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Synthesis of Heteroatom Substituted SBA-15 by the "pH-Adjusting" Method

Shuo Wu, Yu Han, Yong-Cun Zou, Jiang-Wei Song, Lan Zhao, Yan Di,
Shu-Zhen Liu, and Feng-Shou Xiao*

Department of Chemistry & State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China

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A simple and effective method denoted "pH-adjusting" is used to graft a large amount of heteroatoms such as Al and Ti to mesoporous silica material SBA-15. The products prepared by this method show highly ordered mesostructures with large surface areas and uniform mesopore size distribution. The results of ICP, EDX, ^{27}Al NMR, calcium ion-exchange capacity, and UV−vis spectra show that almost all the heteroatoms added into the initial reaction mixture can be introduced into the products, and moreover, the heteroatoms introduced by this route locate at mainly tetrahedrally coordinated sites.

Introduction

A series of mesoporous silica materials with various structures have been synthesized in strongly acidic media, such as SBA-15,[1a] SBA-16,[1b] SBA-1, SBA-2,[1c] FDU-1,[2] and so forth. These materials have attracted much attention because of their interesting structures and potential applications in catalysis. However, they are all purely siliceous materials and it is difficult to prepare heteroatom-introduced mesoporous silica under strongly acidic synthesis conditions. This is because, under such conditions, metals will exist only in the cationic form rather than their corresponding oxo species and therefore heteroatoms cannot be introduced into the mesoporous walls via a condensation process with silicon species. As we know, the active sites in molecular sieves are always from heteroatoms; for example, the introduction of Al^{3+} and Ti^{4+} will provide acidic and redox sites into pure silica, respectively.[3] Therefore, it is of great importance to introduce heteroatoms into the walls of these mesoporous silica materials prepared under strongly acidic conditions.

"Direct-synthesis"[4−10] and "postsynthesis grafting"[11−16] are two typical methods used for the introduction of heteroatoms. The procedure of direct-synthesis is relatively simple. For example, Yue et al.[4] have synthesized Al−SBA-15 at the pH value of 1.5; Li et al.[5] have prepared Ti−SBA-15 by controlling the hydrolysis of the siliceous source in the presence of fluoride; Komarneni et al.[6] have prepared Ti−SBA-15 under microwave hydrothermal conditions; Yang et al.[17,18] have prepared mesoporous aluminosilicates and titanosilicates in nonaqueous media. However, the efficiency of direct-synthesis is always low; that is, only a small part of the heteroatoms added into the initial gels can be introduced into the mesoporous products in aqueous solution.

Postsynthesis-grafting procedures have been performed for mesoporous materials prepared under both acidic and basic conditions.[11−16] For example, Mokaya et al.[11] have prepared Al−MCM-41 by the reactions of MCM-41 with either an aqueous solution of aluminum chlorohydrate or with aluminum isopropoxide in nonaqueous media; Ryoo et al.[12] reported a generalized method for the grafting of heteroatoms onto mesoporous siliceous frameworks by stirring the mixture of mesoporous materials and anhydrous inorganic salts in absolute ethanol solutions; Luan et al.[13b] have synthesized Al−SBA-15 by postsynthesis modification with

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* To whom correspondence should be addressed. E-mail: newbloo@sina.com and fsxiao@mail.jlu.edu.cn. Tel: +86-431-8499191. Fax: +86-431-5671974.

(1) (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. (b) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024. (c) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(2) Yu, C.; Yu, Y.; Zhao, D. *Chem. Commun.* **2000**, 575.

(3) Coma, A. *Chem. Rev.* **1997**, *97*, 2373.

(4) Yue, Y.; Cedeon, A.; Bonardet, J.-L.; Melosh, N.; D' Esinose, J.-B.; Fraissard, *J. Chem. Commun.* **1999**, 1697.

(5) Zhang. W.; Lu, Q.; Han, B.; Li, M.; Xiu, J.; Ying, P.; Li, C. *Chem. Mater.* **2002**, *14*, 3413.

(6) Newalkar, B. L.; Olanrewaju, J.; Komarneni, S. *Chem. Mater.* **2001**, *13*, 552.

(7) Han, Y.; Xiao, F.-S.; Wu, S.; Sun, Y.; Meng, X.; Li, D.; Lin, S. *J. Phys. Chem. B* **2001**, *105*, 7963.

(8) (a) Han, Y.; Wu, S.; Sun, Y.-Y.; Li, D.-S.; Xiao, F.-S. *Chem. Mater.* **2002**, *14*, 1144. (b) Han, Y.; Li, N.; Zhao, L.; Li, D.; Xu, X.; Wu, S.; Di, Y.; Li, C.; Zou, Y.; Yu, Y.; Xiao, F.-S. *J. Phys. Chem. B* **2003**, *107*, 7551.

(9) Xiao, F.-S.; Han, Y.; Yu, Y.; Meng, X. J.; Yang, M.; Wu, S. *J. Am. Chem. Soc.* **2001**, *124*, 888.

(10) Liu, Y.; Pinnavaia, T. J. *Chem. Mater.* **2002**, *14*, 3−5.

(11) Mokaya, R. *Angew. Chem.* **1999**, *111*, 3079. *Angew. Chem., Int. Ed.* **1999**, *38*, 2930.

(12) Ryoo, R.; Jun, S.; Kim, J. M.; Kim, M. J. *Chem. Commun.* **1997**, 2225.

(13) (a) Luan, Z.; Maes, E. M.; van der Heide, P. A. W.; Zhao, D.; Czernuszewicz, R. S.; Kevan, L. *Chem. Mater.* **1999**, *11*, 3680. (b) Luan, Z.; Hartmann, M.; Zhao, D.; Zhou, W.; Kevan, L. *Chem. Mater.* **1999**, *11*, 1621. (c) Luan, Z.; Bae, J. Y.; Kevan, C. *Chem. Mater.* **2000**, *12*, 3202.

(14) Sumiya, S.; Oumi, Y.; Uozumi, T.; Sano, T. *J. Mater. Chem.* **2001**, *11*, 1111.

(15) Mokaya, R.; William, J. *Chem. Commun.* **1997**, 2185.

(16) Morey, M.; O'Brien, S.; Schwarz, S.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 898−911.

(17) Yang, P.; Zhao, D.; Margolese, D.; Chmelka, B.; Stucky, G. D. *Nature.* **1998**, *396*, 152.

(18) Yang, P.; Zhao, D.; Margolese, D.; Chmelka, B.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813.

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aluminum isopropoxide in dry hexane, with $AlCl_3$ in dry ethanol, and with an aqueous solution of sodium aluminate followed by calcination, respectively; Luan et al. have also prepared Ti−SBA-15[13a] and V−SBA-15[13c] by incipient-wetness impregnation inside a glovebox under flowing nitrogen; Morey et al. have synthesized both Ti−MCM-48 and Ti−SBA-15 by the reaction of titanium isopropoxide and dehydrated mesoporous materials in dry hexane media in a Schlenk line with the protection of argon.[16] Compared to direct-synthesis, postsynthesis can introduce more heteroatoms into mesoporous silica. However, the postsynthesis routes mentioned above are all relatively complicated, and in some cases the process has to be carried out under conditions that do not include water and oxygen.[13] Another disadvantage of postsynthesis is that the uniform mesostructures are sometimes severely destroyed.[13b] Moreover, it is also difficult to incorporate heteroatoms quantitatively into the materials by postsynthesis because the grafting procedures are mostly processed by immersing solid mesoporous silica into an aqueous or nonaqueous solution followed by filtration and calcinations, and heteroatoms may be partially leached out during filtration. Additionally, not all heteroatoms introduced by postsynthesis locate at the mesoporous walls in 4-coordinated environments and there are always 6-coordinated heteroatom species in the products.[11−14]

Recently, a novel method for the incorporation of heteroatoms (Al and Ti) into the walls of ordered mesoporous silica materials synthesized in strongly acidic media has been reported by Xiao et al.[7−9] and Pinnavaia et al.,[10] where preformed zeolite nanoclusters were used as the inorganic precursor for the synthesis of mesoporous materials. In this way, the heteroatoms were fixed in the framework of the preformed zeolite nanoclusters and directly introduced into the mesostructure along with the nanoclusters. Although the materials obtained by this method showed high activity in catalysis,[7−9] the heteroatom content in these materials is still relatively low.

Herein, we report an effective and convenient method for the grafting of heteroatoms such as Al and Ti onto ordered mesoporous silica materials synthesized in strongly acidic media with high heteroatom content. In this method (denoted “pH-adjusting”), the heteroatom source is added into the initial reaction mixture in strongly acidic media ($pH < 0$), just as in the case of direct-synthesis; when the mesostructure is basically formed, the pH value of the system is adjusted from a strong acid ($pH < 0$) to neutral ($pH = 7.5$), followed by a hydrothermal treatment for another period of time, during which a large amount of heteroatoms can be introduced into the mesophase. In this study, SBA-15 is presented as an example as a mesoporous silica material prepared under strongly acidic conditions and highly ordered Al−SBA-15 and Ti−SBA-15 with high Al (or Ti) contents are then successfully synthesized using the pH-adjusting method.

Experimental Section

Synthesis. The synthesis of Al−SBA-15 using the pH-adjusting method was carried out as follows: (1) 0.8 g of triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) was dissolved in 25 mL of HCl solution (2 M), followed by the addition of 1.7 g of TEOS. The mixture was stirred at 40 °C for 4 h, and then a requisite amount of $Al_2(SO_4)_3{\cdot}18H_2O$ was added to the mixture, followed by additional stirring at 40 °C for 20 h. The mixture was then transferred into an autoclave for further condensation at 100 °C for 2 days. (2) After the procedure described above, the pH value of the synthesis system was adjusted up to 7.5 by adding ammonia dropwise at room temperature and the obtained mixture was hydrothermally treated again at 100 °C for another 2 days. The final solid was collected by filtration, washed with water, and dried at room temperature. The surfactants were removed through either the solvent extraction method or by calcination. The samples are designated Al−SBA-15_X, where X stands for the Si/Al ratios in the initial gels.

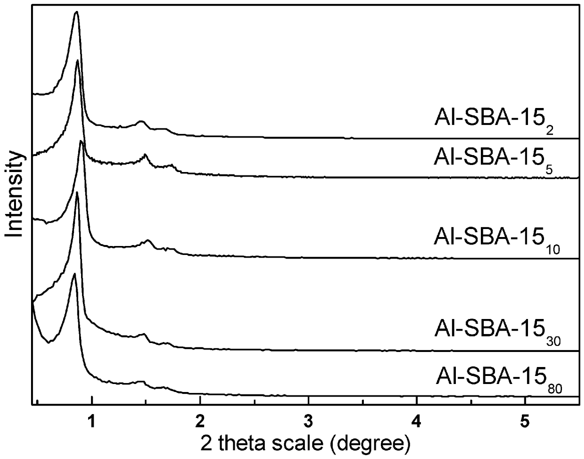

Figure 1. XRD patterns of as-synthesized Al−SBA-15_X samples prepared by pH-adjusting method.

A series of Ti−SBA-15samples were synthesized through the same route as shown above except that the heteroatom source was $TiCl_4$ instead of $Al_2(SO_4)_3{\cdot}18H_2O$. The obtained products are denoted Ti−SBA-15_X, where X stands for the Si/Ti ratios in the initial gels.

For comparison, the semi-product of Al−SBA-15_{10} designated as SBA-15-A, which was filtered before the pH value was adjusted, was prepared.

Characterization. X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 diffractometer using Cu Kα radiation. Transmission electron microscopy experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The isotherms of nitrogen were measured at 77 K using a Micrometeritics ASAP 2010 system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution was calculated using the Barrett−Joyner−Halenda (BJH) model. ^{27}Al NMR spectra were recorded on Varian Infinity plus 400 spectrometer and chemical shifts were referenced to $Al(H_2O)_6^{3+}$. UV−vis spectra were measured with spectrometer PE Lambda 20, and $BaSO_4$ was used as an internal standard. The ratios of Si/Al and Si/Ti in solid samples were determined by the results of inductively-coupled plasma analysis (ICP, Perkin-Elmer 3300DV) and energy-dispersive X-ray spectroscopy (EDX, EDAX Phoenix 30T). The ion-exchange capacity is measured by a CyberScan pH/Ion 510 Bench pH/Ion/mV Meter and an Orion 9300BN calcium electrode.

Results and Discussions

Figure 1 shows the X-ray diffraction (XRD) patterns of Al−SBA-15 samples prepared by pH-adjusting with various Si/Al ratios. Although the d spacing of the first strong reflection changes slightly from sample to sample, all samples exhibit well-resolved diffraction peaks that can be indexed as the (100), (110), (200) diffractions associated with $p6mm$ hexagonal symmetry, and there is no decrease observed in peak intensity with the increase of Al content even if the Si/Al ratio decreases to 2.0. This result indicates that the pH-adjusting method allows a large amount of Al content to be grafted while retaining a highly ordered mesostructure.

Generally, the structural ordering of mesoporous aluminosilicate is not as good as that of its pure silica analogue and will be further diminished with the increase of Al content. For example, Al−MCM-41 materials have been reported to suffer from poor and unpredictable structural ordering;[19] Ryoo et al.[20] have found that direct introduction of Al into purely siliceous MCM-41 would result in a drastic reduction in the intensity and resolution of XRD peaks. This is because the aluminates added in the synthesis system would affect the interaction between surfactants and silicates therefore to form a relatively disordered surfactant−silicate mesostructure. Luan et al.[13b] and Sadanabu et al.[14] have prepared Al−SBA-15 with Si/Al ratios at 13.8 and 4.8, respectively, but no XRD patterns were shown to justify the structural ordering of the products in their papers.

Previous investigations observed that the $d_{(100)}$ spacing of Al-containing mesoporous silica materials generally increases with the amount of aluminum introduced, likely due to the longer Al−O bond length compared to the Si−O bond. However, the $d_{(100)}$ spacing of the Al−SBA-15 samples reported in this paper gradually decreases from 106 to 99 Å with the increase of Al content (Si/Al ratio from 80 to 10), and the trend is just the reverse when the Al content is further increased (Si/Al ratio from 10 to 2, Figure 1). The reason for this phenomenon is not clear as of yet.

The high-resolution transmission electron microscope (HRTEM) images of as-synthesized Al−SBA-15_{10} show well-ordered hexagonal arrays of mesopores with one-dimensional channels, indicating a 2-D hexagonal (*P*6*mm*) mesostructure (Figure 2). The other Al−SBA-15 samples prepared by pH-adjusting have TEM images (not shown) similar to Al−SBA-15_{10}. This is fully consistent with the results of the XRD studies and confirms that the pH-adjusting method is favorable for maintaining the highly ordered mesostructure even when a large amount of Al species is grafted.

Figure 3 shows the N_2 adsorption/desorption isotherms and pore size distributions of Al−SBA-15_{10} and SBA-15-A. Both samples show typical IV adsorption/desorption isotherms. The surface area, micropore volume, and micropore area of Al−SBA-15_{10} (795 m^2/g, 0.02 cm^3/g, and 73.5 m^2/g) are all less than those of SBA-15-A (951 m^2/g, 0.07 cm^3/g, and 176.2 m^2/g). These results indicate that the micropore volume and micropore area are reduced after the pH-adjusting treatment, which is probably due to the filling of the micropores during the pH-adjusting procedure.[21] However, the total surface area, pore size distribution, and pore volume of Al−SBA-15_{10} are still comparable with those of pure silica SBA-15. Therefore, pH-adjusting is a good method for the alumination of mesoporous silica with highly ordered mesostructures.

Besides the advantage in maintaining the mesostructured ordering, the pH-adjusting method shows high efficiency for the introduction of heteroatoms. That is, almost all heteroatom species added in the initial reaction mixture could be eventually introduced into the final products. Evidence for this is provided by the results of element analysis performed by both inductively-coupled plasma analysis (ICP) and energy-dispersive X-ray spectroscopy (EDX). Figure 4 shows the EDX spectra of Al−SBA-15_{30}, Al−SBA-15_{10}, and Al−SBA-15_2. The marked circle with a radius of 150 nm in Figure 2a shows the region of incident electron beams. Obviously, the marked circle is in the inner section of the hexagonal mesoporous materials. Thus, the EDX data gathered are not strongly influenced by the aluminum species on the external surface. It is clear that the intensity of the signals associated with Al species (150 eV) is proportionally enhanced with the increase of the Al content added, and the Si/Al ratios in the products are near to the values in the initial reaction mixtures. For example, the Si/Al ratios for Al−SBA-15_{30}, Al−SBA-15_{10}, and Al−SBA-15_2 are 25.5, 12.8, and 3.2, respectively. These

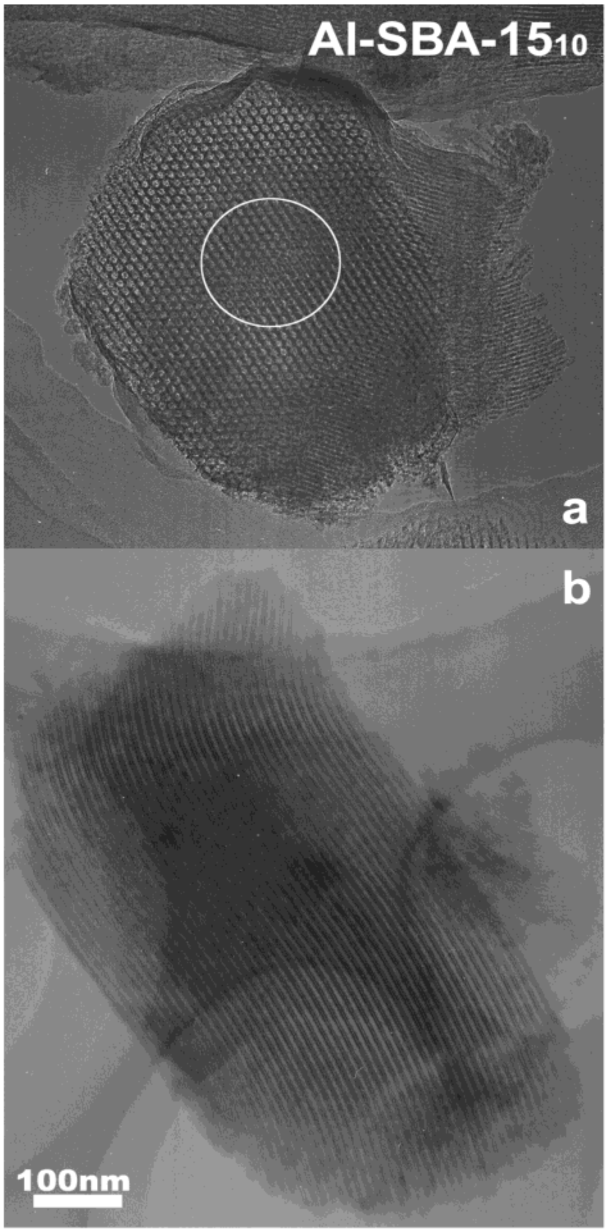

Figure 2. TEM images of as-synthesized Al−SBA-15_{10} prepared by the pH-adjusting method. The marked circle in Figure 2a is the incident region of the electron beam.

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(19) Mokaya, R.; Jones, W. *Chem. Commun.* **1998**, 1839.
(20) Ryoo, R.; Ko, C. H.; Howe, R. F. *Chem. Mater.* **1997**, *9*, 1607.
(21) Ryoo, R.; Ko, C. H. *J. Phys. Chem. B* **2000**, *104*, 11465.

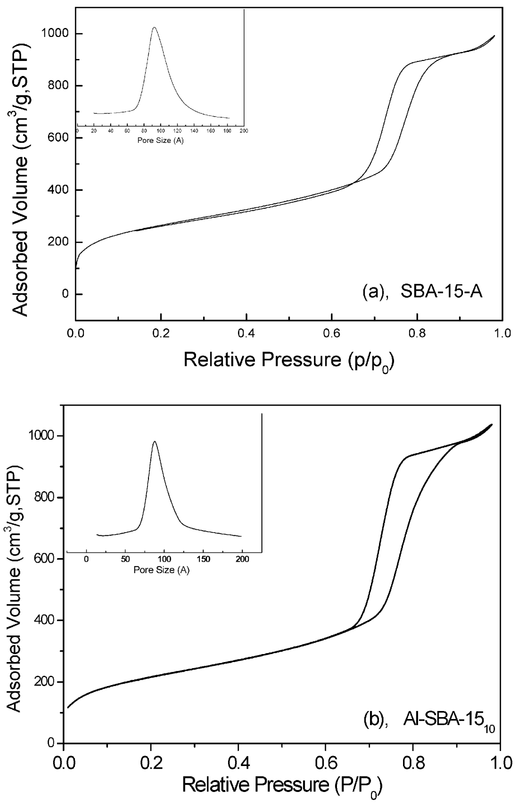

Figure 3. N_2 isotherms and pore size distribution of calcined SBA-15-A obtained before the pH-adjusting treatment (a) and calcined Al−SBA-15$_{10}$ prepared by the pH-adjusting method (b).

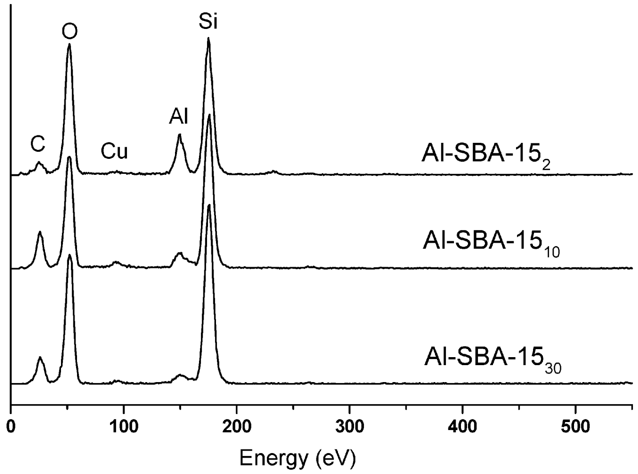

Figure 4. EDX spectra of calcined Al−SBA-15$_X$ samples prepared by the pH-adjusting method. The signals of Cu and C are from the supporting membranes under the specimen.

Table 1. Si/M (M = Al, Ti) Ratios of Al−SBA-15$_X$ and Ti−SBA-15$_X$ Samples Prepared by the pH-Adjusting Method

	Al−SBA-15					Ti−SBA-15		
Si/M (in initial gel)	80	30	10	5	2	80	40	20
Si/M (in product^a)	78	32	9.5	4.7	2.4	71	44	22
Si/M (in product^b)		25.5	12.8	4.2	3.2		36	

[a] The Si/M (M = Al, Ti) ratios in products are determined by ICP. [b] The Si/M (M = Al, Ti) ratios in products are determined by EDX.

results are approximately consistent with those obtained by ICP (Table 1) and support the conclusion that nearly all Al species in the initial mixture can be grafted to the product by the pH-adjusting method. In contrast, the traditional direct-synthesis routes are always low in efficiency for the introduction of heteroatoms.[4,5]

In mesoporous aluminosilicates, there are mainly two kinds of Al species: tetrahedral Al and octahedral Al. Since only the tetrahedral Al species contribute to the ion-exchange ability and the Bronsted acidity of the materials, it is usually desired to obtain materials with more 4-coordinated Al species. ^{27}Al MAS NMR spectroscopy is a widely used technique for discriminating between 4-coordinated and 6-coordinated Al. Figure 5 shows the ^{27}Al NMR spectra of Al−SBA-15 samples with various Si/Al ratios prepared by the pH-adjusting method. Notably, all samples have 100% tetrahedral Al (53 ppm) except for Al−SBA-15$_2$, in which octahedral Al (0 ppm) instead of tetrahedral Al is the primary species. This result indicates that not only a large amount of Al species could be introduced into pure silica SBA-15 by pH-adjusting,but also the Al species introduced by this method are inclined to locate at 4-coordinated sites. At least, Al−SBA-15 with a low Si/Al ratio (about 4.5 in the product, Table 1) and 100% tetrahedral Al (Al−SBA-15$_5$) can be prepared by the pH-adjusting method. In contrast, using other alumination methods, octahedral Al species are almost inevitable if such a high Al content is introduced.[11−13]

The calcium ion-exchange capacity of as-synthesized Al−SBA-15$_{10}$ and Al−SBA-15$_{10}$ extracted with ethanol (designated as Al−SBA-15$_{10}^{r}$) has been measured by a CyberScan pH/ion 510 Meter for 15 min at room temperature. The calcium ion-exchange capacity of Al−SBA-15$_{10}$ is 14.2 mg of $CaCO_3$/g and of Al−SBA-15$_{10}^{r}$ is 64.3 mg of $CaCO_3$/g. The results indicate that when the pores are full of template, the large amount of active ions in the pores cannot be ion-exchanged by Ca^{2+} ions. However, when the template is extracted from the pores, almost all the active ions participate in the ion-exchange reaction. Therefore, the calcium ion-exchange capacity for Al−SBA-15$_{10}^{r}$ is much larger than that of Al−SBA-15$_{10}$. In contrast, if all the aluminum species are anchored to the external surface, the calcium ion-exchange capacity of the samples will not be affected by the blockage of the template and the two data should be the same. However, experimental data show that calcium ion-exchange capacity of Al−SBA-15$_{10}^{r}$ is much higher than that of Al−SBA-15$_{10}$, indicating that most aluminum ions prefer to locate in the interior of the particles rather than only in the external surface.

It is proposed that when an Al source is added into the initial reaction mixture, the Al species are dispersed homogeneously in the synthesis system in the form of Al^{3+} cations because of the strongly acidic conditions ($pH < 0$). Possibly, Al^{3+} cations permeate the interstitial regions between the silica-block copolymer before the pH-adjusting treatments. The metal ions may be coated with silica-block copolymer mesophase, but have almost no linkage with the silicates in strongly acidic media. Therefore, before pH-adjusting treatment, when the semi-product is filtered, only pure silica SBA-15 is obtained, which has been confirmed by XRD (Figure 6), ICP, EDX, and^{27}Al NMR techniques. However, when the pH value is adjusted from strong acid ($pH < 0$) to neutral ($pH = 7.5$), the metal ions in the interstitial

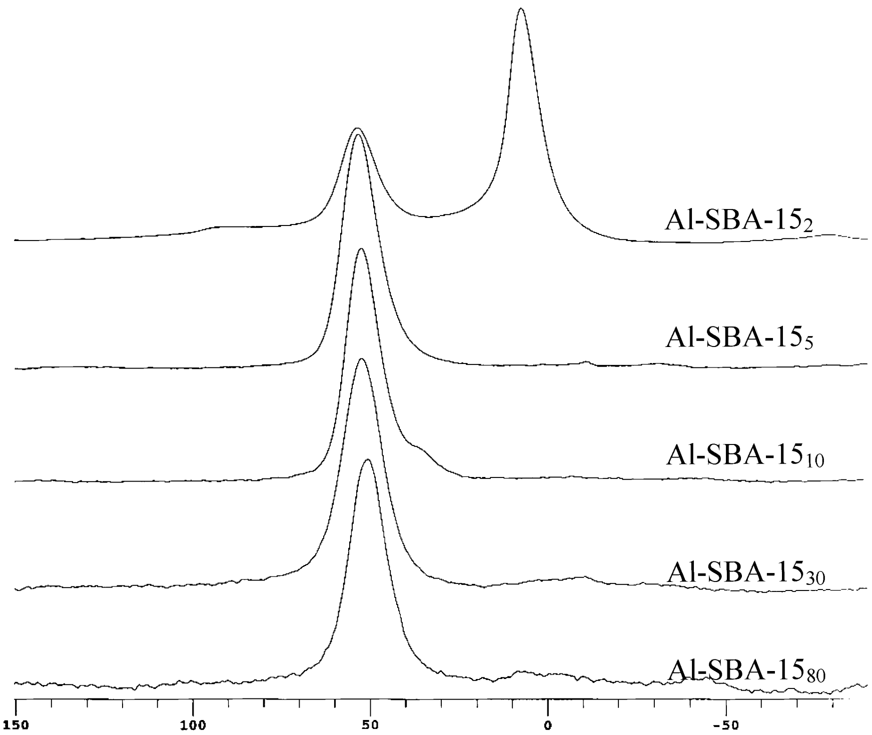

Figure 5. ^{27}Al NMR spectra of as-synthesized Al−SBA-15$_X$ samples prepared by the pH-adjusting method.

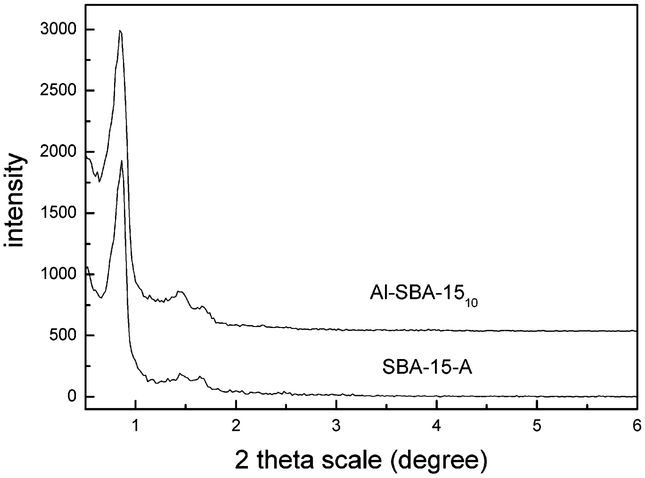

Figure 6. XRD patterns of as-synthesized Al−SBA-15$_{10}$ samples prepared by the pH-adjusting method and the semiproduct designated as SBA-15-A obtained before the pH-adjusting treatments.

regions change into the oxo form and condense with the adjacent silanols, resulting in the introduction of metal atoms to the mesoporous walls.

Compared with traditional postsynthesis, the SBA-15 sample synthesized for introducing the Al species in the pH-adjusting procedure does not require either filtration or calcinations (the treatments will result in shrinkages of the silanols. In contrast, in the case of postsynthesis, the parent materials are calcined and the silanol groups are reduced) before the pH values are adjusted; therefore, it can introduce many more heteroatoms onto the mesoporous walls by the pH-adjusting method. Moreover, because the grafting of Al species is completed under mild hydrothermal conditions rather than the severe calcinations generally used in the case of postsynthesis, it is beneficial for maintaining the ordered mesostructure.

It should be pointed out that the adjusted pH value has significant effects on the products. Figure 7 shows the XRD patterns and the ^{27}Al NMR spectra of three Al−SBA-15$_{30}$ samples prepared from different pH values (6.0, 7.5, and 8.5). It is observed that the sample obtained from the highest pH value (8.5) treatment shows no XRD peaks, whereas the other two samples ($pH = 7.5$ and $pH = 6.0$) have multiple well-resolved XRD peaks, indicating that a higher pH value ($pH > 8.5$) is unfavorable for maintaining the preformed mesostructure of SBA-15. This is likely because the presence of OH^- gives rise to the hydrolysis of the preformed SBA-15 mesostructure. SBA-15 is synthesized under acidic conditions via a $S^0(H^+)X^-I^+$ route and its framework is electrically neutral ($S^0H^+X^-I^0$).[1] Those mesoporous silicates prepared from basic media through a S^+I^- route such as MCM-41, however, possess a negatively charged framework. Therefore, it is not surprising that the as-synthesized SBA-15 loses its structure easily by hydrothermal treatment under weakly alkaline conditions, while as-synthesized MCM-41 will not suffer structure breakdown under the same treatment (since it can be synthesized by using such conditions). This may be attributed to the fact that the alkaline hydrolysis (catalyzed by OH^- anions) of a negatively charged framework is difficult because of the electric charge repellency.

On the other hand, the ^{27}Al NMR spectra show that there are both tetrahedral and octahedral Al species in the sample prepared at the lowest pH value of 6.0 while all the Al species are tetrahedral in the other two samples. This result shows that if 100% tetrahedral Al species are desired, a lower pH value should be avoided and may be attributed to the fact that the degree of polymerization of aluminates at a pH value of 6.0 is higher than that under neutral or basic conditions.

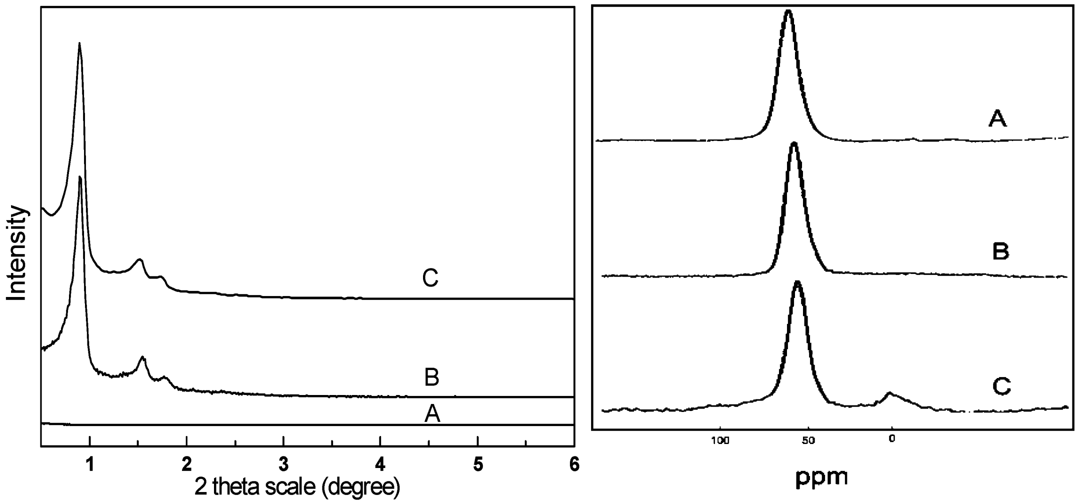

Figure 7. XRD patterns (a) and ^{27}Al NMR spectra (b) of as-synthesized Al$-$SBA-15$_{30}$ prepared by the pH-adjusting method at different pH values: 8.5 (A), 7.5 (B), and 6.0 (C).

A high polymeric degree makes it difficult for the Al species to combine with silanol groups in the isolated 4-coordinated form and therefore results in some octahedral Al species. On the basis of the XRD data and ^{27}Al NMR, the optimal pH region for the introduction of Al into SBA-15 is finally determined to be 7.2$-$7.8, in which highly ordered mesostructures with 100% tetrahedrally coordinated Al could be obtained.

It is notable that although Al species are completely tetrahedrally coordinated in the as-synthesized Al$-$SBA-15$_X$ samples (except for Al$-$SBA-15$_2$), some octahedral Al species are observed in the corresponding calcined samples, which is associated with the collapse of Al atoms from tetrahedral sites in the mesoporous walls during the calcination. If more tetrahedral Al species are preferred, the solvent extraction method should be chosen for the removal of surfactants to obtain open mesopores.

As for the introduction of Ti species into the mesoporous silica materials prepared from acidic media, the conventional postsynthesis method always requires complex and strict conditions (for example, inside a glovebox under flowing nitrogen) to avoid the rapid hydrolysis and polymerization of the Ti source. The pH-adjusting method, however, provides a simple and direct way to introduce Ti into purely siliceous materials, which is verified by UV$-$vis diffuse reflectance spectroscopy (Figure 8). The spectra of Ti$-$SBA-15$_{80}$ and Ti$-$SBA-15$_{40}$ both show a broad absorption band centered at 225 nm that is characteristic for Ti introduction and generally assigned to isolated Ti species in the amorphous mesoporous walls.[3,13a,22] However, besides the main adsorption at 225 nm, a very small shoulder at 270 nm assigned to Ti atoms with penta- or octahedral coordination, appears for the sample Ti$-$SBA-15$_{40}$. If the amount of Ti is further increased to Si/Ti at 20 (Ti$-$SBA-15$_{20}$), the maximum absorption shifts to 240 nm and the shoulder absorption peak at 270 nm is clearer. These results suggest that the pH-adjusting method can effectively introduce a certain amount of Ti (Si/Ti > 40) into SBA-15. Besides the ease of operation, other advantages of the pH-adjusting method, including well-ordered products and a high efficiency for the introduction of Ti, are also observed, just as in the case of the introduction of Al shown above. We suggest that the mechanism proposed for the formation of Al$-$SBA-15 can also explain how Ti species are introduced to SBA-15 by the pH-adjusting method. That is, Ti species are dispersed homogeneously in the system in the form of Ti^{4+} at first, and after the pH value is adjusted, the Ti species change their form to oxo titanates and are consequently grafted to the mesoporous walls through condensations with the silanol groups.

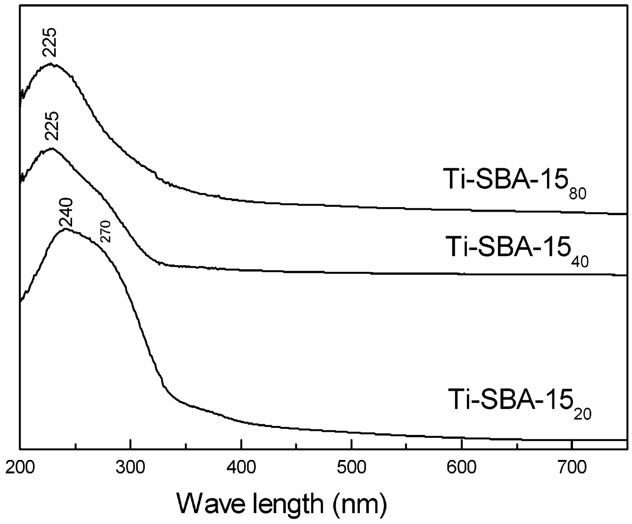

Figure 8. UV$-$vis spectra of as-synthesized Ti$-$SBA-15$_X$ samples prepared by the pH-adjusting method.

In summary, we have proposed an effective method for the grafting of heteroatoms such as Al and Ti into SBA-15. Interestingly, this synthetic approach shows a possibility for the introduction of other hetroatoms such as Ga, V, B, and Cr with various mesostructures such as SBA series,[1] FDU-1,[2] and JLU-20.[23]

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(22) Zhang, W.; Froba, M.; Wang, J.; Wong, J.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9164.

(23) Han, Y.; Li, D.-F.; Zhao, L.; Song, J.; Yang, X.; Li, N.; Di, Y.; Li, C.; Wu, S.; Xu, X.; Meng, X.; Lin, K.; Xiao, F.-S. *Angew. Chem., Int. Ed.* **2003**, *42*, 3633.

Conclusions

In summary, “pH-adjusting” is a novel method for the grafting of heteroatoms to mesoporous silica materials prepared from strongly acidic media. The procedure of pH-adjusting is as simple as the general “direct-synthesis” method; however, it shows remarkable efficiency that is even much higher than traditional “postsynthesis” routes. Using this method, heteroatoms including Al and Ti have been successfully introduced onto the mesoporous walls of SBA-15 in large amounts. The obtained Al−SBA-15 (Si/Al > 5) and Ti−SBA-15 (Si/Ti > 40) have relatively large surface areas, relatively uniform mesopore size distributions, and almost all 4-coordinated heteroatoms species. Moreover, this route can potentially be expanded to the introduction of other heteroatoms into mesoporous silica materials with various mesostructures.

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