pH 对两步法非离子模板合成 MSU-X 类硅基介孔结构的影响

金政伟^{1,*} 刘长玲² 梁 浩³

(¹ 天津科技大学包装与印刷工程学院, 天津 300222; ² 吉林化工学院化工与材料工程学院, 吉林 吉林 132022;
³ 北京化工大学制药工程系, 北京 100029)

摘要: 采用两步法以非离子型表面活性剂 Tween 20 为模板剂合成硅基介孔材料, 研究了 pH 对介孔材料结构的影响. 结果表明, 没有氟离子存在且模板剂浓度较低(约为 2%(w))的条件下, 在弱酸性环境中(pH=3.32–4.26)可以制备有序的 MSU-X 类硅基介孔材料, 本研究中的简单合成体系有助于查明 MSU-X 合成机理. 对所得介孔材料测试表明, 在同样的合成体系中, 随着体系 pH 的变化, 所得硅基介孔材料的形貌和孔壁结构都发生了变化.

关键词: 两步法; MSU-X; 硅基介孔; Tween 20
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Effects of pH on the Structure of Non-Ionically Templated MSU-X Mesoporous Silica *via* a Two-Step Synthesis

JIN Zheng-Wei^{1,*} LIU Chang-Ling² LIANG Hao³

(¹*School of Packaging and Printing Engineering, Tianjin University of Science and Technology, Tianjin 300222, P. R. China;*
²*College of Chemical and Materials Engineering, Jilin Institute of Chemical Technology, Jilin 132022, Jilin Province, P. R. China;*
³*Department of Pharmaceutical Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China)*

Abstract: Highly ordered MSU-X type mesoporous silica was synthesized by using ethoxylated derivatives of fatty esters of sorbitan (Tween 20) as template *via* a two-step pathway under mildly acidic conditions (pH=3.32–4.26) without the addition of fluoride. The template concentration (ca 2% (w)) is much lower than for conventional synthetic routes and the synthetic medium is much simpler than that used for other two-step pathways. The obtained materials have high specific surface areas, large pore volumes, and thick pore walls. Transformations of exterior morphologies and inner structure of mesoporous silica were found by varying the pH and keeping all other conditions constant.

Key Words: Two-step synthesis; MSU-X; Mesoporous silica; Tween 20

The first synthesis of M41S-type mesoporous silica was reported in 1992 by researchers in the Mobil Oil Corporation who discovered the remarkable features of this novel type of material and opened up a whole new field of research^[1]. Since then, such highly ordered mesoporous silica materials have been intensively studied with regard to synthetic methods, mesostructure, surface modification, and applications as functional materials and in catalysis.

Presently, besides M41S molecular sieves, a variety of highly ordered mesoporous silica materials, such as SBA^[2–6], FSM^[7], FDU^[8], JLU^[9,10], KIT^[11], and MSU^[12,13], have been successfully

synthesized with anionic, neutral, and nonionic surfactants through various assembly routes. One of the most studied systems is MSU-X type mesoporous silica, synthesized by condensation of alkoxysilanes such as tetraethoxysilane (TEOS) in the presence of commercially available anionic, neutral, and poly (ethylene oxide) nonionic as templates. These materials have unique 2-dimensional (2D) or 3-dimensional (3D) wormhole-like mesostructure and are generally more active as heterogeneous catalysts^[12–15]. Although considerable efforts have been made to investigate the mechanism of MSU-X type silica, and some possible mechanisms have been proposed^[16–20], the detail mecha-

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*Corresponding author. Email: jzhengw@tust.edu.cn; Tel: +8622-60271980.

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nisms of the MSU-X type are much less clear than those for the synthesis of the MCM-41 type materials under basic conditions. Moreover, to maximize the utility of mesoporous silica materials, especially for separations and optoelectronic devices, several synthesis strategies have also been used to control the morphology of MSU-X mesoporous silica^[21]. Usually, when poly (ethylene oxide) (PEO)-based surfactants were used to synthesize MSU-X type mesoporous silica in near neutral conditions without addition of fluoride, the surfactant concentrations in aqueous solution were much high (25%–50%) (*w*) to compensate the weak interaction between template and silica precursor^[22–24]. Apparently, such synthetic methods with high concentration of surfactant are directly related to the final cost of product. With the aid of fluoride, Prouzet *et al.*^[25] reported a two-step synthesis of ordered MSU-X mesoporous silica by using nonionic PEO-based surfactants (ca 3.3% (*w*)) in the pH range of 2–4.

Cui *et al.*^[4–6] have successfully synthesized the well-ordered SBA-15 type and SBA-16 type silica materials under mildly acidic conditions by templating Pluronic polymers *via* a two-step synthetic method separating the hydrolysis and the condensation steps of silica source in controlled pH range. In this paper, we also report a two-step synthesis of mesoporous silica materials based on the template of ethoxylated derivatives of fatty esters of sorbitan (Tween 20) under mildly acidic medium.

1 Experimental

Tween 20 (analytical reagent) was commercially obtained from Aldrich Company. Tetraethoxysilane (analytical reagent) and hydrochloric acid (analytical reagent) were supplied by Beijing Chemical Reagents Company. All of the chemicals were used without further purification. A typical two-step synthetic method is described as follows. In the first step, the mixture of 1.05 g Tween 20 was dissolved in 40.00 g deionized water with stirring in a beaker at 22 °C to form a transparent template solution. In another beaker, the mixture of 5.0 mL TEOS and 5.00–10.00 g HCl aqueous solution with controlled acidity ($\text{pH} < 3$) was stirred at 35 °C until TEOS hydrolyzed thoroughly. In the second step, the solutions of above two beakers were mixed with stirring for 48 h. Subsequently, the mixture was aged at 100 °C for another 24 h, and the final pH value was recorded. The precipitated white product was washed with deionized water and dried in air for a week at room temperature, and then calcined at 500 °C for 6 h. The pH values of experimental solution at different stages were carefully measured by Sartorius PB-10 acidity instrument, and the results are shown in Table 1.

Powder X-ray diffraction (XRD) was performed with a Japan Rigaku, D/max-rC diffractometer (40 kV, 50 mA) with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154$ nm). Transmission electron microscopy (TEM) images were obtained on a Japan Hitachi H-800 transmission electron microscope with an acceleration voltage 200 kV. Morphologies of the samples were observed on Japan Hitachi S-4700 scanning electron microscopy (SEM). ^{29}Si MAS (magic-angle-spinning) NMR spectra were measured at 79.4 MHz with

Table 1 pH values of experimental solutions at different reaction stages

Sample	pH at the first step		pH at the second step		
	Template solution	Hydrolyzed TEOS solution	Initial	Intermediate	Final
1	7.03	2.21	2.78	2.98	3.11
2	7.03	2.71	3.12	3.21	3.32
3	7.03	3.48	3.94	4.08	4.26
4	7.03	3.68	4.09	4.35	4.89

a Germany Bruker MSL-400 spectrometer. Nitrogen adsorption and desorption isotherms were measured at -196 °C using a Nova 4200e surface analyzer (Quantachrome Instruments, USA). The data of diameter distribution were calculated from the adsorption branch of the isotherm using Barrett-Joyner-Halenda (BJH) method. The specific surface area were calculated by Brunauer-Emmett-Teller (BET) mode. The pore wall thickness (T_{wall}) was calculated from the formula $T_{\text{wall}} = a_0 - D_{\text{pore}}$, where D_{pore} and a_0 were the pore diameter and lattice parameter, respectively.

2 Results and discussion

Fig.1 shows the powder XRD patterns of the as-synthesized and calcined samples synthesized through the two-step pathway at various pH values. For the as-synthesized sample synthesized at pH 3.11, no peaks can be found. While for the as-synthesized samples prepared at pH 3.32–4.26 a single diffraction peak is exhibited at low 2θ corresponding to a pore-pore correlation distance of 8.40 to 8.82 nm. These are typical patterns for worm-like mesostructures and are similar to those of MSU-X type mesoporous silica synthesized with PEO-based surfactant as template^[25]. Calcination at 500 °C caused a structural shrinkage, as indicated by the above peaks shifting to higher 2θ with enhancing intensity. For the sample synthesized in the least acidic medium with pH 4.89, a wild diffraction peak which is observed at low 2θ angle disappears after calcination, indicating a disordered

Fig.1 Powder XRD patterns of samples synthesized at various pH values through the two-step pathway

(A) as-synthesized samples, (B) calcined samples

Fig.2 TEM images of the calcined samples synthesized at various pH values

pH: (a) 3.32; (b) 4.26; (c) 4.89

mesostructure. The shrinkage ratios of the interplane distances upon the calcination were 21.7% and 26.4% for the samples at pH 3.32 and 4.26, respectively. Such large shrinkages of the structural spacing may be attributed to the relative low condensation degree of Si—OH species during the synthesis process, which can be further confirmed by ^{29}Si MAS NMR spectra.

TEM images of the calcined samples synthesized at various pH values are shown in Fig.2. From Fig.2(a, b), one can clearly observe a highly ordered worm-like structure for the samples prepared at pH 3.32 and 4.26, respectively. However, the sample prepared at pH 4.89 displays the mixture of ordered and disordered mesopores as shown in Fig.2(c), indicating a disordered mesostructure. These TEM images are in agreement with the ordered worm-like mesoporous structure deduced from the corresponding XRD results.

Morphologies of the samples synthesized at various pH values were studied by SEM as shown in Fig.3. The sample synthesized at pH 3.32 exhibits sphere morphologies having relatively uniform sizes of ca 0.6 μm (Fig.3(a)). However, these macro-sized spheres aggregate together seriously and form randomly shaped agglomerations with increasing the pH value. The above phenomena are in accordance with our former results which can be explained by the rate of the phase separation^[426]. Comparing with the higher pH value, a lower one (pH=3.32) results in a lower condensation rate, and the rate of phase separation will be slower. In this case, the surface free energy will have considerable influence on the morphology; the morphology with large curvature (e.g., spheres) is generated in order to minimize the surface energy. The condensation rate increases with increasing the pH

value, and then the formation of the randomly shaped agglomerations will occur from a competition between the surface free energy and the total free energy. Finally, the macro-sized spheres will form through a further condensation between the preformed silica particles resulting in one large particle, still minimizing its surface free energy. The conversion of the morphology can be imputed to the formation of a greater amount of crystal silica with increasing the condensation rate resulted by higher pH value.

It is easy to synthesize the ordered MSU-X type mesoporous materials under various conditions with the aid of fluoride. In this study, the well-ordered MSU-X type mesoporous silica was synthesized *via* the two-step pathway by templating Tween 20 (low concentration of 2.0% (*w*)) without addition of fluoride. When the nonionic templates are used to synthesize mesoporous materials in acidic medium, the assembly is expected to proceed through an intermediate of $(\text{S}^0\text{H}^+)(\text{X}^-\text{I}^+)$ double-layer hydrogen bonding interaction, where S^0 is the nonionic surfactant, X^- is the halide anion, and I^+ is silicate precursor cation. In the first step at $\text{pH} < 3$, the rate of hydrolysis of the TEOS is faster than the rate of condensation, so that the hydrolysis reaction is dominant in this step. In the second step, mixing the hydrolyzed silica precursor solution with the surfactant one reduces the concentration of hydrogen and results in a rise in pH. This leads to an increase in the rate of condensation of inorganic precursor and the alcoholysis and oxolation reactions become dominant. However, the condensation rate and degree under these conditions are much lower than those in the presence of F^- , which presents enough time for assembly and adjusting of interaction between

Fig.3 SEM images of the calcined samples synthesized at various pH values

pH: (a) 3.32; (b) 4.26; (c) 4.89

template micelle and the silica precursor. With increasing the

the

Fig.4 ^{29}Si MAS NMR spectra of the as-synthesized samples synthesized at various pH values
pH: (a) 3.32; (b) 4.26; (c) 4.89

Fig.5 ^{29}Si MAS NMR spectra of the calcined samples synthesized at various pH values
pH: (a) 3.32; (b) 4.26; (c) 4.89

Table 2 Physical properties of the samples synthesized at various pH values

Condition	pH (final solution)	d/nm	$V_{\text{pore}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$D_{\text{pore}}/\text{nm}$	$T_{\text{wall}}/\text{nm}$
as-synthesized	3.32	8.40	0.71	762	3.21	3.37
calcined		6.58				
as-synthesized	4.26	8.82	0.65	659	3.85	2.64
calcined		6.49				
as-synthesized	4.89	6.30	—	—	—	—
calcined		—				

d : interplane distance, V_{pore} : total pore volume, S_{BET} : specific surface, D_{pore} : mean pore diameter, T_{wall} : pore wall thickness

pH to 3.32–4.26, this interaction turns weak and the three-layered hybrid micelles are formed^[18], in which the worm-like mesostructure is obtained for synthesis of the MSU-X type mesoporous silica. In this study, the weak interaction between surfactant template and inorganic species (OI) is dominant under suited pH values (pH=3.32–4.26), which makes it possible for inorganic silica species assemble around the template and then solidify to form an ordered matrix. But the slight change of pH in the synthetic solution results in the un-matching of this action and the interaction between surfactants (OO) and inorganic species (II) is dominant, which leads to the fast condensation of inorganic species. As a result, a disordered mesostructure is obtained and then solidify to form the disordered mesoporous silica.

The ^{29}Si MAS NMR spectra of the as-synthesized and calcined samples are also collected to confirm the condensation degree of TEOS, as shown in Fig.4 and Fig.5. For the ^{29}Si MAS NMR spectra (Fig.4) of as-synthesized samples at pH=3.32–4.89 exhibit three resonances at chemical shifts around δ -92, -100, and -110, which can be assigned to $\text{Si}(\text{—O—Si—})_2(\text{—OH})_2$ (Q^2), $\text{Si}(\text{—O—Si—})_3(\text{—OH})$ (Q^3), and $\text{Si}(\text{—O—Si—})_4$ (Q^4), respectively. Calcination at 500 °C causes the further condensation degree of Si—OH species, which leads to the varieties of the amount and the intensity of these resonances for all the samples (Fig.5). It can be observed that the spectrum of the sample synthesized at pH 3.32 has a strong Q^4 resonance at chemical shifts (Fig.5a). The samples prepared at pH 4.26 and 4.89 have two strong resonances which can be assigned to be Q^3 and Q^4 (Fig.5

(b, c)). Moreover, the sample prepared at pH 4.89 shows a clear Q^2 signal around δ -92, suggesting lower levels of silica cross-linking or condensation degree of Si—OH species. It is known that the Q^4 structural units indicate SiO_4 tetrahedrons in the inner of the mesoporous silica walls, while Q^3 and Q^2 structural units represent the wall surfaces associated with silanol groups. The signals for these resonances are the effects of pH on the condensation behaviors of TEOS.

The corresponding physical properties obtained from analysis of the nitrogen adsorption-desorption isotherms are listed in Table 2, from which one can see that the samples synthesized in this study also exhibit high BET specific surfaces, large pore volumes, and thick pore walls, which may generally favor the incorporation of catalytically active heteroatoms in silica frameworks and the functionalization of organic group.

3 Conclusions

The highly ordered MSU-X type mesoporous silica were synthesized with Tween 20 as template *via* the two-step pathway under mildly acidic conditions (pH=3.32–4.26) without addition of fluoride. The template concentration is much lower than those conventional synthetic routes, and the synthetic medium is much simpler than other two-step pathways. The obtained materials have high specific surface areas, large pore volumes, and thick pore walls. The transformations of the morphologies from sphere to irregular shapes and the effects of pH value on the structure of pore wall were found with a variation of controlling pH whilst keeping all other conditions constant. These discoveries based on the two-step synthesis provide new insights into the

mechanism of mesostructure formation in mesoporous silica for their simple synthesis reactants.

References

- 1 Kresge, C. T.; Leoniwics, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, **1992**, **359**: 710
- 2 Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science*, **1998**, **279**: 548
- 3 Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.*, **1998**, **120**: 6024
- 4 Jin, Z.; Wang, X.; Cui, X. *Micropor. Mesopor. Mater.*, **2008**, **180**: 183
- 5 Jin, Z.; Wang, X.; Cui, X. *J. Non-Cryst. Solids*, **2007**, **353**: 2507
- 6 Cui, X.; Zin, W. C.; Cho, W. J.; Ha, C. S. *Mater. Lett.*, **2005**, **59**: 2257
- 7 Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc. Chem. Commun.*, **1993**: 680
- 8 Fan, J.; Yu, C.; Gao, F.; Lei, J.; Tian, B.; Wang, L.; Luo, Q.; Tu, B.; Zhou, W.; Zhao, D. *Angew. Chem. Int. Ed.*, **2003**, **42**: 3146
- 9 Yang, X.; Zhang, S.; Qiu, Z.; Tian, G.; Feng, Y.; Xiao, F. *J. Phys. Chem. B*, **2004**, **108**: 4696
- 10 Di, Y.; Meng, X.; Wang, L.; Li, S.; Xiao, F. *Langmuir*, **2006**, **22**: 3068
- 11 Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.*, **1996**, **100**: 17718
- 12 Boissiere, C.; Larbot, A.; Prouzet, E. *Chem. Mater.*, **2000**, **12**: 1937
- 13 Liu, J.; Liao, S.; Jiang, G.; Zhang, X.; Petrik, L. *Micropor. Mesopor. Mater.*, **2006**, **95**: 306
- 14 Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science*, **1995**, **269**: 1242
- 15 Prouzet, E.; Cot, F.; Boissiere, C.; Kooyman, P. J.; Larbot, A. *J. Mater. Chem.*, **2002**, **12**: 1553
- 16 Casagrande, M.; Moretti, E.; Storaro, L.; Lenarda, M.; Gersich, J.; Stievano, L.; Wagner, E. F. *Micropor. Mesopor. Mater.*, **2006**, **91**: 261
- 17 Herrier, G.; Blin, J. L.; Su, B. L. *Langmuir*, **2001**, **17**: 4422
- 18 Boissiere, C.; Larbot, A.; Bourgaux, C.; Prouzet, E.; Bunton, C. A. *Chem. Mater.*, **2001**, **13**: 3580
- 19 Kim, S. S.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Commun.*, **2000**: 835
- 20 Jin, Z. W.; Wang, X. D. *Acta Phys. -Chim. Sin.*, **2008**, **24**: 1519 [金政伟, 汪晓东. 物理化学学报, **2008**, **24**: 1519]
- 21 Biswas, K.; Ray, J. C.; Choi, J. K.; Ahn, W. S. *J. Non-Cryst. Solids*, **2008**, **354**: 1
- 22 Blin, J. L.; Leonard, A.; Su, B. L. *J. Phys. Chem. B*, **2001**, **105**: 6070
- 23 Prouzet, E.; Pinnavaia, T. J. *Angew. Chem. Int. Ed.*, **1997**, **36**: 516
- 24 Zhang, W.; Glomski, B.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Commun.*, **1999**: 1803
- 25 Boissiere, C.; Larbot, A.; van der Lee, A.; Kooyman, P. J.; Prouzet, E. *Chem. Mater.*, **2000**, **12**: 2902
- 26 Yu, C.; Fan, J.; Tian, B.; Zhao, D. *Chem. Mater.*, **2004**, **16**: 889