Efficient Incorporation of Metal Oxides into Neutral Surfactants-templated Mesoporous Silicas

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We provided a two-step synthetic method for convenient and efficient incorporation of metal oxides into the mesoporous silicas templated with neutral surfactants at room temperature.

Recently, the neutral surfactant-templated mesoporous silicas have attracted much attention because the neutral surfactants are usually biodegradable and natural friendly. Moreover, the neutral surfactant-templated mesoporous silicas possess thicker wall thickness than the cationic surfactant-prepared MCM-41.[1] In general, a highly acidic condition (pH < 2.0) was required to synthesize the neutral surfactant-templated silicas. It is well known that most of metal ions are well dissolved in highly acidic solution but fast condenses to metal oxides in neutral and alkaline aqueous solution. The metal oxides introduced into the neutral surfactant-made mesoporous silica is relatively difficult to be achieved in a highly acidic solution. Although post-grafting[2,3] or hydrothermal treatment[4–11] was performed to introduce the metal oxides on or into the mesoporous silica, an efficient synthetic method applied systematically to the metal oxides incorporation is still desired. In this study, we proposed a two-step method to effectively incorporate the heteroatom of Al, Ti, or Zr into mesoporous silica materials templated with triblock copolymer in a near neural media (pH ≈5.0) at room temperature.

Basically, the metal oxide incorporated mesoporous silicas were synthesized via an acid-hydrolysis of the tetraethyl orthosilicate and metal alkoxides in the presence of neutral surfactants at pH ≈1.0, and then a fast self-assembling reaction between surfactant and silica and a rapid precipitation of metal oxides would occur simultaneously in an aqueous solution of pH value around 5.0. Typically, 1.0 g of P123($EO_{20}PO_{70}EO_{20}$) was dissolved into (30.0–60.0) g of water and combined with (7.08–9.44) g 37 wt % HCl, 4.6–5.8 g of tetraethyl orthosilicate (TEOS) and desired amount of metal oxide precursors to form a clear solution. The silica/metal molar ratio in the gel-solution was adjusted within a range of 20–60. The precursors of aluminum, titanium, and zirconium oxides are, aluminum isopropoxide, titanium(IV) isopropoxide, and zirconium(IV) isopropoxide, respectively. After stirring for 6–10 min, that clear solution was poured directly into 300 mL of an aqueous solution at pH value of 4.5–5.5, prepared with 8.12 g of CH_3COONa, (1.0–2.0) g of NaOH and 300 mL of water. Then, white precipitate was formed within seconds. Filtration, washing, and drying gave the solid product. The yield is typically higher than 80% based on silica recovery. The organic template was removed by calcination at 560 °C for 6 h in air.

Figure 1a shows the XRD patterns of the calcined metal oxides incorporated mesoporous silicas (denoted as M–MS; M = Al, Ti, Zr) synthesized from P123-HCl-H_2O-TEOS-metal alkoxides components with the silica/metal molar ratio of 20. At the low-angle range of 0.5–2°, one can clearly find a broad peak, which can be assigned to the disordered mesostructure. However, at high angle range of 25–50° no apparent peaks were observed, which indicates that no crystal phase of metal oxide was formed during the synthetic or calcination process. In parallel to the broad XRD patterns, the representative TEM images of the M–MS particles show that the mesostructure is wormhole-like and the particle size distribution is broad from tens to 200 nm (as shown in supplementary materials; Figure S1). With the analysis of the N_2 adsorption–desorption isotherms (Figure

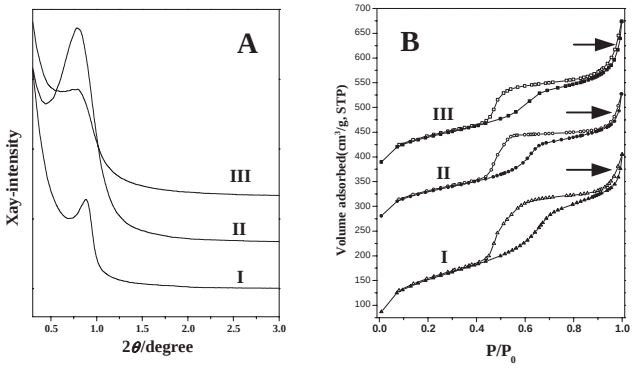

Figure 1. The XRD patterns (A) and N_2 adsorption–desorption isotherms (B) of calcined different metal oxides incorporated into mesoporous silica of the silica/metal molar ratio = 20 synthesized from P123-H_2O-HCl-TEOS-metal alkoxides-(AcONa + NaOH) compositions around pH value of 5.0. Sample I. Aluminum oxide; II. Titanium oxide; III. Zirconium oxide. The N_2 adsorption isotherms of samples II and III were vertically shifted by 150 and 300 $cm^3 g^{-1}$, respectively.

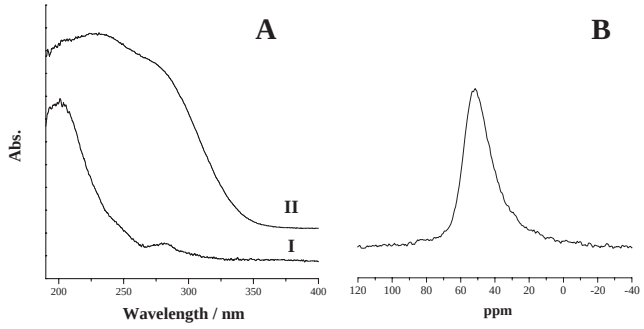

Figure 2. (A) The reflectance UV–vis spectrum of the calcined mesoporous sample with Si/M molar ratio of 20. Sample I. Zr–MS; Sample II. Ti–MS; (B) The ^{27}Al MAS NMR spectrum of the calcined Al–MS sample with Si/Al molar ratio of 20.

1b), all samples show a capillary condensation at $P/P_0 \approx 0.6$ as the conventional P123-templated mesoporous silica, and an extra absorption at $P/P_0 \approx 0.9$ (denoted by arrows). The appearance of the additional adsorption at $P/P_0 \approx 0.9$ is ascribed to the filling of the textural mesoporosity resulting from the inter-aggregation of the fundamental nanoparticles.[12] In addition, all these samples possess the microporosity of abut $0.05\,cm^3g^{-1}$. The thermogravimetric analysis (TGA) plots of the as-synthesized M–MS samples show that the weight loss by the use of P123 surfactant between 150 and 250 °C is about 50–55 wt % (Figure S2). The high surfactant content indicates that the P123 surfactants can thermodynamic-favorably self-assemble with the mixture of silica and metal oxides. The physical properties of the M–MS mesoporous silica were listed in Table 1. All M–MS samples possess the advantages of high surface area ($450–530\,m^2\,g^{-1}$) and large pore size (5.0–5.7 nm) and pore volume ($0.4–0.63\,cm^3g^{-1}$) as well as the pure-silica ones. Comparing the Si/M ratios in the gel and in the products, one can see that the metal content is almost the same with the added amount. Only in the Al–MS, the aluminum content is relatively lower. This is because the aluminum-incorporation leads to partial negative charge on the silica framework. The more negative charged inorganic has less self-assembling capability with the $–CH_2CH_2–O^{\delta-}$ chain in the P123 surfactants. Consequently, we can use the convenient method to obtain the nano-sized M–MS materials by using neutral surfactant as template at room temperature.

Table 1. The physical properties of the different metal oxides incorporated mesoporous silicas synthesized with P123 surfactant

Entirety[a]	Si/M (gel)	Si/M (M–MS)	d_{100}/ nm	S_{BET}/ cm^2g^{-1}	V_p/ cm^3g^{-1}	W_{BJH}/ nm
Pure silica	∞	∞	9.3	468	0.48	5.0
Si/Al	20	30	8.5	528	0.63	5.7
Si/Ti	20	19	9.5	441	0.50	5.3
Si/Zr	20	18	9.3	484	0.41	5.1

[a]S_{BET}, the BET specific surface area, V_p, total pore volume obtained from $P/P_0 = 0.99$; W_{BJH}, the pore diameter calculated using the BJH method. The Si/M ratios in the M–MS were recorded by ICP and EDS analysis.

To further identify the homogeneous incorporation of the metal oxide, the UV–vis spectra of Ti–MS and Zr–MS samples with M/Ti ratio of 20 were shown (Figure 2a). The absorption band maximum is observed at about 226 and 270 nm in the Ti–MS sample, and that is characteristic for the tetrahedral- and octahedral-coordinated Ti species among the amorphous silica framework. The Zr–MS sample is found to have an absorption band around 210 nm, which are usually attributed to O^{2-} to an isolated Zr^{4+} in a tetrahedral configuration. Moreover, Figure 2b shows the ^{27}Al MAS NMR spectrum of the calcined Al–MS sample with the Si/Al = 20. Notably, only framework aluminum oxide (at ≈51 ppm) was detected. This result indicates that Al species was stably introduced into the siliceous framework at four-coordinated sites. The catalytic activities of Al–MS sample towards the cumene cracking reaction have been examined. We found that the Al–MS can catalyze cumene conversion and the conversion increases with the temperature to about 14% at 400 °C (Figure S3). Accordingly, the M–MS catalysts have been successfully prepared with the neutral surfactant P123.

Here we try to explain the main concepts of our synthetic method. From our previous work,[13] we recognized that the P123 neutral surfactant could mutually combine with silica species at pH around 5.0 to form the mesostructured silicas in seconds.[13] Moreover, most of the metal oxides fast precipitate at neutral pH value. With the matching on the reaction rates between the self-assembling of silica and P123 neutral surfactant and the precipitation of metal oxides, the metal oxides, therefore, could be homogeneously incorporated into the silica framework of the P123-templated mesoporous silicas. When the pH value is less than 3.0 or higher than 6.0, the self-assembling reaction of neutral surfactant and silica is faster than the metal oxide precipitation and then the mesoporous pure silica was obtained instead. At pH > 6.0, the silica species possess a highly negative-charged surface and no mesostructured silica was formed.

In conclusion, we provided a theoretically designed synthetic method to prepare metal oxides incorporated mesoporous silicas efficiently and conveniently. This route could be extended widely to prepare other M–MS materials of different metal oxides, pore size and forms with other metal oxides precursors and different neutral surfactants. Since the particle size is close to nano-dimension and the wall thickness is thick, the stable M–MS would possess the better framework accessibility and connectivity to be much higher catalytic activity toward large-molecule reactions.

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