

Synthesis of Zr-Incorporated SBA-15 Mesoporous Materials in a Self-generated Acidic Environment

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An environmentally friendly process of synthesizing Zr-incorporated mesoporous SBA-15 silica materials with the Zr content up to 0.1 Zr/Si atomic ratio and of well-ordered pore structure, high surface area, and narrow pore-size distribution was developed, where no addition of mineral acids was necessary. The main strategy of this method was to utilize the acidity self-generated in the aqueous solutions of the zirconium precursors as the catalyst for TEOS hydrolysis. In addition, the zirconium precursors also contributed to salt effect in increasing the ordering of the mesostructure. SBA-15 materials of highly ordered pores were obtained without the addition of mineral acids when the Zr/Si ratios were around 0.05. For those with the Zr/Si ratios smaller or greater than this value, the introduction of some salts, such as NaCl, in the synthesis gel was found essential in order to obtain mesostructure of high ordering and narrow pore size distribution. The amount of Zr incorporated in SBA-15 synthesized under such a mild condition was greater than that synthesized in a strong acidic environment. Moreover, the Zr content, up to Zr/Si ratio of 0.1, was close to that started with in the gel. The morphology of the Zr–SBA-15 material was found to vary with the acidity of the synthesis gels. Rodlike shape morphology was observed when no mineral acids were used, in contrast to the hexagonal platelet morphology for the material synthesized in a strong acidic environment.

Introduction

Mesoporous silica of high surface area and highly ordered uniform pores has been shown to be important in catalysis, sorption, and nanoscience.^{1,2,3–9} The SBA-15 of hexagonal-ordered pore structure, synthesized using amphiphilic triblock copolymers as the pore-directing agents,¹⁰ has received great attention in recent years because of its relatively large pore diameter and high hydrothermal stability in comparison to MCM-41, its analogue in the M41S family. To introduce functionality and broaden its applications, various metal ions have been incorporated into the framework of SBA-15,

such as Al,⁸ Ti,¹¹ and Zr.^{12–15} The Zr-incorporated SBA-15 was shown to have good catalytic activities in selective oxidation reactions.¹² Unfortunately, the normal synthesis condition of SBA-15 is so acidic (ca. 2 M HCl) that the amount of metal ions incorporated in the SBA-15 framework is usually low. Recently, Newalkar and co-workers¹⁵ utilized a microwave-assisted hydrothermal method to synthesize Zr–SBA-15. However, the ordering of mesostructure still decreased markedly as the Zr/Si atomic ratio in the synthesis gel was greater than 5% and the mesostructure was nearly disorganized when the ratio approached 10%. Moreover, no elemental analysis results were given concerning the amount of Zr really incorporated in the mesostructure. In this study, we developed an environmentally friendly and efficient method to synthesize highly ordered Zr-incorporated SBA-15 with up to 10% Zr/Si content in the framework. The physicochemical properties of the resultant materials were characterized with X-ray powder diffraction, X-ray absorption spectra of Zr L_3 -edge, solid state ²⁹Si NMR, thermo-gravimetric analysis, transmission and scanning electron microscopy, ICP-AES and EDX elemental analysis, and nitrogen physical adsorption.

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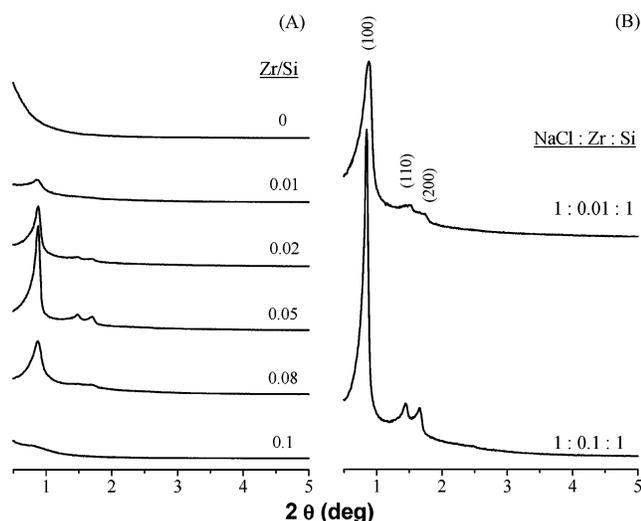


Figure 1. Small-angle X-ray diffraction patterns of (A) calcined Zr–SBA-15 with varied Zr/Si atomic ratios (in gel) synthesized by acid-free conditions. (B) Zr–SBA-15 crystallized in the presence of NaCl.

Experimental Methods

Synthesis of Zr–SBA-15 Mesoporous Silica. In our synthesis conditions, no mineral acid was added to the synthesis mixtures, which contained only the amphiphilic triblock copolymer P-123 (EO₂₀PO₇₀EO₂₀, Aldrich) as the pore-directing agent, silica (TEOS, Acros), zirconium precursor (ZrOCl₂·8H₂O), and water in an atomic ratio of 0.017:1.0:(0–0.1):220 P123:Si:Zr:H₂O. The mixture was stirred at 35 °C for 1 day and then hydrothermally reacted at 90 °C for another day in static conditions. The product was filtered, washed with a large amount of deionized water to remove the weakly adsorbed ions, and dried at 50 °C. The as-synthesized Zr–SBA-15 samples were heated at 250 °C for 3 h and at 500 °C for another 3 h to obtain the calcined samples. Samples were named as *x*Zr–SBA-15, where *x* is the atomic ratio of Zr/Si.

Characterization. XRD patterns were recorded in the 2θ range of 0.5–10° using a Philip X'pert Pro diffractometer with Cu Kα radiation operated at 40 mA and 45 kV. The pore structures of the samples were analyzed by nitrogen physical adsorption at liquid N₂ temperature using a Micromeritics TriStar 3000 system. Prior to the experiments, samples were outgassed at 200 °C for 6–8 h under vacuum (10^{−3} Torr). The elemental contents in bulk were determined by ICP-AES (ELAN 5000) on the mixed HF/HCl solution dissolved samples. The thermogravimetric (TG) analysis was carried out on a DuPont 950 TG analyzer. The heating rate was 10 °C/min and the carrier gas was dried air with a 50 mL/min flow rate. The ²⁹Si NMR spectra were measured using a Bruker MSL-300 spectrometer with zirconia rotors spun at 5 kHz. Data were acquired at 59.6 MHz, 20 μs pulse width, and 12 s recycle delay. The chemical shifts are given in ppm, using TMS as the standard. The X-ray absorption near edge spectroscopic (XANES) experiments were performed at beam line 15B at National Synchrotron Radiation Research Center facility at Hsinchu, Taiwan. Standard operating conditions were 1.5 GeV and 120–200 mA. Photon energies were calibrated using the L-edge of pure Zr foil.

Results and Discussion

Figure 1a shows the XRD patterns of the Zr–SBA-15 samples with Zr/Si atomic ratios varied in 0–0.1. It can be seen that the optimal ordering of the 2D-hexagonal *P6mm* structure was obtained for the mesoporous silica with Zr contents around Zr/Si = 0.05. The ordering decreased as the Zr contents were either greater or smaller than this ratio, and those with Zr/Si

Table 1. Elemental Analysis and Physical Properties of Zr-Incorporated SBA-15 Mesoporous Materials with Well-Ordered Structure

Zr/Si (gel)	pH (gel)	Zr/Si (solid)		BET S.A. (m ² /g)	pore vol. (cm ³ /g)	Φ _p ^a (nm)	PSD (nm)	W _t ^b (nm)
		ICP-MS	EDS					
0.01 ^c	2.25	0.017	0.018	802	0.891	6.9	1.8	5.0
0.02 ^c	2.20	0.020	0.029	860	0.857	7.0	1.9	5.2
0.03	1.68	0.029	0.047	756	0.783	6.4	2.3	5.3
0.04	1.46	0.044	0.067	811	0.988	6.6	2.4	5.2
0.05	1.40	0.059	0.078	779	0.902	6.6	2.0	5.0
0.06	1.42	0.061	0.087	738	0.835	6.1	4.1	5.6
0.06 ^c	1.70			859	0.983	6.3	1.8	5.5
0.07	1.40	0.072	0.101	711	0.791	3.6	4.0	8.1
0.07 ^c	1.65			837	0.951	6.2	2.3	5.3
0.08	1.33	0.081	0.100	710	0.810	3.6	4.2	7.5
0.08 ^c	1.37	0.089	0.119	841	0.907	6.6	2.2	5.8
0.10 ^c	1.23	0.108	0.151	769	1.062	6.2	2.0	5.4

^a Pore sizes were calculated from the N₂ desorption branch by the BJH method with Halsey equation. ^b Wall thickness. ^c Synthesized with NaCl.

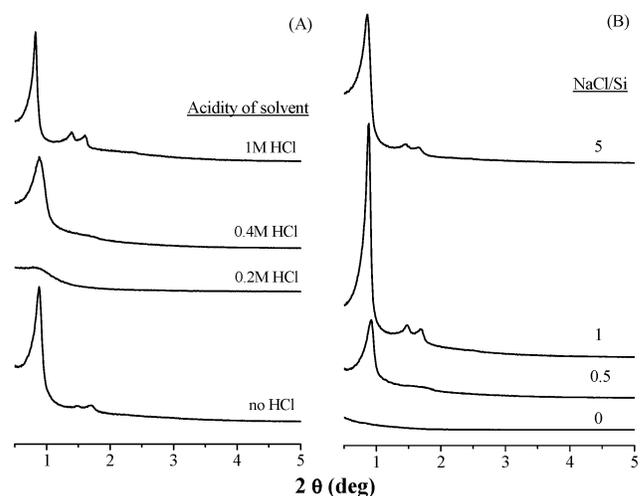


Figure 2. XRD patterns of (A) 0.07Zr–SBA-15 synthesized with various amounts of HCl and (B) 0.10Zr–SBA-15 synthesized with different amounts of NaCl salt.

ratio lower than 0.02 or higher than 0.08 were disorganized. Nevertheless, the ordered structure of the Zr–SBA-15 samples could be greatly improved by the addition of NaCl salt into the synthesis gel. Figure 1b demonstrates that the Zr–SBA-15 samples of very low (0.01) or relatively high (0.1) Zr/Si became highly ordered when NaCl was added.

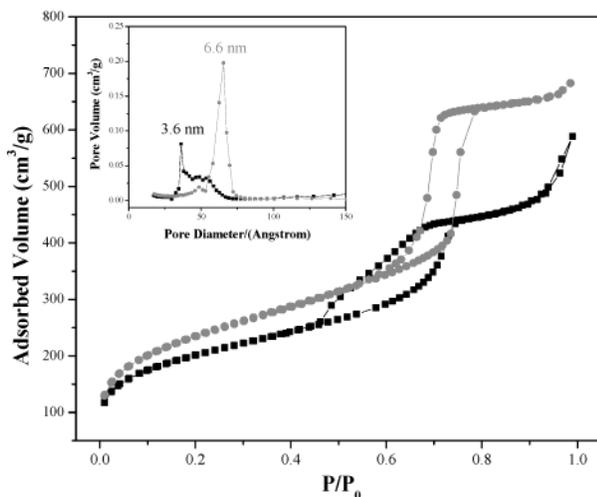
The phenomenon that a suitable amount of Zr alone present in the synthesis gel would lead to highly ordered SBA-15 structure is elucidated by the aqueous solutions of Zr(IV) salts probably providing enough acidity for TEOS hydrolysis. The pH values of the synthesis solutions are listed in Table 1. As the Zr content was increased from Zr/Si = 0.01 to Zr/Si = 0.1, the pH value of the solution was lowered from ca. 2.25 to 1.23. However, too much Zr seemed to hinder the self-assembly of the micelle and the silica precursor.

To further investigate the role of Zr, a series of experiments was carried out by synthesizing 0.07Zr–SBA-15 with various amounts of HCl. Figure 2a shows that a highly ordered sample was obtained using 1 M HCl, but the ordering was markedly decreased as the amount of HCl was reduced to 0.2 M. In contrast, a highly ordered sample could be obtained without any HCl. The pH value of the latter solution was ca. 1.4,

Table 2. Elemental Analysis by ICP-AES of Zr–SBA-15 Crystallized in Solutions of Different Acidities

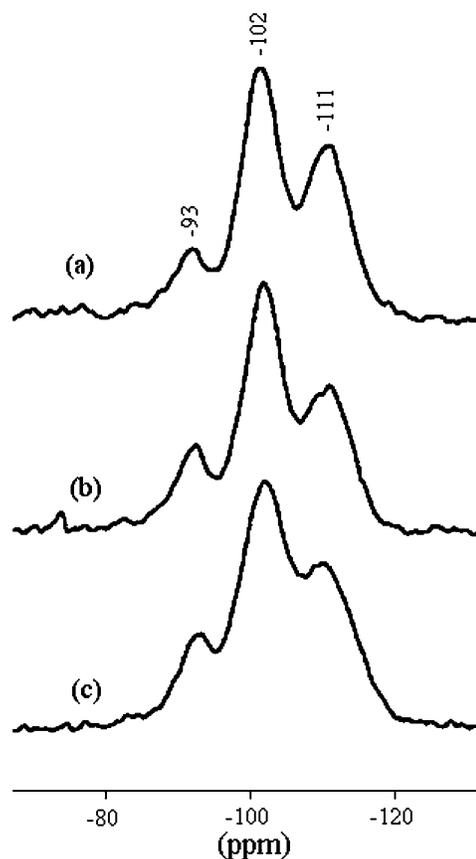
Zr/Si (gel)	Zr/Si (solid)			
	no HCl	0.2 M HCl	1 M HCl	2 M HCl
0.01	0.011		0.010	
0.02	0.025	0.022	0.019	0.017
0.03	0.029	0.030		
0.04	0.044	0.044	0.039	0.031
0.05	0.059	0.056	0.049	0.034
0.06	0.061	0.064	0.053	
0.07	0.072	0.075	0.056	
0.08	0.081	0.083	0.058	
0.09	0.106	0.099	0.055	
0.10	0.113	0.099	0.062	0.050
0.10 ^a	0.108			

^a Synthesized with the addition of NaCl.

**Figure 3.** N₂ sorption isotherms and pore size distribution of 0.8Zr–SBA-15 synthesized (●) with and (■) without NaCl.

which was more basic than the solution containing 0.2 M HCl. A similar influence of the amount of HCl on the ordering of the mesostructure was observed for Zr–SBA-15 with a Zr/Si atomic ratio in the range of 0.03–0.08. Based on these results, the role of Zr is likely more than just providing the acidity. It further reveals that protons and zirconyl ions are probably in a competitive position in self-assembly of the organic template and the inorganic precursor, which leads to the formation of ordered mesostructure. In a synthesis mixture of acidity greater than the isoelectric point of silica (pH ~ 2), the main interaction for the self-assembly of the polymer micelle and the silica precursor should be the I⁺X⁻S⁺ type electrostatic interaction, where I⁺ is the protonated surfactant, S⁺ is the protonated silanol group, and X⁻ is a counteranion. Therefore, well-ordered SBA-15 mesostructure is usually synthesized in a high concentration of HCl (>1 M). Without the addition of mineral acids such as HCl, the proton concentration is low. It is proposed that the zirconyl cation, when its concentration is great enough in the solution, may take the place of protons and adhere to either the hydrophilic side of the polymer micelle or the silanol group to form cationic species, which participate in the self-assembly process.

The zirconium contents in the highly ordered Zr–SBA-15 materials were determined by both ICP-AES and EDX techniques and the results are summarized in Table 1. The former technique provides the elemental

**Figure 4.** ²⁹Si MAS solid-state NMR spectra of as-made SBA-15 sample with Zr/Si atomic ratios of (a) 0, (b) 0.05, and (c) 0.10.

analysis of the bulk, while the latter gives composition information mainly concentrated on the surface. The atomic ratios of Zr/Si in the solids analyzed by both methods were found to be slightly higher than that in the synthesis gels. These results might be due to the incomplete hydrolysis of TEOS because the pH values of our synthesis mixtures were around 1.23–2.25 and near the isoelectric point of silica. It was reported that the hydrolysis rate of the silanol groups was slow under such conditions.¹⁶ In addition, the Zr contents analyzed by EDX were all greater than those by ICP-AES. It reveals that the zirconium species were likely more concentrated near the surface of the mesostructure framework than inside the bulk.

Table 2 compares the Zr contents in the Zr–SBA-15 samples crystallized in solutions of different acidities. All the samples, except 0.10Zr–SBA-15*, were prepared without the addition of NaCl. The Zr contents in the solid samples were proportional to those in the synthesis gel. However, the values increased when a relatively lower amount of HCl, such as 0.2 M HCl or no acid, was used instead of 1 M or 2 M HCl. On the other hand, the addition of NaCl salt in the synthesis gel, where no HCl was used, was found to have no significant influence on the amount of Zr incorporated in the SBA-15 mesostructure.

Figure 2b shows the ordered structure of 0.1Zr–SBA-15 as a function of the amount of NaCl added in the

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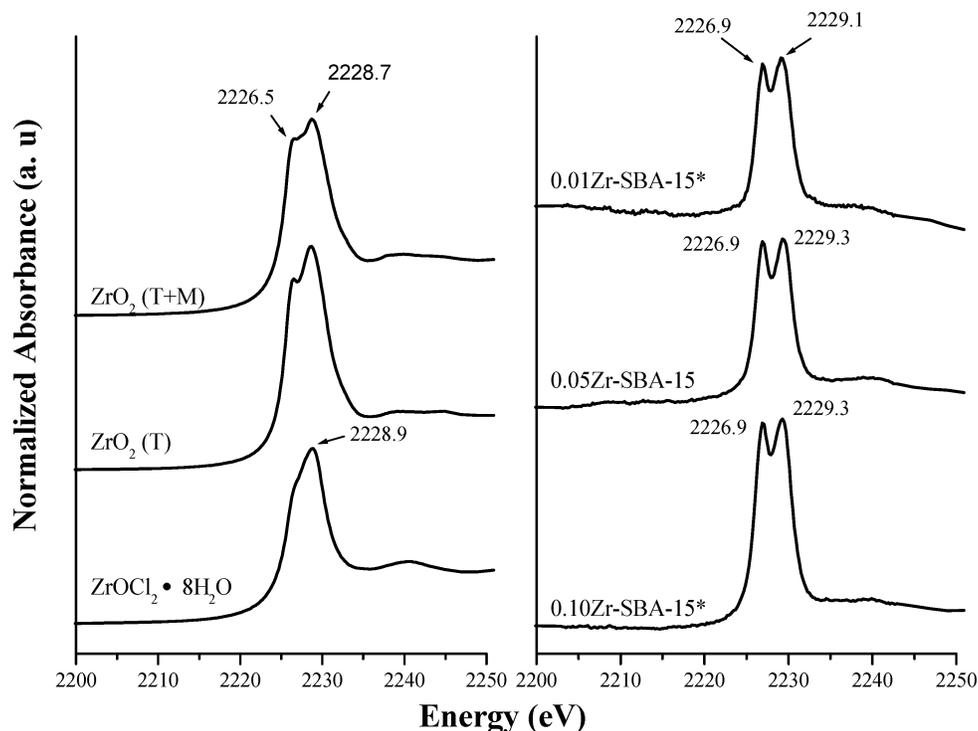


Figure 5. Zr L_3 -edge XANES of Zr-SBA-15 material of different Zr loadings and the reference samples.

synthesis gel. The optimal amount of NaCl used to achieve best order was the NaCl/Si atomic ratio being around 1. Moreover, the pore size distribution of Zr-SBA-15 was found to be markedly narrowed down when NaCl was added. Figure 3 shows that a sharp pore size distribution (PSD) was obtained for the sample prepared in the presence of NaCl, in comparison to the broad PSD for the sample without NaCl. Several other salts, such as LiCl, KCl, CsCl, NaBr, NaI, NaSCN, $\text{Na}_2(\text{SO}_4)$, and $\text{K}_2(\text{SO}_4)$, were also found to have a similar effect, but NaCl was the most efficient in improving the ordering of the mesostructure. It is also the most economical one among the salts. In the cationic surfactant¹⁷ or polymer^{18–23} templated system, it was well-documented that the ordered structure of the mesostructure materials could be improved by the addition of salts into the synthesis gels. The presence of salt in the synthesis gel was proposed to decrease the critical micelle concentration (CMC) and therefore facilitate the ordered arrangement of the mesostructures. Different from the recent reports of two research groups, which showed cubic $Ia3d$ mesoporous silica or organosilica were obtained in the presence of NaCl, only 2D hexagonal $p6mm$ phase was observed for Zr-SBA-15 in the present studies.^{22,23} To the best of our knowledge, this is the first example to prepare highly ordered mesoporous silica with metal

substitution by the addition of inorganic salts and under such mild synthesis condition.

The physical properties of the Zr-SBA-15 samples determined by N_2 sorption were summarized in Table 1. All the Zr-SBA-15 materials were found to have high BET surface area (711–860 m^2/g) and large pore volume (0.78–1.0 cm^3/g). Narrow PSD of ~ 2 nm and a narrow range of wall thickness of 5.0–5.8 nm were also observed for all samples except those with Zr/Si greater than 0.06 but synthesized without NaCl. Moreover, no significant blockage of the pore or reduction in pore diameter was found on the Zr-SBA-15 samples. These results imply that the Zr species should be incorporated in the silica framework instead of forming extraframework zirconia particles.

Figure 4 compares the ^{29}Si MAS solid-state NMR spectra of Zr-SBA-15 with that of pure siliceous SBA-15. No significant changes in the intensity of Q_2 , Q_3 , and Q_4 peaks, which appeared at -93 , -102 , and -111 ppm, respectively, can be seen. However, the peaks became broader and more seriously overlapping with each other as the Zr content in SBA-15 was increased, indicating that the local environment of Si became less regular when the Zr content in SBA-15 was increased. This is also an indication that Zr was probably incorporated in the framework of SBA-15.

Synchrotron radiation-based X-ray absorption spectra at the Zr L_3 -edge were taken because the data provided information on the local coordination symmetry of Zr. Figure 5 shows the X-ray absorption near edge spectra (XANES) of Zr-SBA-15 of different Zr loadings as well as those of the reference samples: ZrO_2 (tetragonal phase and a mixture of tetragonal and monoclinic) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The L_3 -edge spectrum of Zr(IV) is characterized by two absorption peaks, which are assigned to the electron transition from an initial state of 2p level to the excited states of predominantly 4d character. It

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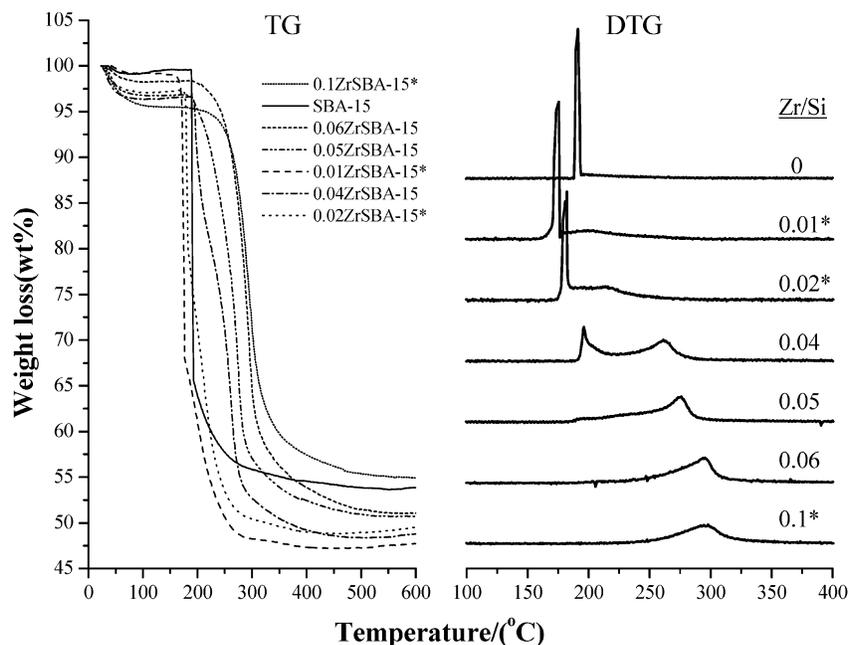


Figure 6. Thermogravimetric analysis profiles and their differential curves of Zr-SBA-15, synthesized without additional mineral acids, with various amounts of Zr. * synthesized with NaCl.

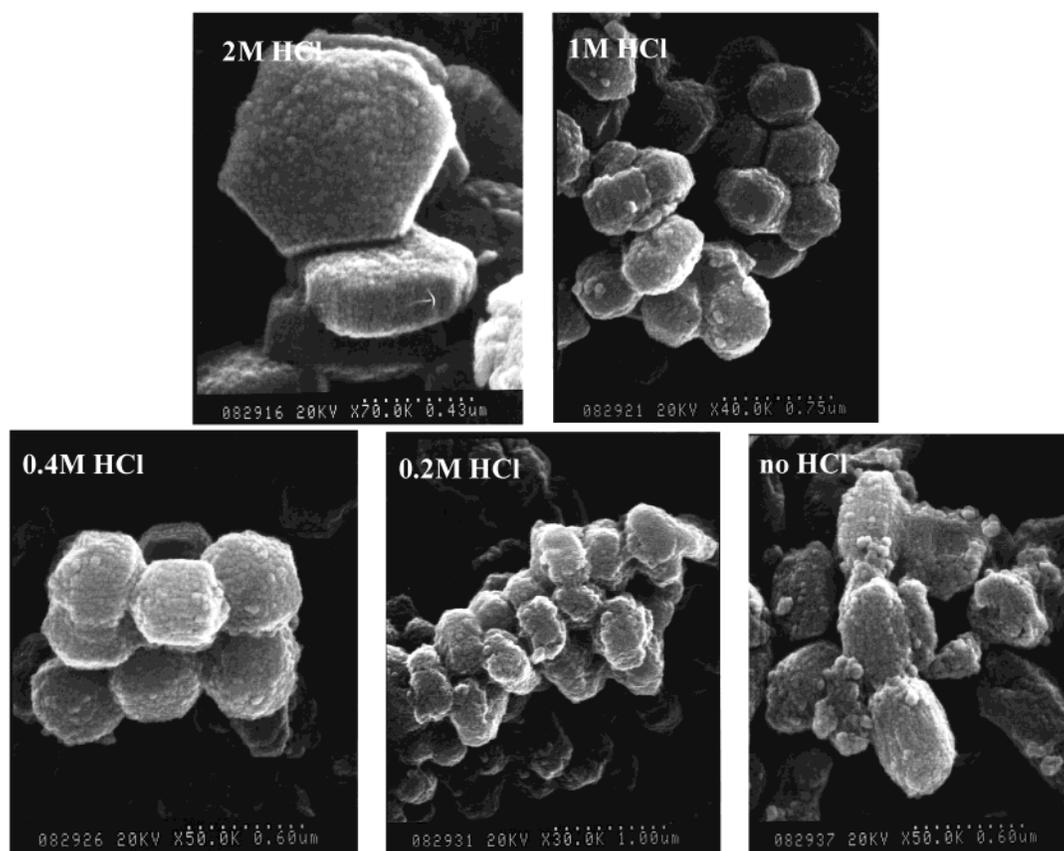


Figure 7. Morphologies of Zr-SBA-15 synthesized in solutions of different acidity; Zr/Si atomic ratio = 0.05, solvent = 0–2 M HCl.

is noticed that the two peaks for Zr-SBA-15 samples are better resolved than those of the references. Moreover, the intensities of these two peaks are almost the same for Zr-SBA-15, while those for the references are not. These results imply that Zr incorporated in SBA-15 should not be either forming ZrO_2 or present as zirconyl cation.

In $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Zr is in a distorted square antiprismatic arrangement of eight O atoms around Zr.²⁴ In tetragonal ZrO_2 , Zr is 8-coordinated and there are two sets of 4 Zr-O (at 0.2065 and 0.2455 nm) forming

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flattened and elongated tetragonal groups. In monoclinic ZrO_2 , Zr is 7-coordinated. The 4d orbitals of Zr in such low symmetric environments are split into several energy levels, and the splitting among the d-orbitals should be smaller than that of a highly symmetric field, such as t_{2g} and e_g in an octahedral field. That accounts for the poorly resolved peaks in the XANES of ZrO_2 and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The well-resolved peaks observed on Zr-SBA-15 samples imply that Zr is in a relatively symmetric coordination environment. Moreover, since the XANES spectra of Zr-SBA-15 did not have significant changes upon increasing the Zr loading, it is suspected that the Zr is octahedrally coordinated. The tetrahedral or cubic coordination is ruled out because the splitting between the 4d orbitals would be smaller than that of the octahedral one.

The thermal analysis technique was used to understand the interaction between the P123 triblock copolymer and the framework of the Zr-SBA-15 materials (Figure 6). Pure siliceous SBA-15 synthesized under strong acidic conditions (2 M HCl) was used as the reference sample. A sharp and single-step weight loss (~ 54 wt %) of P123 with decomposition temperature (T_d) around 180–200 °C was observed on the pure siliceous SBA-15, which was consistent with the literature results.¹⁰ When a small amount of Zr was incorporated into SBA-15, there was another weight loss that appeared in the range of 170–300 °C, indicating the presence of two kinds of interactions between the polymer template and the framework. The original weight loss shifts slightly toward lower temperature (ca. 170 °C), while another weight loss appeared at temperatures higher than that of pure siliceous SBA-15. Moreover, the low-temperature weight loss shrunk while the high-temperature one enlarged when the Zr loading was increased. When the Zr/Si ratio was greater than 0.6, only the weight loss at higher temperature (270–300 °C) was observed. The part of weight loss at lower temperature (170–210 °C) was suggested due to the decomposition of P123 interconnected with the silica surface. The shift of this peak toward lower temperatures for Zr-incorporated SBA-15 was probably due to a weaker interaction between the insufficient protonated polymer group and the silica surface. On the other hand, the part of weight loss at higher temperature was assigned to the decomposition of the polymer templates interacted with the surface zirconium species. The higher T_d indicates a stronger interaction between the zirconium species and the polymer template. These results are in consistency with that of the elemental analysis, which shows that the zirconium seems to concentrate on the surface of the silica mesopores.

It was also noticed that the addition of NaCl in the synthesis gels has little effect on the decomposition temperature of the surfactant (TG profiles not shown). These results in combination with the elemental analysis, which showed a negligible amount of Na^+ was incorporated in the mesoporous material, imply that the NaCl salt probably just varies the ionic strength of the synthesis gel and has no direct interaction with the species involved in the self-assembly of the micelle and silica precursor.

It was noticed that the morphologies of Zr-SBA-15 material changed as a function of the acidity of the

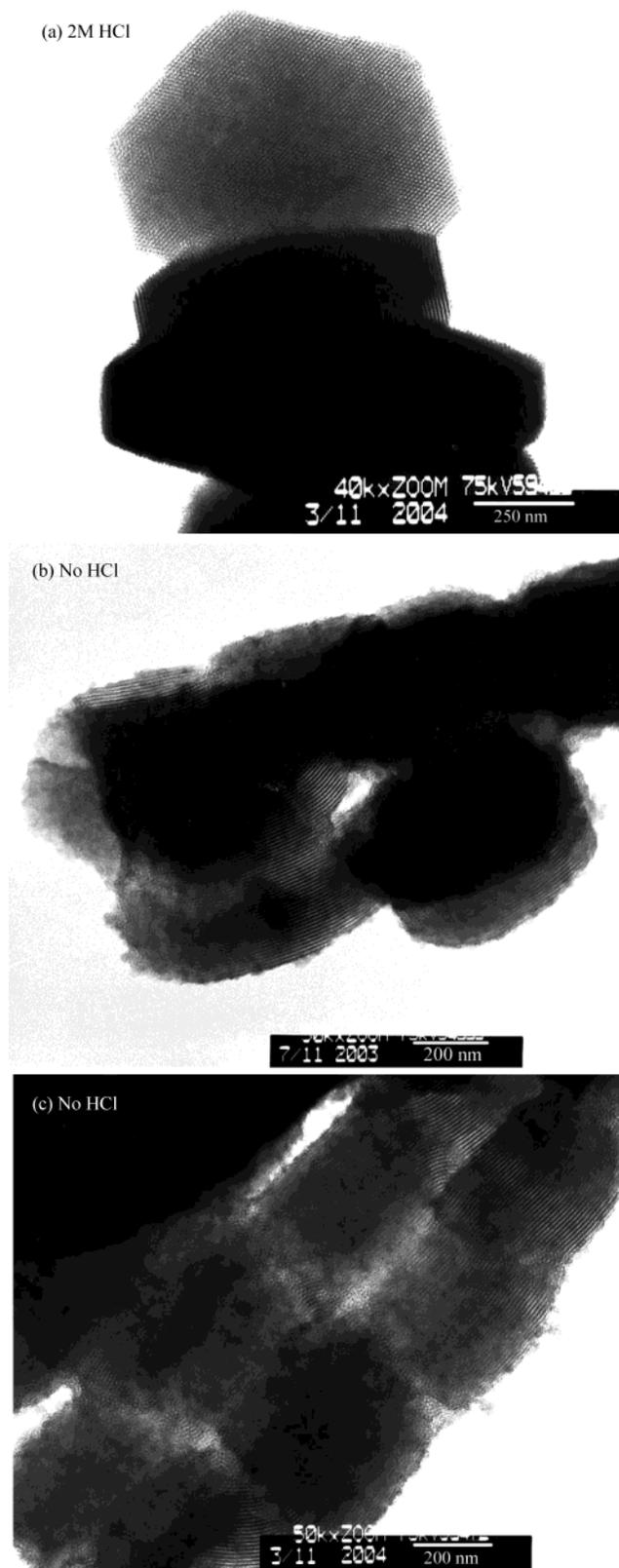


Figure 8. TEM images of Zr-SBA-15 samples of different Zr loadings and prepared in solutions of different acidity: (a), (b) Zr/Si = 0.05, and (c) Zr/Si = 0.10.

synthesis gels. The SEM photographs in Figure 7 show the variation in morphology of 0.05Zr-SBA-15 synthesized in 0–2 M HCl. With 2 M HCl, the material is a hexagonal platelet of ca. 0.5 μm width and 0.08 μm thickness. The material elongates along the thickness

and shrinks in hexagonal width as the acidity decreases. When the material was synthesized without the addition of HCl, a rodlike shape was obtained.

The TEM images in Figure 8 show the arrangement of channel pores in the samples of different morphologies. For 0.05Zr-SBA-15, the sample prepared in 2 M HCl has the channel pores well-aligned along the thickness of the hexagonal platelet, and the hexagon is the (001) plane. Figure 8a shows that the well-ordered hexagonal-arranged pores are clearly seen from the top of the hexagon and so are the channels along the side of the platelet. When the Zr-SBA-15 material was prepared without HCl, the morphology turned to a rodlike shape and the channel pores were aligned along the long axis of the rod. Moreover, in contrast to the strong dependence of the morphology and the pore arrangement on the acidity of the synthesis gel, the Zr content in Zr-SBA-15 has little effect. Figures 8b and 8c show that the Zr-SBA-15 material synthesized without HCl with Zr/Si of 0.05 and 0.10, respectively, has very similar rodlike shape and pore arrangement.

Conclusions

Highly ordered Zr-incorporated SBA-15 with Zr/Si atomic ratio up to 0.1 can be synthesized without the addition of mineral acids. The acidity self-generated by the Zr precursor should be enough to catalyze the hydrolysis of TEOS. The zirconyl ions might also play

an important role in self-assembly of the polymer surfactant and the silica through the $I^+X^-S^+$ type electrostatic interaction by adhering to either the polymer micelle or the silanol group and formation of cationic species. The addition of inorganic salts, especially NaCl, was found to efficiently enhance the ordered structure of the mesoporous Zr-SBA-15 materials. Moreover, the pore size distribution was greatly sharpened with the addition of NaCl. This synthesis method is environmental friendly and efficient in incorporating Zr(IV) ions into the framework of the mesoporous silica sieves. It was also found that this method could also be applied to other systems where the metal precursors can generate proper acidity in the synthesis solutions. We have also successfully synthesized a series of Al, and Fe-incorporated SBA-15, by a similar method. The details of the work will be reported in the future.

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