

[Communication]

Novel Templating Route to Mesoporous Silica Molecular Sieves

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Since Mobil researchers reported the discovery of a new family of silica-based mesoporous molecular sieves (M41S) materials in 1992^[1,2], there has been a growing interest in using these nanoporous materials as heterogeneous catalysts, catalyst supports, and nanocomposite host materials for novel applications^[3-7]. All these applications have stimulated many researchers to synthesize mesoporous materials *via* different templating schemes. So far, ionic and neutral surfactants including neutral alkylamine^[8], polyethylene oxide^[9], genimi^[10], and amphiphilic triblock copolymer^[11] have been the most commonly used as templates for the synthesis of mesoporous molecular sieves. Here, we present a low-cost and biodegradable amphoteric templating route to mesoporous materials. Using low-cost and biodegradable amphoteric tetradecyl betaine ($C_{14}H_{29}N^+(CH_3)_2CH_2COO^-$) as template, we successfully synthesized the mesoporous silica molecular sieves under acidic conditions at mild temperature.

A typical synthesis was carried out as follows: the appropriate amount of tetradecyl betaine (TB) was dissolved in water, when the turbid mixture became clear, aqueous HCl was added to adjust the pH of this solution to 2.2. With magnetic stirring, the designed amount of tetraethylorthosilicate (TEOS) was introduced dropwise into the above mixture. The final composition of the reaction mixture was 1 TEOS: 0.35 TB: 0.000173HCl: 40.5 H₂O. After allowing the re-

sulting gel to age at 323 K under gentle stirring for 24 h, the resulting solid product was recovered by filtration, washed with distilled water and air-dried.

Template removal was achieved by solvent extraction and calcination. The solvent extraction was performed by stirring 1g of the air-dried product in 80 mL ethanol (EtOH) and water mixture (1/1, V/V) for 2 h. Then, it was filtered and washed with another 50 mL EtOH and water. This extraction procedure was repeated four times (the final washing with water). The extracted product was finally air-dried and calcined in air at 973 K for 6 h.

The amphoteric surfactant tetradecyl betaine (TB) has quaternary ammonium and carboxylate functionalities for the head group and can therefore bond with both negatively and positively charged species. Under the low pH conditions of the reaction, the quaternary ammonium group of TB is positively charged, and the carboxylate group is partly protonated. Therefore, the charged silicate species may bond with the quaternary ammonium cation and carboxylate anion *via* static electrical interaction, or with the carboxyl *via* hydrogen bonding interaction. Concurrent surfactant bonding with the inorganic and aggregation of the micellar structures lead to the formation of the mesoporous phase.

Fig. 1 shows the powder X-ray diffraction (XRD, Rigaku, D/Max-2400, with Cu K_α radiation;

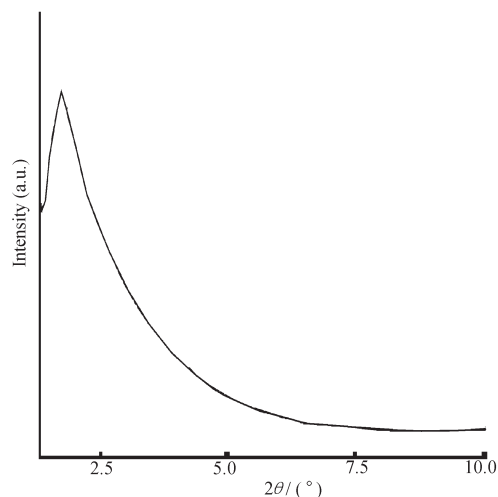


Fig. 1 The powder XRD pattern of calcined STO mesoporous silica molecular sieves

$\lambda = 0.15418$ nm) pattern of calcined mesoporous silica (designed STO). It exhibits an intense reflection corresponding to 5.3 nm at low angle, while higher order Bragg reflections are not resolved. The absence of higher order reflections is attributed to the lack of long-range order or finite size effects^[10]. The strong electrostatic interactions and charge matching are essential for the formation of the long-range ordered mesostructure phase. The single XRD reflections and small X-ray scattering domain sizes of the obtained materials suggest that their formation be governed by weak interactions. Furthermore, the XRD pattern of the obtained sample showed the typical MSU wormhole structures assembled from polyethylene oxide as template^[9]; this result is supported by the transmission electron microscopy (TEM, Philips CM-120) in Fig. 2. It can be clearly seen from Fig. 2 that STO possesses the typical wormhole-like framework of the MSU mesoporous molecular sieves^[12]. The BET specific surface area and BJH pore diameter of the obtained STO are $1013 \text{ m}^2 \cdot \text{g}^{-1}$ and 3.6 nm, respectively. The N_2 adsorption-desorption isotherms (Micromeritics ASAP 2010 sorptometer) (Fig. 3) clearly exhibits the type IV isotherms with an obvious hysteresis loop, three well-distinguished regions of the adsorption isotherm are evident: (i) monolayer-multilayer adsorption, (ii) capillary condensation, and (iii) multi-

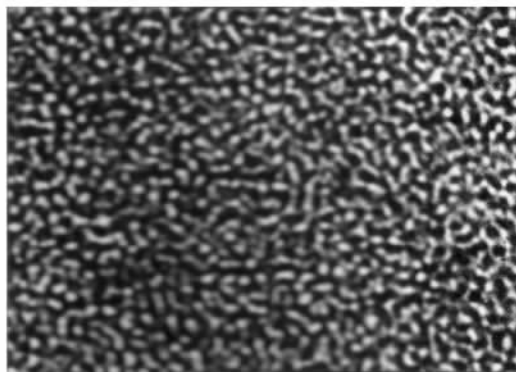


Fig. 2 TEM image of calcined STO mesoporous silica molecular sieves

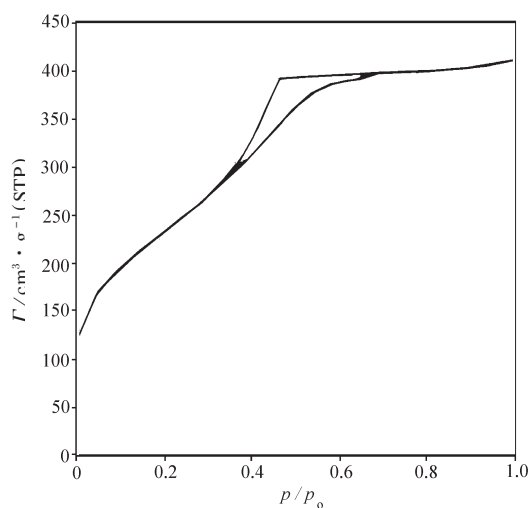


Fig. 3 N_2 adsorption-desorption isotherms of calcined STO mesoporous silica molecular sieves

player adsorption on the outer particle surface.

Fig. 4 depicts the TG curves (Perkin-Elmer) for the as-synthesized and solvent-extracted samples. Both of the samples show similar weight loss during about 20 °C to 150 °C stage, due to the desorption of water or EtOH. In the second stage from 150 °C to 460 °C, the weight loss of the as-synthesized sample is attributed to the decomposition of the organic template; we noted that the solvent-extracted sample had little weight loss, suggesting that nearly 100% template removal was achieved by direct solvent-extraction and the surfactants was permitted to recover and re-use. We have used such recycled amphoteric tetradecyl betaine to synthesize the high quality STO showing characteristics properties identical to those presented above. The weight loss during the third stage from 450 °C to 600

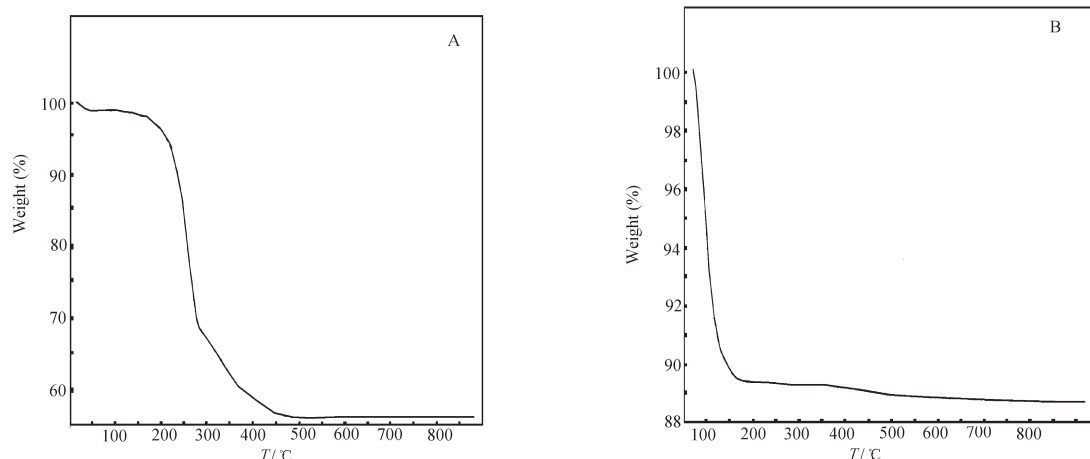


Fig. 4 Thermogravimetry curves of (A) as-synthesized and (B) solvent-extracted STO samples

°C shows the dehydroxylation of silanol groups^[13]. After calcinations at 973 K for 6h, the reflections are fairly retained, confirming that these materials are thermally stable.

In summary, a mesoporous silica molecular sieve has been successfully synthesized with the low-cost and biodegradable amphoteric tetradecyl betaine as the structure-directing agent under acidic conditions. Physicochemical characterization proved that the samples obtained possess a wormhole-like framework typical of MSU. Thermogravimetry (TG) revealed that nearly 100% surfactant removal was achieved by direct solvent-extraction. Systematic investigations for the mechanisms in the synthesis and applications of the titled materials are still in progress and will be reported in the full paper followed this letter.

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以新型模板方法合成中孔 SiO₂ 分子筛

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摘要 以廉价、生物可降解的两性表面活性剂十四烷基甜菜碱作为模板剂, 以正硅酸乙酯为硅源, 在酸性条件下成功地合成了具有螺旋状孔道结构的 SiO₂ 中孔分子筛. 热重表征结果说明, 采用溶剂萃取(乙醇的水溶液为萃取剂)的方法, 近乎 100% 的模板剂可以脱除回收.

关键词: 两性表面活性剂, 模板剂, SiO₂ 中孔分子筛, 合成