Synthesis of Mesoporous Silica Molecular Sieves *via* a Novel Templating Scheme

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Abstract: Mesoporous silica molecular sieves have been synthesized under mild conditions by using *in situ* prepared N, N-dimethyldodecylamine oxide as template.

Keywords: Mesoporous silica molecular sieves, N, N-dimethyldodecylamine oxide, Synthesis.

The discovery of M41S family of mesoporous molecular sieves by Mobil researchers [1,2] has stimulated considerable interest in the use of these materials as catalysts, catalyst supports, as well as adsorbents[3,4]. In the original report[1,2], MCM-41 was prepared from a self-assembly process which involves electrostatic interactions between positively charged quaternary ammonium micelles (S^+) and inorganic anions (I^-) used as framework precursors. Huo *et al* [5] extended the electrostatic assembly approaches by proposing four complementary synthesis schemes (S^+I^-, S^-I^+, $S^+X^-I^+$, and $S^-X^+I^-$). Recently, a number of surfactants, including neutral alkylamines [6], polyethylene oxides[7], gemini surfactants [8], and amphiphilic triblock copolymers[9], have been used as the structure directing agents for the synthesis of mesoporous molecular sieves. Otherwise, several other surfactants are of potentials as the templates for the synthesis of mesoporous materials. Among those surfactants, tertiary amine oxide might be a good candidate, because it contains two different hydrogen-bonding centers (N and O) and exhibits cationic nature under acidic conditions and nonionic nature under neutral and basic conditions. Like alkylamines and polyethylene oxides, it can be used to direct the formation of mesostructures through hydrogen-bonding forces between inorganic precursors and tertiary amine oxide. As far as we are aware, however, it has not been involved in the synthesis of the mesopores yet.

In this paper, it was shown that N, N-dimethyldodecylamine oxide (DAO) is really a promising template for the mesoporous silica molecular sieves. Furthermore, a novel and convenient templating scheme was also established where the DAO was synthesized *in situ* from N, N-dimethyldodecylamine and aqueous H_2O_2.

In a typical synthesis, 2.0 ml N, N-dimethyldodecylamine was dispersed in 5.0 ml H_2O at 60 °C. With magnetic stirring, 1.0 ml H_2O_2 (30%wt) was added dropwise into the above mixture. The reaction was carried out at 60 °C for 3.5 h, then at 75 °C for 12 h. This template solution was then cooled to room temperature. Under vigorous stirring, the determined amount of tetraethylorthosilicate (TEOS) was introduced dropwise by following recipe 1 TEOS: 0.5 DAO: 25 H_2O. Allowing the resultant gel to age under moderate stirring at room temperature for 48 h, the product was centrifuged, washed with de-ionized water, air-dried, and calcined in air at 873 K for 5 h to remove the organic template. On the other hand, template removal was also achievable by solvent extraction where 1 g of the as-synthesized product was suspended in 50 ml solvent (ethanol or acetone) under stirring for about 1 h. Then the sample was centrifuged, washed with extracting solvent, and air-dried at 353 K.

Powder x-ray diffraction (XRD) patterns of the as-synthesized, solvent-extracted, and calcined products (designated as LZC, LZC-EE, LZC-AE, and LZC-C, respectively) are depicted in **Figure 1**. All patterns were similar and exhibited a broad single diffraction peak corresponding to the d spacing of 4.24, 3.98, 3.90, and 4.12 nm, respectively. Higher order Bragg reflections were not resolved. Analogous diffraction patterns have been observed for hexagonal mesostructures prepared both by electrostatic and neutral templating schemes[6,7]. The absence of higher order reflections is attributed to the lack of long-range crystallographic order and/or small scattering domain size effect[7,8]. After the removal of template by calcination or by solvent extraction, the d spacing shifts to a small value, which suggests that the as-synthesized mesostructures were promoted by calcination and solvent extraction process. However, the intensity of LZC-C was remarkably high with respect to those of the others, which means that the calcination can improve the ordering of the silica framework and thereby it might be a more effective method for removing the template.

Figure 1 Powder XRD Patterns of as-synthesized (LZC), ethanol-extracted (LZC-EE), acetone-extracted (LZC-AE), and calcined sample (LZC-C).

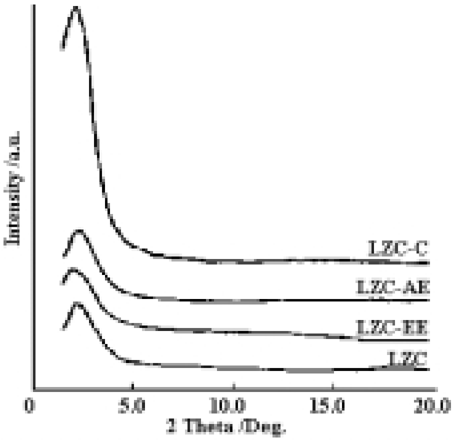


Figure 2. Transmission electron micrograph of LZC-C silica.

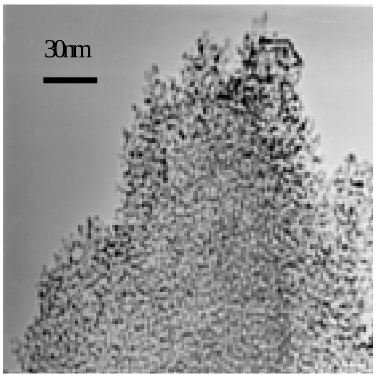
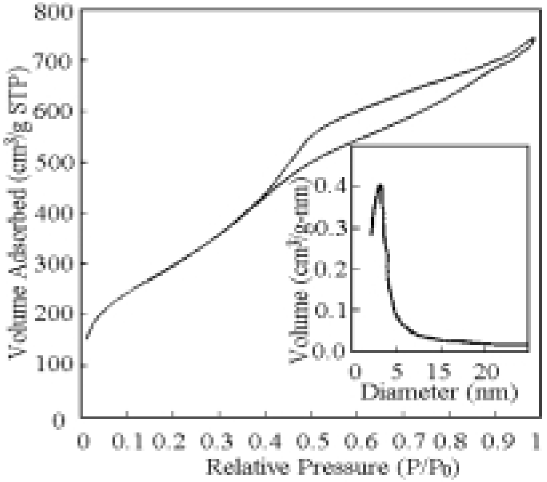


Figure 2 shows the transition electron micrograph (TEM) image of the calcined LZC sample. There was a large number of worm-like channels in its structure, but lack of long range packing order. The channels of LZC-C are interconnected. These might be due to the weak hydrogen bonding forces between N, N-dimethyldodecylamine oxide head-group and silicon precursor.

The N_2 adsorption-desorption isotherms and the corresponding pore size distribution curve for LZC-C are presented in **Figure 3**. There was a large adsorption-desorption hysteresis loop at high relative pressure, suggesting the capillary condensation in the disordered channels. The pore size distribution curve revealed a comparatively narrow distribution in pore diameter, which was also observed in TEM image. The BET specific surface area, BJH mean pore diameter, and pore volume are 1102 m^2/g, 3.9 nm, and 1.24 cm^3/g, respectively.

Figure 3. N_2 adsorption/desorption isotherms for LZC-C silica. (Inset) The corresponding Barrett-Joiner-Halender pore size distribution determined from N_2 adsorption isotherm. Before analysis, the sample was degased at 423 K and 1.07×10^{-3} KPa for 12 h. The isotherms were obtained on a Micromeritics ASAP 2010 Sorptometer.



N, N-dimethyldodecylamine is insoluble in water, while DAO has a good solubility. Thus for the formation of LZC mesostructure in aqueous media, it is DAO rather than N, N-dimethyldodecylamine that acts as the structure directing agent. The interaction forces for the formation of LZC mesophase, probably, were the hydrogen bonding between silicon precursor and head-group of N, N-dimethyldodecylamine oxide. It might be the reason why the templates in the silica channels could be removed by solvent extraction in principle. In fact, the retaining of XRD patterns after solvent extraction and the thermogravity analysis result could confirm it. There were about 17.34% template in the as-synthesized sample. After ethanol or acetone extraction, the template contents dropped to 9.44% or 13.51%, respectively, *i.e.*, the templates can be partly removed by solvent extraction.

In conclusion, disordered mesoporous silica molecular sieves can be synthesized at mild conditions, involving the *in situ* prepared N, N-dimethyldodecylamine oxide as structure directing agent. This synthesis strategy was a convenient alternative templating pathway for the preparation of mesoporous silicas.

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