第22卷 第4期　分　子　催　化　Vol. 22, No. 4
2008年8月　JOURNAL OF MOLECULAR CATALYSIS(CHINA)　Aug.　2008

Article ID: 1001-3555(2008)04-0315-05

Facile Synthesis of Stable Mesoporous Silica MCM-41 Via a Dual Templating of CMC and CTAB

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Abstract: Highly ordered mesoporous molecular sieve MCM-41 with hexagonal structures (p6mm) and enhanced stability has been successfully synthesized via a dual templating of carboxymethyl cellulose (CMC) and cetyltrimethylammonium bromide (CTAB). The TEM images show the samples were with high order hexagonal mesostructure. Moreover, the lattice distance contraction (Sample synthesized via a dual templating of CMC and CTAB) of as low as 3.1% is considerably less than the value (about 9.7%) obtained for MCM-41 materials synthesized by pure CTAB, indicating that mesoporous material synthesized via a dual templating of CMC and CTAB were with higher thermal stability. The interaction between the CMC and the intermediate silicate species Si-$(OH)_x$ may increase the concentration of Si-$(OH)_x$ around the cylindrical surfactant, which make the arrangement of Si-$(OH)_x$ is more closely.

Key words: mesoporous; template; CMC; MCM-41
CLC number: O 643.3　　**Document code**: A

Since the discovery of the M41S family of ordered mesoporous adsorbents by scientists at Mobil Oil[1,2], these materials have attracted considerable attention, due to its peculiar characteristics: large internal surface area and favorable uniformity but easily controlled size of the pore, the ordered mesoporous molecular sieves. Such a novel mesoporous solid might be desirable as shape/size selective adsorbents, hosts for quantum structures, catalysts, and catalyst supports. In most of the studies, cationic quaternary ammonium[3,4] and neutral surfactants[5,6] have been employed as templates, which direct the mesophase formation based on the electrostatic and hydrogen-bonding interactions, respectively. However, the range of application has been limited by the instability of the pore structure of the mesoporous materials.

Recently, glucosamine molecules were found to direct the formation of novel zinc phosphate phases[7]. Organic compounds have been used as dopants or pore fillers in silicate sol-gel materials for studying pore environment and molecule-matrix interactions[8]. The high affinity and appropriate hydrophilicity of D-fructose (and/or its derivatives) for the intermediate silicate species might act as a stabilizer for the cubic micelle over a wide range of reaction temperatures, so the high thermal stability mesoporous materials are obtained[9]. Herein, we report a successful synthesis of highly ordered hexagonal structure MCM-41 with enhanced stability has been successfully synthesized via a dual templating of carboxymethyl cellulose (CMC) and cetyltrimethylammonium bromide (CTAB).

1 Experimental

1.1 Synthesis of the mesostructured MCM-41

A typical gel was prepared by adding sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) to an aqueous solution containing cetyltrimethylammonium bromide (CTAB), CMC and H_2SO_4. After further stirring for about 4 hr at room

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Received date: 2008-05-29; Revised date: 2008-07-14

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temperature, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 110℃ in a Teflon-lined autoclave for 72 hr. The molar composition of the initial gel was $SiO_2/CTAB/H_2O$ = 1.0:0.12:60.0. For the samples A, B, C, the molar ratio of CTAB and CMC were 1:0.24, 1:0.32, 1:0.50, respectively. Sample D was the MCM-41 using pure CTAB template. The solid product was obtained followed by filtration, washed with deionized water, dried in vacuum atmosphere at 110℃ for 24 hr and calcined in air at 550℃ for 6 hr to remove the CTAB and CMC.

1.2 Characterization of the mesostructured silica

XRD measurements were performed on a Rigaku D/max-IIIA diffractometer using Co K(radiation at 30 kV and 15 mA. TEM images were obtained by FEI Tecnai F20 electron microscope. Nitrogen sorption isotherms of samples were obtained by a Micromeritics TriStar 3000 analyzer at 77 K. The Brumauer-Emmett-Teller (BET) surface area was calculated using experimental points at a relative pressure of P/P_o = 0.05-0.25. The total pore volume was calculated by the N_2 amount adsorbed at the highest P/P_o ($P/P_o \approx 0.99$). The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) were carried out in a WCT-2 system in a static air atmosphere at a heating rate of 10℃ per minute.

2 Results and discussion

Transmission electron microscope (TEM) images of A (a, b); B (c, d); C (e, f); D (g, h) were shown in Fig. 1. The TEM images viewed from the [0 0 1] (a, c, e, g) and [1 1 0] (b, d, f, h) directions show the samples A, B, C and D were with high order hexagonal mesostructure. These results indicated the highly ordered messtructured MCM-41 was synthesized via a dual templating of CMC and CTAB even though the molar ratio of CTAB and CMC increased from 1:0.24 to 1:0.50.

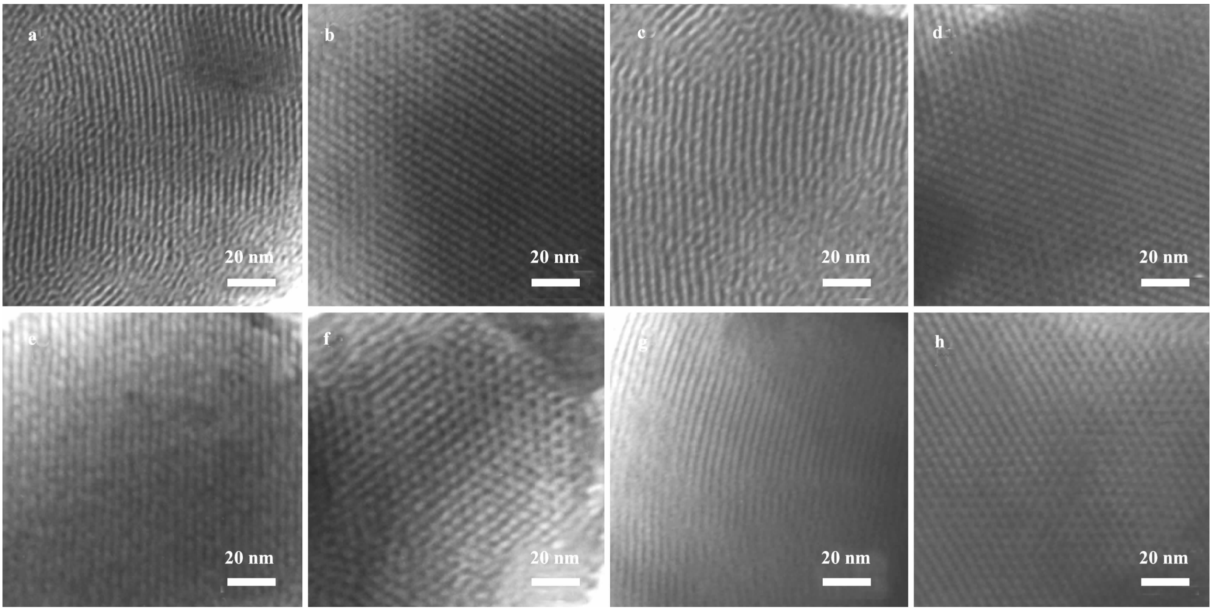

Fig. 1 TEM images of MCM-41 samples A (a, b); B (c, d); C (e, f); D (g, h) viewed from the [0 0 1] (a, c, e, g) and [1 1 0] (b, d, f, h) directions

Low angle X-ray diffraction pattern (XRD) patterns of dried samples and calcined samples were shown in Fig.2 and Fig.3. A high-intensity diffraction peak of (100) and three additional well-resolved diffraction peaks of (110), (200), (210) were observed, which can be assigned to a two-dimensional hexagonal mesostructure (space group p6mm). This suggests a long range ordering of the porous structure and well-formed hexagonal pore arrays can be prepared via a dual templating of CMC and CTAB. Upon calcinations at 550℃ for 6 h, the intensity of the XRD peaks increased, and the resolution of the higher order peaks is improved (Fig. 2b and Fig. 3b), as compared to the as-synthesized sample. These results reflect that the degree of ordering is dramatically improved by the removal of the surfactant and CMC. Meanwhile, as the amount of CMC increases (sample A, B and C), the (100) diffraction peak widens and the (210) diffraction peak disappears in sample B and C, which indicates that the mesoporous structure becomes slightly nonsymmetrical and poorly ordered. This is consistent with the TEM results. Moreover, the lattice distance contraction (Sample A, B and C) of as low as 3.1% is considerably less than the value (about 9.7%) obtained for MCM-41 materials synthesized by pure CTAB (Table 1), indicating that mesoporous material synthesized via a dual templating of CMC and CTAB were with higher thermal stability.

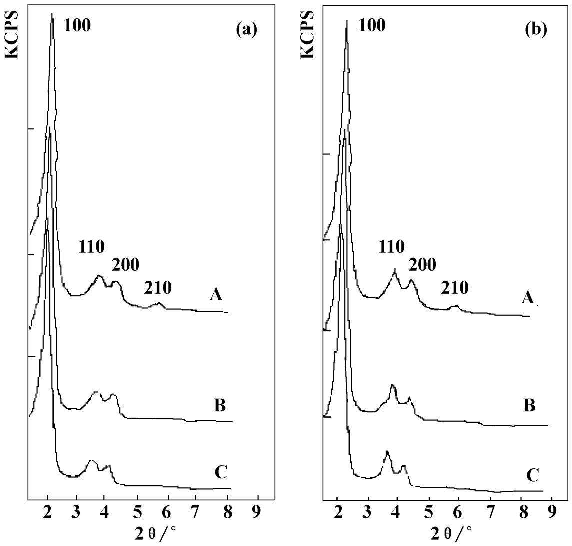

Fig. 2 Low angle XRD patterns of (a) dried samples (A, B and C); (b) calcined samples(A, B and C)

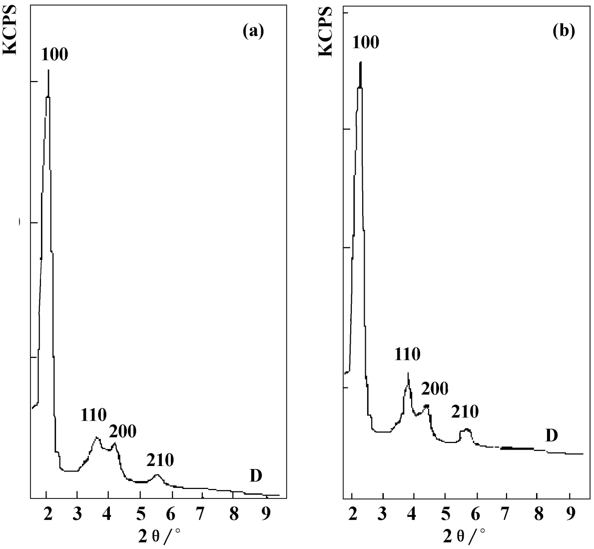

Fig. 3 Low angle XRD patterns of (a) dried sample D; (b) calcined samples D

Nitrogen sorption isotherms of calcined A, B, C and D samples in Figure 4 show a type-IV curve with a well-defined capillary condensation step, thus further confirming the existence of uniform channel-like mesopores [10]. The narrow and sharp pore-size distribution curves calculated by the Barrett-Joyner-Halenda (BJH) model (inset of Fig. 4) suggest that the mesopores have very uniform sizes. Their structural parameters are also summarized in Table 1. With an increasing of molar ratio of CTAB and CMC from 1∶0.24 to 1∶0.50, the Brumauer-Emmett-Teller (BET) surface area decreases from 1031.2 to 992.8 $m^2\ g^{-1}$, the pore volume decreases from 0.99 to 0.90 $cm^3\ g^{-1}$, respectively. Interestingly, the wall thickness of A, B and C (~1.9 nm) synthesized via a dual templating of CMC and CTAB is thicker than that of D (~1.4 nm).

Table 1 Physical properties of products calcined at 823 K

Sample	d/nm				a_o /nm	S(BET) $m^2 \cdot g^{-1}$	V(BJH) $cm^3 \cdot g^{-1}$	D(BJH) /nm	Wall thickness /nm
	d_{100}	d_{110}	d_{200}	d_{210}					
A	4.09	2.41	2.08	1.59	4.72(4.87)	1031.2	0.99	2.74	1.98
B	4.04	2.36	2.05	1.56	4.66(4.81)	1022.4	0.94	2.76	1.90
C	4.03	2.34	2.03	1.54	4.65(4.81)	992.8	0.90	2.77	1.88
D	3.79	2.41	2.07	1.60	4.38(4.85)	1044.4	1.02	2.70	1.38

a_o: the lattice parameter, from the XRD data using the formula, $a_o = 2d_{100}/\sqrt{3}$, the data in parentheses is a_o before calcination; S(BET): the BET surface area; V(BJH): BJH adsorption cumulative pore volume; D(BJH): the maxima in the BJH pore size distribution; Wall thinckness = a_o - D(BJH).

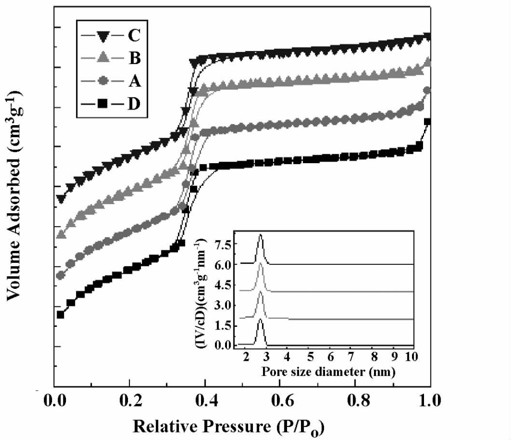

Fig. 4 N_2 adsorption/desorption isotherms and pore size distribution from desorption branch of samples A, B, C and D obtained by a Micromeritics TriStar 3000 analyzer at 77 K. Isotherms of A, B and C have been offset by 100, 200 and 300 cm^3g^{-1} along the vertical axis for clarity, respectively.

The TG-DTA profiles of as-synthesized sample B and D after washing are shown in Fig. 5 (a) and Fig. 5 (b). It was previously reported that thermogravimetric analysis of MCM-41 materials show three or more weight losses [11,12]. While, the high-resolution TGA curves for the as-synthesized samples B and D after washing show three weight losses. The weight loss steps are located in the following temperature ranges: 1) from 25 to 230 ℃ (thermodesorption of physically adsorbed water); 2) from 230 to 310 ℃ (surfactant CTAB decomposition), and 3) from 310 to 600 ℃ (residual surfactant decomposition and CMC decomposition). There is no weight loss upon heating from 600 to 1 000 ℃, which indicated the complete removal of CMC and surfactant after calcinations in air at 600 ℃. Meanwhile, this confirms that the synthesized MCM-41 by the CMC modification is thermally stable.

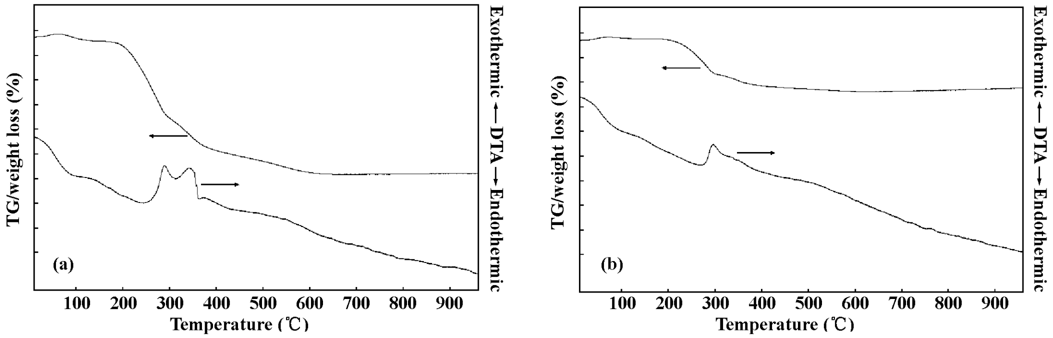

Fig. 5 TG-DTA profiles of (a) as synthesized sample B; (b) as synthesized sample D

The non-surfactant templates, which have been investigated so far, include glucose, maltose, cyclodextrins, tartaric acid derivatives and agarose[13,14]. They are generally the compounds having high affinity for intermediate silicates, appropriate hydrophilicity and solubility, and low volatility. Furthermore, it's reported that the templates should be present in forms of aggregates or assembly of the aggregates, whose interactions with the silicate species through hydrogen bonding play an important role in directing the mesophase formation prior to and/or during the gelation[15]. In the present synthesis route, the high affinity and appropriate hydrophilicity of CMC for the intermediate silicate species might act as a stabilizer for the MCM-41 structure.

The hydrogen bonding between the CMC (see Fig. 6), and the intermediate silicate species, Si-$(OH)_x$, brings the two components together and forms a homogeneous sol. Meanwhile, the cylindrical surfactant and the aggregates of silicate and CMC are simultaneously formed, and further silicate condensation mediates the ordering of the cylindrical surfactant into the hexagonal arrangement. The interaction between the CMC and the intermediate silicate species Si-$(OH)_x$ may increase the concentration of Si-$(OH)_x$ around the cylindrical surfactant, which make the arrangement of

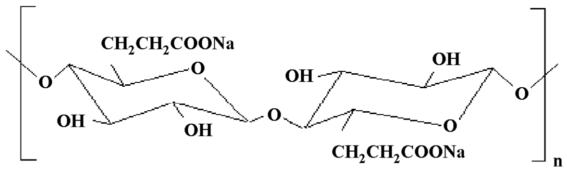

Fig. 6 the molecular structure of CMC

$Si\text{-}(OH)_x$ is more closely. And it make the lattice distance contraction (Sample A, B and C) of as low as 3.1% is considerably less than the value (about 9.7%) obtained for MCM-41 materials synthesized by pure CTAB. The results indicated that the MCM-41 with hexagonal structures and enhanced stability has been successfully synthesized via a dual templating of CMC and CTAB.

3 Conclusion

In conclusion, we have presented a novel synthesis route for the preparation of highly ordered mesoporous molecular sieve MCM-41 with hexagonal structures and enhanced stability. This strategy offers the opportunity to prepare MCM-41 with enhanced stability. Thus, these improvements in the MCM-41 synthesis open new opportunities to facilitate the more widespread use of this unique mesophase in materials research.

References

[1] a. Kresge C T, Leonowicz M E, Roth W J, *et al. Nature* [J], 1992, **359**: 710
b. Liu Xin-mei(刘欣梅), Yan Zi-feng(阎子峰), G. Q. Lu. *J. Mol. Catal.* (China)(分子催化)[J], 2006, **20**(1): 84 ~ 94
c. Jiang Jie(姜　杰), Song Chun-min(宋春敏), Xu Ben-jing(徐本静), *et al. J. Mol. Catal.* (China)(分子催化)[J], 2007, **21**(6): 605 ~ 611

[2] Beck J S, VartUli J C, Roth W J, *et al. J. Am. Chem. Soc*[J], 1992, **114**: 10834

[3] Tanev P T, Pinnavaia T J. *Science*[J], 1995, **267**: 865

[4] Tanev P T, Liang Y, Pinnavaia T J. *J. Am. Chem. Soc.* [J], 1997, **119**: 8616

[5] Templin M, Franck A, Chesne A D, *et al. Science* [J], 1997, **278**: 1795

[6] Dongyuan Zhao, Jianglin Feng, Qisheng Huo, *et al. Science*[J], 1998, **279**: 548

[7] Nenoff T M, Thoma S G, Provencio P, *et al. Chem. Mater.* [J], 1998, **10**: 3077

[8] a. Dunn B, Zink J I. *Chem. Mater.* [J], 1997, **9**: 2280
b. Song Chun-min(宋春敏), Jiang Jie(姜　杰), Qiao Ke(乔　柯), *et al. J. Mol. Catal.* (China)(分子催化)[J], 2006, **20**(4): 294 ~ 299

[9] Hsien-Ming Kao, Chun-Chiang Ting, Anthony S. T. Chiang, *et al. Chem. Commun.* [J] 2005, **8**: 1058 ~ 1060

[10] On D T, Zaidi S M J, Kaliaguine S. *Micropor. Mesopor. Mater.* [J], 1998, **22**: 211 ~ 224

[11] Mokya R, Jones W. *Chem. Commun.* [J], 1996, **8**: 981

[12] Araujol A S, Jaroniec M. *Thermochimica Acta* [J], 2000, **363**: 175 ~ 180

[13] Wei Y, Jin D L, Ding T Z, *et al. Adv. Mater.* [J], 1998, **3**: 313

[14] Wei Y, Jin D L, Ding, T Z. *J. Phys. Chem.* [J], 1997, **101**: 3318

[15] Yen Wei, Jigeng Xu, Hua Dong, *et al. Chem. Mater.* [J]. 1999, **11**: 2023 ~ 2029

CMC 和 CTAB 双模板法合成具有稳定结构的 MCM-41 中孔分子筛

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摘　要：以羧甲基纤维素和十六烷基三甲基溴化铵为双模板，制备出了具有更高稳定性并且具有高度有序二维六方结构的 MCM-41 介孔分子筛．透射电镜和 X 射线衍射结果表明，以双模板制备的 MCM-41 介孔分子筛具有高度有序的二维六方(p6mm)孔道结构．此外，以双模板制备的 MCM-41 介孔分子筛焙烧前后的 X 射线衍射结果表明，在焙烧过程中其晶胞收缩比例为 3.1%．与以纯表面活性剂为模版制备的 MCM-41 介孔分子筛(晶胞收缩比例为 9.7%)相比，双模板制备的 MCM-41 介孔分子筛具有更高的稳定性能．MCM-41 介孔分子筛稳定性能的提高可能是由于在硅物种、表面活性剂以及羧甲基纤维素在自组装过程中，羧甲基纤维素表面丰富的羟基与硅物种 $Si\text{-}(OH)_x$ 的相互作用促进了 $Si\text{-}(OH)_x$ 的缩聚．

关键词：中孔；模版法；羧甲基纤维素；MCM-41