

NEW ROUTES FOR IMPROVING HYDROTHERMAL STABILITY OF ORDERED MESOPOROUS MATERIALS AND SYNTHESIS OF MESOPOROUS ZEOLITES

FENG-SHOU XIAO

College of Chemistry, Jilin University, Changchun 130012, China

In comparison to industrial zeolite catalysts, ordered mesoporous materials exhibit relatively low hydrothermal stability, which severely hinders their practical applications in industrial catalytic reactions such as petroleum refining. In this paper, several new routes for improving hydrothermal stability of ordered mesoporous materials are summarized, including (1) hydrothermally stable mesoporous aluminosilicates and titanosilicates assembled from preformed zeolite precursors; (2) high-temperature synthesis of ordered mesoporous silica-based materials with high silica condensation; (3) introduction of promoters for silica condensation in the synthesis of ordered mesoporous materials. Furthermore, we focus on synthesis of mesoporous zeolites because mesoporous zeolites have the advantages of both zeolites and mesoporous materials. In this paper, a facile route for synthesis of mesoporous zeolites from cationic polymers is described.

1. Introduction

Since the first discovery of ordered mesoporous materials by Mobil scientists [1], a series of novel ordered mesoporous materials have been successfully synthesized [2-10]. However, compared with zeolites, these mesoporous materials exhibit low catalytic activity and hydrothermal stability due to their amorphous walls [2]. Therefore, increasing catalytic activity and hydrothermal stability are great tasks for rational synthesis of ordered mesoporous materials. In this work, we have mainly reviewed our recent development for synthesis of ordered mesoporous materials with improved hydrothermal stability, which include (1) catalytically active and hydrothermally stable mesoporous aluminosilicates and titanosilicates assembled from preformed zeolite precursors; (2) high-temperature synthesis of ordered mesoporous silica-based materials with high silica condensation; (3) introduction of promoters for silica condensation in the synthesis of ordered mesoporous materials.

Additionally, mesoporous zeolites are also a hot topic for synthesis of porous materials recently [15] because the mesoporousity in zeolites is favorable for mass transfer. Very importantly, these crystalline mesoporous zeolites exhibit

much higher hydrothermal stability than the amorphous mesoporous materials. In this work, we also show a facile synthesis of mesoporous zeolites from mesoscale template of cationic polymer in the presence of small organic ammonium salts [15.].

2. Improving Hydrothermal Stability of Ordered Mesoporous Materials

2.1. *Strongly Acidic and Hydrothermally Stable Ordered Mesoporous Aluminosilicates from Preformed Aluminosilicate Zeolite Precursors*

It is well known that zeolites are hydrothermally stable and catalytically active, and one of reasons for their excellent properties is the existence of primary and secondary zeolite building units (PSBU) in zeolites [16]. Of course, the preformed zeolite precursors contain PSBU. Fortunately, when preformed aluminosilicate zeolite precursors are assembled with the templating micelle, strongly acidic and hydrothermally stable ordered mesoporous aluminosilicates have been synthesized successfully [19-24]. The early works for synthesis of ordered mesoporous aluminosilicates are carried out in alkaline media [19-21]. However, under alkaline media, mixed phases would often be obtained if the synthetic conditions are not controlled very well. In order to prevent the formation of mixed phases, the assembly of preformed zeolite precursors with the templating micelle is explored to strongly acidic media. Under this condition, crystallization of zeolites will be avoided, and the products therefore would be pure mesoporous materials [22-24].

It is worthy to mention that the quality of preformed zeolite precursors play a key role for the synthesis of strongly acidic and hydrothermally stable ordered mesoporous aluminosilicates. If the sizes of the preformed zeolite precursors are too big, it is difficult to form an ordered mesostructure due to the rigidity of nanocluster assembly. If the sizes of the preformed zeolite precursors are too small, it is difficult to obtain strongly acidic and hydrothermally stable mesoporous aluminosilicates due to a significant increase of amorphous silica in the samples. In our case, the quality of the preformed zeolite precursors (zeolite seeds solution) is usually checked by the synthesis of zeolites in the absence of organic template. For example, addition of a small amount of the preformed Beta zeolite precursors with a good quality into alumina-silica gel at 140 °C for 2-4 days led to Beta zeolite with high crystallinity in the absence of organic templates [25]. The preformed aluminosilicate precursors appear to serve as seeds for the crystallization of Beta zeolite.

Recently, various types of the preformed zeolite precursors such as MFI and L nanoclusters was also used to synthesize ordered mesoporous aluminosilicates, and these mesoporous materials also exhibit higher hydrothermal stability and acidity than conventional MCM-41 [26, 27].

2.2. Catalytically Active and Hydrothermally Stable Ordered Mesoporous Titanosilicates from Preformed Titanosilicate Precursors

Since the discovery of TS-1 zeolite by Enichem Company [28], a series of microporous crystals of titanosilicates, have been reported which have remarkable catalytic properties. However, the pore sizes (<0.8 nm) of these microporous titanosilicates too small for access by bulky reactants of the kind important in fine chemical and pharmaceutical industries. The solution for this problem is to synthesize mesoporous titanosilicates with pore sizes of 3~8 nm [29]. Unfortunately, when compared with TS-1, the oxidation ability and hydrothermal stability are relatively low, which severely hinders their practical applications. The relatively low oxidation ability and hydrothermal stability, e.g. of Ti-MCM-41, can be attributed to the difference in the titanium coordination environment (amorphous nature of the mesoporous wall) [2]. In our case, an ordered mesoporous titanosilicate (MTS-9) has been assembled from the preformed TS-1 precursors in strongly acidic media, and its mesostructure is hydrothermally stable [30], compared with that of Ti-MCM-41. For hydroxylation of phenol with hydrogen peroxide, the activity and selectivity are similar to TS-1. However, for hydroxylation of bulky molecules like trimethylphenol, TS-1 is inactive, while mesoporous MTS-9 has very high activity. The increased activities, especially for bulky reactants, and higher stability are novel catalytic properties that may lead to new applications [30].

Recently, the synthesis of ordered mesoporous titanosilicates from the preformed TS-1 precursors is extended to alkaline media [31, 32], and obtained products exhibit excellent properties for the conversion of bulky reactants. For example, in non-aqueous solvent decane epoxidation of cyclohexene was tested and compared with conventional Ti-MCM-41 and TS-1. It is clear that the much higher conversion cyclohexene to the epoxidation product of the mesoporous materials assembled from the preformed TS-1 precursors, demonstrating their superiority of catalytic properties [32]. Furthermore, ordered mesoporous ferrosilicates are also synthesized from the assembly of the preformed ferrosilicate zeolite precursors with surfactant micelle in strongly acidic media, and obtained products exhibit much higher hydrothermal stability than Fe-MCM-41 [32]. Obviously, the assembly of the preformed zeolite precursors with the templating

micelle is a good route for synthesis of catalytically active and hydrothermally stable ordered mesoporous materials.

2.3. High-temperature Synthesis of Hydrothermally Stable Ordered Mesoporous Silica-based Materials with High Silica Condensation

It has been reported that a critical factor in increasing hydrothermal stability is to have more silica condensation on the mesoporous walls [33]. Conventionally, the synthesis of ordered mesoporous materials is at low temperatures (80-150 °C) because there is no surfactant that can be used as template at high temperature (160-220 °C). The low-temperature synthesis usually results in imperfect silica condensation of mesoporous materials with a large amount of terminal OH group which make the mesostructure unstable [2]. Fortunately, when the mixture of an ordered polymer surfactant micelle (P123) with a fluorocarbon surfactant (FC-4, $C_3F_7O(CFCF_3CF_2O)_2CFCF_3CONH(CH_2)_3N^+(C_2H_5)_2CH_3I$) is used as a template, ordered hexagonal mesoporous silica-based materials with good hydrothermal stability, designated JLU-20, are successfully synthesized in strong acidic media at high temperature (160-220 °C) [34]. XRD pattern of calcined JLU-20 generally shows four clearly well-resolved peaks that can be indexed as the (100), (110), (200), and (210) diffractions associated with the $P6mm$ hexagonal symmetry, and TEM images of JLU-20 sample confirm this mesostructure. Interestingly, JLU-20 is much more hydrothermally stable than SBA-15. Upon hydrothermal treatment, JLU-20 remains well-ordered, whereas SBA-15 loses most of its mesostructure. Furthermore, the ^{29}Si MAS NMR spectrum of the as-synthesized JLU-20 provides direct evidence of the extent of silica condensation. JLU-20 is primarily made up of fully condensed Q^4 silica units (-112 ppm) with a small contribution from incompletely cross-linked Q^3 (-102 ppm), giving very high Q^4/Q^3 ratio (6.5). In contrast, SBA-15 has typical peaks correspond to Q^2 , Q^3 , and Q^4 silica species respectively, and the ratio of Q^4/Q^3+Q^2 is 1.9, suggesting the presence of large amounts of terminal hydroxyl group in the mesoporous walls. These results demonstrate that JLU-20 has fully condensed mesoporous silica walls, which should be attributed directly to the contribution of high-temperature synthesis [34].

Recently, the synthesis of JLU-20 at high-temperatures was investigated by 1H , ^{13}C , and ^{19}F NMR spectroscopy, and obtained results show that the ammonium head in the mixture of FC-4 and P123 play a key role for the high-temperature synthesis. Accordingly, it is suggested that ordered silica mesoporous materials could be synthesized at high temperature without the use of fluorocarbon chains. Therefore, we can design fluorocarbon-free templates for the synthesis of ordered mesoporous silica materials at high temperatures (>180°C). Fortunately, when a mixture of tetraethylammonium hydroxide (TEAOH) with P123 is used as a template, ordered hexagonal silica-based

materials (JLU-20-TEA) is successfully synthesized at high-temperature (180 °C). The ^{29}Si MAS NMR spectrum of the as-synthesized JLU-20-TEA shows high Q^4/Q^3 ratio at 4.2, and hydrothermal treatments of the samples show that JLU-20-TEA is more stable than conventional mesoporous silica of SBA-15.

2.4. Introduction of Promoters for Silica Condensation in the Synthesis

SBA-15 is a first example of ordered mesoporous silica materials templated from 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 is still a problem for improving its hydrothermal stability. Recently, we systemically investigate the effect of anions on silica condensation in acidic, neutral, and alkaline conditions at conventional temperatures such as 100 °C, and it is found that sulfate is a good promoter for silica condensation in aqueous solution under neutral condition. Therefore, when an inorganic anion of sulfate is added into the starting gel for synthesis of SBA-15 under neutral condition, hydrothermally stable and well ordered hexagonal mesoporous SBA-15 materials (SBA-15-SO_4^{2-}) have been successfully synthesized at conventional temperature (100 °C). As we have expected, as-synthesized SBA-15-SO_4^{2-} exhibit very high degree of silica condensation, giving Q^4/Q^3 ratio of 6.3. Interestingly, after treatment in 100% steaming at 780 °C for 3 h, SBA-15-SO_4^{2-} still shows three clear peaks assigned to (100), (110) and (200) reflections of hexagonally ordered mesostructure. In contrast, the treated SBA-15 gives rise to a broad peak assigned to (100) reflection. These results confirm that the hydrothermal stability of SBA-15-SO_4^{2-} is significantly improved, compared with that of SBA-15. Furthermore, this approach has been extended to synthesize hydrothermally stable mesoporous materials with various substituted heteroatoms such as aluminum, zirconium, titanium, iron, tin, and vanadium. For example, ordered hexagonal Al-SBA-15 synthesized in the presence of urea exhibits much higher hydrothermal stability than conventional Al-SBA-15.

3. Mesoporous Zeolites Templated with a Mixture of Small Organic Ammonium and Mesoscale Cationic Polymer

Although those mesoporous materials mentioned above have much improved stability, they are less hydrothermally stable than zeolites. Therefore, our group is to develop new route to synthesize mesoporous zeolites. Mesoporous zeolites should have the advantages of both mesoporous materials for fast diffusion of

molecules and microporous zeolites for highly active sites [11, 12]. Generally, microporous crystals of zeolites such as Beta and ZSM-5 are synthesized from small organic templates such as tetraethylammonium hydroxide (TEAOH) and tetrapropyl ammonium hydroxide (TPAOH). Recently, mesoporous zeolites are successfully templated from nanosized carbon templates in the presence of small organic templates [13, 14], but their industrial applications are limited due to the complexity of synthetic procedure and hydrophobicity of carbon templates. In our case, we show a unique, facile, controllable, and universal route for the synthesis of hierarchical mesoporous zeolites templated from a mixture of both small organic ammonium and mesoscale cationic polymer [15], which are well characterized by HR TEM, nitrogen isotherms, HR SEM, XRD, and probing catalytic reactions. In this route, the choice of mesoscale template of cationic polymer is one of keys for the formation of mesoporous zeolites, which is mainly related to three points in the following: (1) good thermal and hydrothermal stability in the temperatures (up to 200 °C) under the condition of zeolitic synthesis; (2) very low cost; and (3) very strong interaction between cationic polymers with negative silica species in alkaline media.

Figure 1 shows TEM image of mesoporous ZSM-5 zeolite synthesized from cationic polymer. Obviously, there is hierarchical mesoporosity in the range of about 10-30 nm for the sample. Notably, this route is “one-step” hydrothermal synthesis, and the template mixture is homogeneously dispersed into synthetic gel. Notably, these novel mesoporous zeolites exhibit excellently catalytic properties, compared with conventional zeolites. For example, while there is a little activity for cracking of triisopropylbenzene in conventional ZSM-5, high conversion was obtained with mesoporous ZSM-5 zeolite. Very interestingly, one-pot synthesis of mesoporous zeolites is also successful from various mesoscale organic templates such as silane-functionalized polymer [35] and organic-inorganic hybrid surfactant [36] recently.

Additionally, when palladium species were loaded into mesoporous Beta zeolite (Beta-H), the Pd particles could be located in both mesopores and micropores (Pd/Beta-H). The presence of Pd particles in the mesopores offers an opportunity for catalytic hydrotreating of bulky molecules. As a model reaction, the deep hydrogenation of bulky aromatic pyrene shows that the Pd/Beta-H exhibits *much higher activity and selectivity for products of deep hydrogenation* than a conventional Beta zeolite-supported Pd catalyst (Pd/Beta) and Pd catalysts supported on MCM-41 (Pd/Al-MCM-41), which is greatly important for increasing fuel quality and controlling the undesirable emissions in exhaust gases [37].

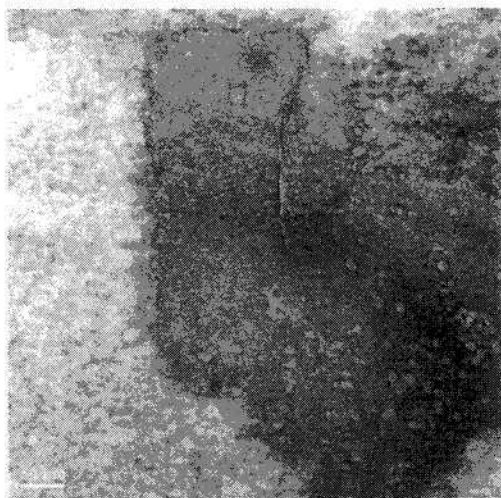


Figure 1. TEM of hierarchical mesoporous ZSM-5 zeolite templated from cationic polymer in the presence of TPAOH.

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