Synthesis of Transition-metal Containing MSU Mesoporous Silica Molecular Sieves

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Novel Zr-, V-, and Ti-containing mesoporous MSU silica molecular sieves are prepared by the hydrolysis of tetraethylorthosilicate and transition-metal ion precursors in an acidic media (pH=2), with polyoxyethylene stearyl ether as template.

Recently, the discovery of mesoporous molecular sieves has attracted great attention in the fields of catalysis, separation, ion-exchange, and advanced material science. A series of mesostructures, including M41S (MCM-41 and MCM-48),[1] HMS,[2] and SBA-n,[3] have been synthesized successfully with different templating schemes. More recently, Pinnavaia and co-workers[4] have prepared another mesoporous materials (MSU) by using nonionic, nontoxic, low-cost, and biodegradable polyethylene oxide surfactants as the structure-directing (templating) agents. Attard et al[5] have shown that nonionic polyethylene oxide (N^0) surfactants in liquid crystalline form function as authentic templates for the synthesis of M41S silicas with hexagonal, cubic, and lamella structure. Bagshaw et al[6] have prepared mesoporous alumina molecular sieves via N^0I^0 pathways. All these mesoporous molecular sieves may have significant benefits in catalytic application, since the catalytically important metal atoms can be incorporated into the templated silica framework. Although Ti-,[7,8] Zr-,[9] and V-substituted[10,11] MCM-41 and HMS silicas have been prepared successfully, and found to be active as catalysts in oxidation reactions with both H_2O_2 and tert-butyl hydroperoxide (TBHP) as oxidants, very few transition-metal other than Ti[12] substituted MSU mesoporous molecular sieves have been reported.

In contrast to the synthesis conditions used previously[4] for MSU silicate mesophases, here we report on the synthesis of MSU materials in acidic media with pH=2, which is the iso electric point of silica.[13] Under this condition, the driving force for the formation of mesoporous structures may be the hydrogen-bonding force between neutral silicon precursor and the template micelles. In addition, Zr, V, and Ti atoms are incorporated into the silica-based MSU structure by this improved method, and physical characterization confirmed that the transition-metal atoms were highly dispersed in the framework structures.

MSU metallosilicates were prepared from tetraethylorthosilicate (TEOS) as the silicon source. Aqueous solutions of NH_4VO_3 and $ZrOCl_2$, as well as tetrabutylorthotitanate (TBOT) in isopropyl alcohol served as the transition-metal ion precursors. Polyoxyethylene (10) stearyl ether ($C_{18}EO_{10}$) was used as template. In a typical synthesis, $C_{18}EO_{10}$ was dissolved in deionized water with magnetic stirring at 50 °C, the pH value of the solution was adjusted to 2 with aqueous hydrogen chloride acid (HCl). Under vigorously stirring, a portion of TEOS was added into the $C_{18}EO_{10}$ solution. While the clear solution became turbid, the mixture of the remained TEOS and determined amount of transition-metal ion precursor was added dropwise under vigorously stirring. The final composition of the reaction mixture was: 1TEOS: $0.27C_{18}EO_{10}$: $200H_2O$: 0.02M, where M was the transition-metal ion precursors. This sol-gel system was stirred vigorously at 50 °C for 36 h. Then products were centrifuged, washed with deionized water, air-dried, and calcined in air at 873 K for 5 h to remove organic template.

Table 1. The chemical composition and structural properties of the samples

Samples	Si/M[a] Gel	Product.	d_{100} /nm	a_0[b] /nm	BET Area /m²/g	BJH Pore size /nm	Wall Thick-ness /nm
MSU	—	—	4.3(4.6)[c]	4.9(5.4)	960	2.7	2.2
Zr-MSU	50	53	4.8(5.1)	5.6(5.9)	979	3.0	2.6
V-MSU	50	50	4.4(4.9)	5.1(5.7)	956	2.6	2.5
Ti-MSU	50	52	4.7(5.3)	5.4(6.1)	966	2.6	2.8

[a] M=Zr, V, and Ti respectively. [b] $a_0=2\times d_{100}/\mathrm{sqrt}(3)$.
[c] The figures in parenthesis are for as-synthesized samples.

Table 1 lists the chemical compositions and some structural properties of the calcined MSU mesoporous molecular sieves. For calcined Zr-, V-, and Ti-containing MSU mesoporous materials, the Si/M ratios were very close to those used in the precursor gels, indicating a high transition-metal efficiency in such cases.

Figure 1 shows the adsorption/desorption isotherms and the Barrett-Joiner-Halender pore size distribution for calcined Zr-MSU, which can be taken as the representative of the other samples. The BET areas, BJH pore sizes, as well as wall thickness are listed in Table 1. The well-defined step in the adsorption isotherms at P/P_0=0.2-0.4 is the characteristics of

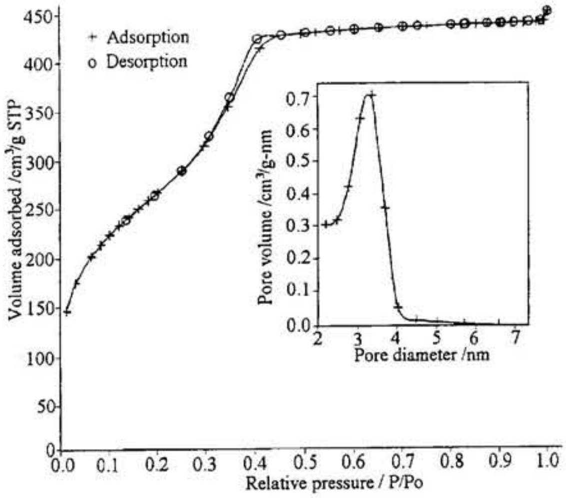

Figure 1. Nitrogen adsorption and desorption isotherms for calcined Zr-MSU. (Inset) Corresponding Barrett-Joiner-Halender Pore size distribution determined from thr N_2 desorption isotherm. Prior to measurement the sample was evacuated at 423 K and 6.67×10^{-4} Kpa for 12h.

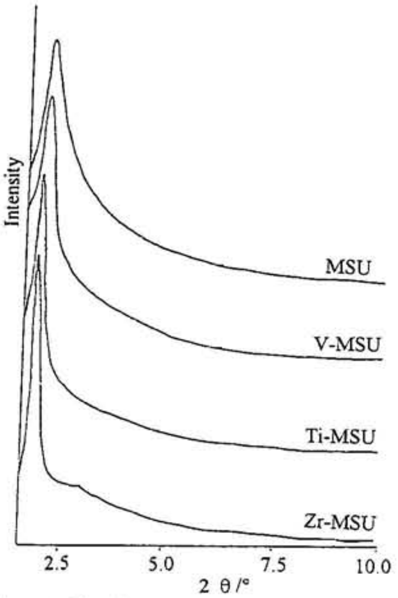

Figure 2. The XRD patterns of the calcined samples.

framework-confined mesoporous filling. The BET specific surface areas and BJH pore size, which determined by the micelles, are close to each other.

Like to the mesostructures prepared by both electrostatic and neutral templating pathways, the synthesized MSU mesoporous materials have the structure of hexagonal-packing. Powder X-ray diffraction (XRD) patterns of the calcined pure silica and transition-metal containing MSU mesoporous materials are shown in Figure 2. The XRD patterns for all these samples exhibit single low-angle diffraction peak, which were consistent with those previously reported for MSU mesoporous molecular sieves,[4] but different from the MCM-41 materials. The absence of higher order Bragg reflections might be due to the weak hydrogen-bonding forces that govern the neutral N^0I^0 templating process and the small scattering domain size effect.[4] The removal of organic templates by calcination lead to the decreasing of the d_{100} spacing and the increasing of the scattering intensity. These suggest that the calcination process may promote the further condensation of silica-based framework structures. Upon introducing of transition-metal atoms, the d_{100} spacing and a_0 shifted to the higher value. Furthermore , the diffraction intensity of transition-metal atom containing samples was higher than that of pure silica analogue. This maybe because the introducing of transition-metal atoms can cause an improvement of the templated silica structures.

The speciation of Zr, V, and Ti was investigated using diffuse reflectance UV-Visible (DR UV-Vis) spectroscopy. Since the DR UV-Vis is very sensitive to the condensed phase of the metal oxide. Figure 3 shows the DR UV-Vis spectra of Zr-, V-, and Ti-containing MSU materials and their pure silica analogue. The absorption intensity of transition-metal containing samples was magnitude stronger than that of pure silica sample. The absence of absorption band in the region of crystalline metal oxide suggested that there were no condensed ZrO_2, V_2O_5 and TiO_2 species. Considering the high transition-metal contents, we can conclude that the Zr, V and Ti atoms might be highly dispersed in the silica-based MSU mesostructures. As for the Zr-, V-, and Ti-substituted MCM-41 and HMS materials, the absorption band at 205 nm, 240 nm, and 225 nm in DR UV-Vis spectra of Zr-MSU, V-MSU, and Ti-MSU might be the characteristic absorption band of Zr, V, and Ti in a tetrahedral environment.[7-11] The absence of crystalline ZrO_2, V_2O_5, and TiO_2 phases was also verified by Raman spectroscopy, which showed no characteristic vibration band corresponding to those metal oxide crystals.

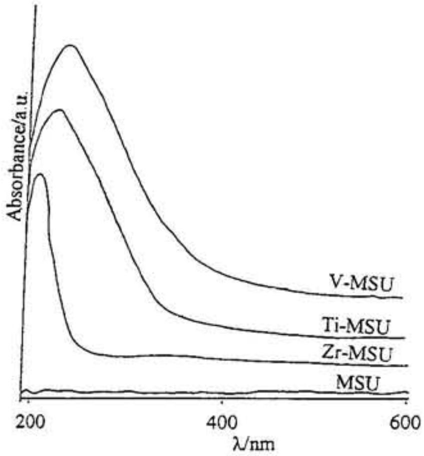

Figure 3. The DR UV-Vis spectra of the calcined samples.

Catalysts based on transition metal substituted forms of MCM-41 and HMS have been reported to be of use in a variety of oxidation reactions, consequently it may be expected that the Zr-, V-, and Ti-MSU materials, described above, may have similar properties. Such studies are underway and will be reported later.

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