Synthesis of Zr-containing SBA-15 with Hollow Spherical Morphology

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Zr-containing SBA-15 materials with hollow spherical morphology were synthesized via adding zirconium into SBA-15 synthesis solution and adjusting pH to about 4–5 with ammonia water. The hollow spherical mesoporous materials were observed in micron scale, and the shell thickness was about 100 nanometers. Zirconium was well dispersed inside the mesoporous structure. The sulfated hollow Zr-doped SBA-15 spheres showed better catalytic activity than conventional SBA-15 spheres in dehydration reactions.

Pure siliceous SBA-15 shows weak catalytic activity due to the charge equilibrium of silicon–oxide tetrahedron,[1] which is unfavorable to the further application of SBA-15. To enhance functionality and applications of SBA-15, various metal atoms have been introduced to the silica framework.[2] And much attention is being focused on zirconium-containing mesoporous materials, concerning their acidity and catalytic activities in organic reactions.[3–8] Several methods have been used to prepare zirconium-containing SBA-15, such as direct synthesis,[3] chemical solution decomposition,[4] microwave synthesis,[5] and NH_3/water vapor-induced internal hydrolysis.[6] We previously reported a direct synthesis of Zr–SBA-15 with a Zr/Si molar ratio ranging from 0 to 2.32 cotemplated by cetyltrimethylammonium bromide (CTAB) and P123.[7] The overall morphology of a mesoporous material is as important as the internal structure for certain practical applications. Thus, developing efficient routes to prepare Zr-doped SBA-15 materials with special morphology has been a challenging topic.

Hollow spherical materials with ordered pore channels are currently attracting attention due to their potential advantages over conventional mesoporous materials in drug delivery, adsorption, and catalysis.[8] Micrometer-range hollow SBA-15 spheres have been previously synthesized via supercritical CO_2 in water emulsion.[9] In this study we demonstrated a facile route to prepare hollow SBA-15 microspheres simultaneously doped with zirconium, which indicated high acid catalytic activity after being sulfated.

Typically, SBA-15 synthesis solution was prepared using block polymer globular aggregates as template and tetraethyl orthosilicate (TEOS) as silica source.[10] The zirconium was directly added to the solution, and then ammonia water was used to adjust pH to 4–5. A gel containing zirconium ammine complex was formed and hydrothermally treated at 100 °C for 48 h. The solid samples were filtered, washed, dried and calcined at 550 °C for 5 h to obtain the final products, hollow mesoporous spheres. Hollow Zr–SBA-15 spheres (noted as ZS01 and ZS03) were prepared corresponding to a Zr/Si molar ratio of 0.1 or 0.3. Pure siliceous SBA-15 was synthesized in the same solution without introduction of zirconium source and was noted as ZS00.

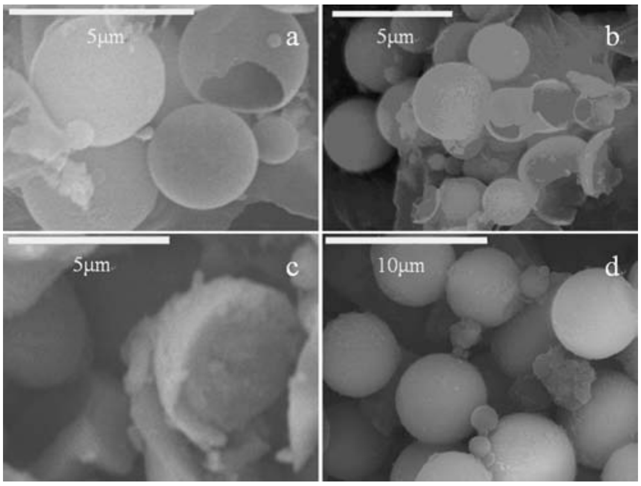

Figure 1. SEM images of Zr–SBA-15 microspheres, ZS03, ZS01 (a), (b) and ZS00 (c), (d).

SEM images of samples showed that the hollow spherical mesoporous Zr–SBA-15 was in microns in diameter and that the shell thickness was about 100 nanometers (Figures 1a and 1b). The Zr/Si ratio and structural properties of samples were determined by inductive coupled plasma emission spectrometry (ICP) and N_2 adsorption–desorption, respectively. The results are listed in Table 1. These microspheres, whether hollow or not, all demonstrate the typical characteristics of mesoporous structure. The well-resolved low-angle XRD patterns (Figure 2a) showed the typical peaks of ordered 2D hexagonal structures.[11] The intensity of diffraction peaks is decreased with the increase of zirconium loading. As shown in Figure 3, the entire zirconium-containing materials exhibit reversible type IV isotherm that is typical of mesoporous materials.[11] The pore size distribution of those ZS samples shows a similar narrow distribution with diameter around 5.8 nm, which is consistent with TEM images.

Typical TEM images of hollow Zr–SBA-15 spheres showed the intactness of the ordered mesoporous structure even after pH-adjustment. Energy dispersive X-ray analysis (EDX) indicated the elemental composition of the sample and the existence of zirconium. (Figure 2b). Wide-angle XRD patterns (inset in Figure 2a) also did not exhibit any peak corresponding to aggregated zirconium. These results proved that the zirconium had to be highly dispersed into the mesoporous structrue of SBA-15.

The hollow Zr-doped SBA-15 materials were treated with aqueous H_2SO_4 ($1\,\mathrm{mol\,L^{-1}}$) overnight. The sulfated Zr–SBA-15 materials were used as catalyst for preparing ketal from the dehydration of cyclohexanone and ethanediol (Table 1). The reaction results demonstrated that the catalytic activity of sulfated Zr-containing SBA-15 materials was much better than the pure siliceous SBA-15 materials (ZS00).

Table 1. Physicochemical properties of samples

Sample	Zr/Si molar ratio		BET surface area	Pore diameter	Pore volume	Ketal yield	Ketal selectivity
	Gel	Product	/$m^2\,g^{-1}$	/nm	/$cm^3\,g^{-1}$	/%	/%
ZS00	0	0	712	6.93	1.06	11.30	100%
ZS01	0.1	0.1	676	5.82	0.67	69.09	100%
ZS03	0.3	0.3	463	5.63	0.52	77.82	100%

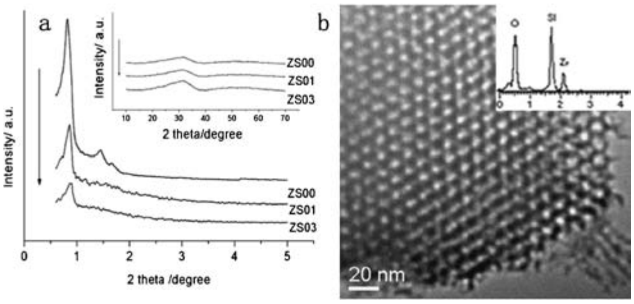

Figure 2. XRD patterns of samples (a); TEM image of ZS03 with EDX (b).

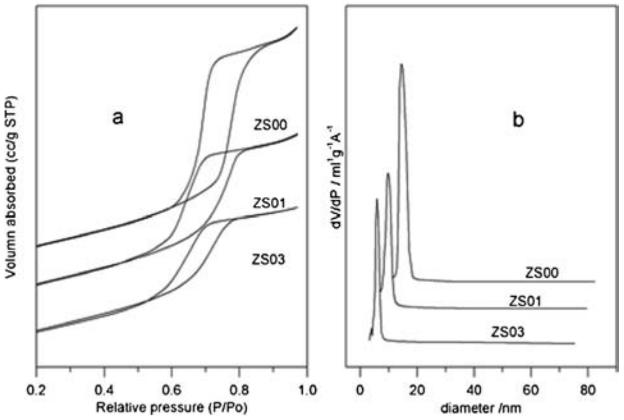

Figure 3. Adsorption–desorption isotherm of nitrogen at 77 K and BJH pore size distribution of samples (a), (b).

The results suggested that the formation of hollow mesoporous microspheres could be immediately involved with zirconium ammine complex. The SBA-15 materials (ZS00) without the zirconium ammine complex were not hollow (Figures 1c and 1d).

The self-assembled polymer–silica colloid system contains hydrophilic domains (solvents, water and ethanol from hydrolyzed silicate ester) and hydrophobic domain (appreciable copolymer coils combined with alkoxy silane).[12] The Zr^{4+} complex species were highly dispersed in the system and probably induced the further polycondensation due to the salting out. On the other hand, zirconium ammine complex may interact strongly with hydrophilic chains of surfactants likely through dative bond, which could compromise interface energy of polymer–silicate composites. Both effects will be beneficial to the homogenous domain self-aggregation and enhance the phase separation between the hydrophilic domains and the hydrophobic domains.[13] Thus the whole colloid system was favorably separated into binary macrophases. The core was solvent and the shell was polymer–silica–metal oxide system. The hollow spherical solids were achieved after solvent evaporated, and the heteroatoms were also dispersed into mesoporous structure of SBA-15.

In summary, hollow Zr-containing SBA-15 microspheres were synthesized via a facile method. The zirconium ammine complex is the key factor in the formation of hollow spheres and dispersion of heteroatom. These hollow mesoporous Zr-containing SBA-15 spheres displayed much better catalytic performance than conventional Si–SBA-15 spheres in dehydration reactions.

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