clearly that the MCM-41 silica has spherical morphology. These spheres are uniform with sizes between 200 and 300 nm. Further evidence for a hexagonal mesostructure is provided by the TEM image showed in Fig. 7, which are representatives of mesoporous silica prepared with CTAB. The pore structure is regular over the whole particle. The morphology of a growing particle depends on the balance between the rate of polymerization of the negatively charged silicate micelles and the rate of mesostructure formation [24]. In case of a slow polymerizing silicate at high alcohol amount (e.g., H_2O/ethanol molar ratio of 10 used in this work), the growth is driven by global surface tension forces to minimize its surface free energy by forming the shape of a sphere, as observed by SEM and TEM images.

4. Conclusions

The preparation at room-temperature of MCM-41 silica using TEOS as silica source under the conditions used in this work was easy, fast and highly reproducible. The structural properties of MCM-41 can be tuned by varying reaction conditions such as synthesis time, molar ratios of CTAB/TEOS and H_2O/ethanol in the initial gel composition. According to nitrogen adsorption–desorption analyses, high ordered mesostructure and thermally stable MCM-41 silica can be obtained using CTAB/TEOS molar ratio of 0.16. These mesoporous MCM-41 molecular sieves presented a uniform size and spherical morphology. The resulting size and shape uniformity of these MCM-41 silica particles should prove potentially useful for applications in catalysis, or as a template to grow nanostructures or nanoparticles inside its pores.

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