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ScienceDirect
Microporous and Mesoporous Materials 112 (2008) 225–234
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

The search of promoters for silica condensation and rational synthesis of hydrothermally stable and well ordered mesoporous silica materials with high degree of silica condensation at conventional temperature

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Received 2 August 2007; received in revised form 23 September 2007; accepted 24 September 2007
Available online 1 October 2007

Abstract

Silica samples condensed at acidic, neutral and alkaline media in the presence of various inorganic anions have been carefully investigated by ^{29}Si MAS NMR spectroscopy. The results show that SO_4^{2-} and CO_3^{2-} could effectively improve the degree of silica condensation under neutral and alkaline media. Accordingly, for example, it is designable to synthesize hydrothermally stable and well ordered hexagonal mesoporous SBA-15 with very high degree of silica condensation in the presence of sulfate and carbonate species under neutral condition. As we expected, hexagonal mesoporous silica materials in the presence of sulfate (SBA-15-S) and carbonate species (SBA-15-U) show high degree of silica condensation, giving Q^4/Q^3 ratios at 6.3 and 4.3, which are much higher than that of conventional SBA-15 ($Q^4/(Q^3+Q^2)$ ratio at 1.8) synthesized in the absence of sulfate and carbonate species. Very interestingly, hexagonal mesoporous SBA-15-S and SBA-15-U shows very high hydrothermal stability, compared with SBA-15. For example, after being treated in 100% steaming at 780 °C for 3 h, SBA-15-S still remains its mesostructure. In constrast, SBA-15 loses most of the mesostructure. Furthermore, heteroatoms-substituted mesoporous materials such as aluminosilicate (Al-SBA-15-U) could also be synthesized in the presence of urea under neutral condition, and Al-SBA-15-U exhibits extraordinary hydrothermal stability. The unique and novel route for syntheses of hydrothermally stable and well ordered mesoporous silica and aluminosilicate materials in the presence of sulfate and carbonate species would be very important for potential application of mesoporous silica (SBA-15) and aluminosilicate materials (Al-SBA-15) as industrially supports and acidic catalysts.

Keywords: Silica condensation; Ordered mesoporous materials; Anionic effect; Hydrothermal stability; ^{29}Si MAS NMR spectroscopy

1. Introduction

Since a discovery of mesoporous materials [1,2], there is a great interest on the improvement of hydrothermal stability of mesoporous silica materials because of the requirement of potential applications [3–60]. Recently, a number of successful routes for synthesis of mesoporous silica-based materials with good hydrothermal stability have been reported, such as thickening mesoporous walls [3], enhancing the degree of silica condensation [4–17], assembling from preformed zeolite nanoclusters or seeds solution [18–31], grafting heteroatoms from post-treatments [32–40], synthesizing under supercritical conditions [41,42], removing surface Si–OH groups from silylation [43–49], and synthesizing by microwave-assistance [50].

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1387-1811/$ - see front matter © 2007 Published by Elsevier Inc.
doi:10.1016/j.micromeso.2007.09.033

As silica-based materials, a critical factor in increasing hydrothermal stability is to have more silica condensation in the pore walls. Recently, it is worth noting that there are couples of successful approaches to improve the degree of silica condensation in mesoporous walls [4–17]. For examples, MCM-41 materials with higher silica condensation are synthesized from repeated pH-adjusting [4,5], addition of inorganic salts [5–7], secondary crystallization [8,9], addition of small organic amines [10], and organic ammonium ions [11]. Notably, although the degree of silica condensation in these mesoporous walls is remarkably increased, there are still many terminal OH groups in the samples, which limit the improvement of hydrothermal stability for ordered mesoporous silica-based materials [12]. Interestingly, MSU-G materials with very high silica condensation has been achieved using neutral gemini surfactants as the templates, but gemini surfactants are difficult to template well ordered mesostructures such as hexagonal or cubic symmetries [13]. More recently, a series of hydrothermally stable and well ordered mesoporous silica-based materials with very high silica condensation (JLU-20, JLU-21, JLU-30, JLU-20-S) have been prepared from high-temperature synthesis (150–240 °C) [14–17,30], but the use of unusual surfactants such as environmentally unfriendly fluorocarbon surfactant (FC-4) and the complexity of high-temperature synthesis severely hinder wide application of this synthetic route. Therefore, a novel and facile approach for synthesizing well ordered mesoporous materials with very high silica condensation at conventional temperature such as 100 °C from usual surfactants such as triblock copolymer of P123 is still challenging.

In last decade, Kumar et al. have reported that the rate of zeolite crystallization could be accelerated by the addition of various inorganic anions such as SO_4^{2-}, CO_3^{2-}, NO_3^- [61], indicating that these anions could speed up the process of silica condensation. Recently, couples of groups try to use inorganic anions as additives in the synthesis under alkaline media to increase hydrothermal stability of ordered mesoporous materials such as MCM-41s [62–66]. For examples, Okabe et al. reported that BF_4^- could promote the interaction between silica species with template micelle in the synthesis of MCM-41 materials [65]. Wang et al. reported that anions such as SO_4^{2-} in the synthesis could improve the hydrothermal stability of MCM-48, but they do not study a relationship between the degree of silica condensation in mesoporous materials and these anions [66].

SBA-15 is a first example of well ordered mesoporous silica materials templated by triblock copolymer surfactant in strongly acidic media, and its good features such as thicker walls and larger pore sizes are very favorable for improvement of hydrothermal stability and diffusion of bulky molecules [3]. However, the relatively low silica condensation in SBA-15 [3] is still a problem for improving its hydrothermal stability.

In this work, we systemically study anionic effect on the degree of silica condensation under various conditions including acidic, neutral, and alkaline media, and we then try to search suitable anionic promoters for silica condensation with very high degree. Finally, based on the dependence of various inorganic anions on the degree of silica condensation, we rationally synthesize hydrothermally stable and well ordered mesoporous silica-based materials with very high degree of silica condensation. For example, hydrothermally stable and well ordered hexagonal mesoporous SBA-15 materials with very high degree of silica condensation (Q^4/Q^3 around 4.3–6.3) have been successfully synthesized in the presence of inorganic anions such as sulfate and carbonate species at conventional temperature (100 °C) from usual polymer template of P123 under neutral condition. Furthermore, this approach has been extended to synthesize heteroatom-incorporated mesoporous materials, and obtained ordered hexagonal Al-SBA-15 synthesized in the presence of urea exhibits much higher hydrothermal stability than conventional Al-SBA-15.

2. Experimental

2.1. Silica samples condensed in the presence of various inorganic anions

Silica samples condensed in the presence of various inorganic anions of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4NO_3 and NH_4Cl are typically in the following: (1) 2.08 g (0.01 mol) of TEOS (tetraethylorthosilicate) was mixed with 30 mL of deionized water, followed by stirring at 45 °C for 30 h to hydrolyze TEOS. (2) 0.02 mol of ammonium salt with various anions was added into the mixture of (1) stirring for another 60 min. (3) Then the mixture was transferred into an autoclave and heated under static condition at 100 °C for 48 h. (4) Finally, the samples were collected by filtering, and dried in air at room temperature. The silica samples condensed in the presence of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4NO_3, and NH_4Cl were designated as S–SO_4^{2-}, S–CO_3^{2-}, S–NO_3^-, and S–Cl^-, respectively (Table 1).

Table 1
Silica samples condensed at 100 °C under various conditions[a]

Sample	Ammonia (28 wt%) (mL)	Water (mL)	Hydrochloric acid (38 wt%) (mL)	Anion	$Q^4/(Q^3+Q^2)$
S	–	30	–	–	
S–Cl^-	–	30	–	Cl^-	2.5
S–NO_3^-	–	30	–	NO_3^-	2.3
S–CO_3^{2-}	–	30	–	CO_3^{2-}	3.5
S–SO_4^{2-}	–	30	–	SO_4^{2-}	3.3
S–SO_4^{2-}-acid	–	25	5	SO_4^{2-}	1.9
S–SO_4^{2-}-base	5	25	–	SO_4^{2-}	3.6

[a] The molar ratio in gel composition of TEOS/Anion/Water is fixed at 1/2/167.