

Synthesis of Microporous Silica in the Presence of Dodecyltrimethylbenzylammonium Chloride Surfactant

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(Received June 26, 2000; CL-000623)

Microporous silicas with pore sizes in the range intermediate between traditional microporous and mesoporous materials have been synthesized by using dodecyltrimethylbenzylammonium chloride as a template. These microporous silicas can be synthesized by either acidic $S^+X^-I^+$ or basic S^+I^- assembly pathways and consist of disordered channels with almost identical pore sizes of 12.2 Å in both cases. Their BET surface areas are larger than 1000 m²/g after being calcined in air.

Since the discovery of M41S mesoporous materials,^{1,2} considerable efforts have been made to modify their structural features, for instance, pore size (in a few nanometers) and morphology (in micron or millimeter scale). Using surfactants with different alkyl chain lengths and expanding the micelles with suitable organic additives, pore sizes of the mesoporous materials can be tuned in the range of 16 to 100 Å. Periodic or crystalline silicates with pore sizes between 10 and 20 Å are likely to be very important for gas separation and shape selective catalysis.³ However there is little to access the synthesis of porous solids with pore diameters in this range, i.e., in the intermediate range between those of the traditional microporous zeolites and mesoporous solids. Mesoporous hexagonal silicates prepared with C₈–C₁₀ alkyltrimethylammonium or primary amine surfactants are known to have pore sizes in the range of 16 to 20 Å.⁴ Recently, Sun and Ying⁵ demonstrated that hexagonal microporous niobia with a pore diameter of less than 20 Å could be prepared by supramolecular templating using short-chain C₄–C₇ *n*-alkylamines. Eswaramoorthy et al.⁶ reported the synthesis of disordered microporous silica and aluminophosphate with pore diameter around 14 Å by making use of supramolecular organization of hexylamine template molecules respectively. Herein we describe the synthesis of microporous tubular silicas with pore sizes of 12 Å by supramolecular templating of dodecyltrimethylbenzylammonium chloride (DDBAC) surfactant solution through electrostatic $S^+X^-I^+$ and S^+I^- assembly pathways⁷ (where S⁺ stands for a cationic surfactant, X⁻ for a counteranion of S⁺ (i.e., halide), and I⁺ and I⁻ for inorganic silica species under acidic and basic systems respectively).

DDBAC (30–40% aqueous solution) was donated by Tianjin Gaoxin Chemical Plant, without any purification before use. All other reagents were received from Beijing Chemical Reagents Company and used without further purification. In a typical basic (S^+I^-) synthesis, 2.9 mL of DDBAC solution was mixed with 15 mL of NH₄OH solution (25%) and 50 mL of water. To this solution, 3.13 g of tetraethyl orthosilicate (TEOS) was added at room temperature with stirring, and the pH value of the final mixture was about 9.2. As to acidic ($S^+X^-I^+$) synthesis of microporous silica, 2.5 mL of DDBAC solution was added in 24 mL of

HCl (5 mol/L) aqueous solution, followed by an addition of 4.2 g of TEOS dropwise under electromagnetic stirring. After further stirring for about 5 h, the solid precipitate was allowed to recover by filtration on a Buchner funnel and dried in air at ambient temperature. The as-synthesized material was calcined in air at a rate of 1 °C/min reaching to a maximum of 520 °C, and then maintained at that temperature for 5 h.

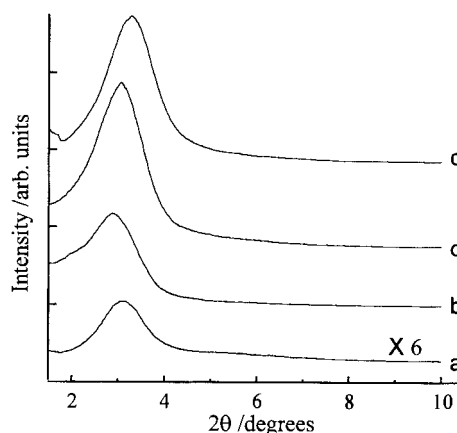


Figure 1. XRD patterns of microporous silicas prepared under acidic system with surfactant DDBAC: (a) as-synthesized; (b) calcined at 250 °C for 3 h in air; (c) calcined at 400 °C for 3 h in air; (d) calcined at 500 °C for 3 h in air.

Figure 1 shows the powder X-ray diffraction (XRD) patterns of the as-synthesized and calcined solid products prepared by the acidic synthesis pathway. The former presents one low-angle peak with a corresponding *d* spacing of 28.7 Å and no significant peaks in the range of 10° to 40° (2θ). This pattern is very similar to that of mesoporous silicates lacking long-range order and is reminiscent of the disordered hexagonal mesoporous silicas prepared by neutral and nonionic surfactant templating^{8,9} and made with cationic surfactant in the presence of organic salts,¹⁰ as well as disordered hexagonal microporous silica reported by Eswaramoorthy et al.⁶ After calcination at 250 °C in air for 3 h, the diffraction peak shifts slightly to a lower 2θ angle, corresponding to a *d* spacing of 30.7 Å. The peak intensity increases, probably due to the process of desorption and decomposition of more than 80% of organic template molecules. After calcination at 400 °C in air for 3 h when almost all organic template molecules were removed, the diffraction peak shifts back to the original position. Calcination at 500 °C in air for 3 h results in a further shift of the peak towards a higher angle, corresponding to a *d* spacing to 26.9 Å. This may be due to further condensing of silanol groups under high-temperature. As to the microporous silicas prepared by the basic route, their XRD patterns are also characteristic of a disordered tubular phase with one diffraction peak around 28.7 Å in as-synthesized pattern. After calcination

in air at 500 °C, the d spacing shifts to 25.5 Å in addition to the substantial increase of the peak intensity. These results do not agree with Eswaramoorthy et al.'s observation,⁶ i.e., calcination in N₂ atmosphere for hexagonal microporous silica prepared with hexylamine did not cause any significant change in the d_{100} spacing in the XRD patterns.

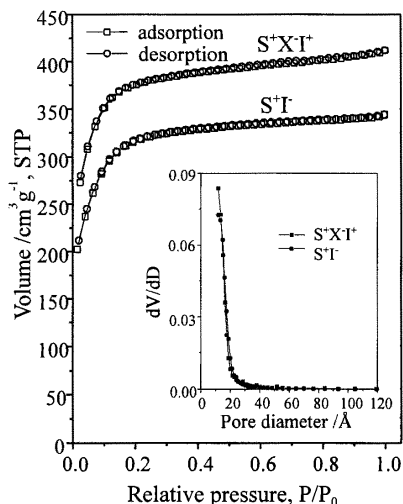


Figure 2. Nitrogen adsorption-desorption isotherms of the calcined silicas prepared by acidic S⁺X⁻I⁺ and basic S⁺I⁻ assembly pathways and their pore size distribution curves calculated by using the BJH method (inset).

Figure 2 shows the N₂ adsorption-desorption isotherms of the porous silicas synthesized by the acidic and basic routes. All the porous silicas from different synthesis pathways show the same isotherm of type I, similar to that found in zeolites and other microporous materials.¹¹ The BET surface areas of the samples synthesized by the acidic and basic routes are 1370 and 1174 m²/g, corresponding to their pore volumes of 0.637 and 0.532 cm³/g, respectively. There is no mesoporosity in our samples as revealed by the pore size distribution curves (Figure 2). Their pore size distributions were calculated by the Horvath-Kawazoe (HK) method¹² (not shown). The pore diameters of the samples from acidic and basic routes are almost the same as 12.2 Å. A similar conclusion was also obtained by using the Barrett-Joyner-Halenda (BJH) method¹³ (Figure 2). The TEM images (Figure 3) of both the samples

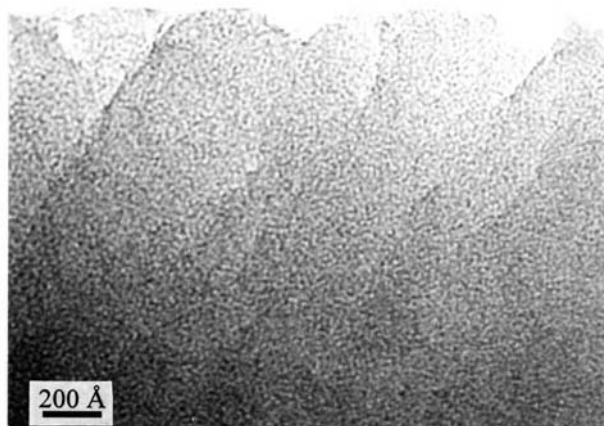


Figure 3. TEM images of microporous silicas calcined at 520 °C.

show the presence of disordered channels. Our XRD and TEM results are similar to those from Eswaramoorthy et al.'s.⁶ The materials contain micropores. However, we believe that these pores are disordered without experimental evidence to show hexagonal symmetry even in a short range scale. It is also well known that it is impossible to measure the pore size directly from the TEM images of disordered porous materials.

The microporous silicas can be synthesized under a wide range of molar compositions through acidic S⁺X⁻I⁺ and basic S⁺I⁻ pathways, respectively. As to the acidic S⁺X⁻I⁺ synthesis process, the pH values of the final mixtures should be smaller than 2. Surf/TEOS ratios can be as low as 0.10. The relative crystallinity of the synthesized microporous silicas increases with Surf/TEOS ratios in the mixtures. H₂O/H⁺ ratios can be in the range of 10 to 20, and H₂O/TEOS ratios in the range of 60 to 450. However, the pore sizes of the synthesized silicas are all in the range of 12 to 13 Å, and their BET surface areas are all larger than 1000 m²/g. As to the basic S⁺I⁻ synthesis process, the optimum pH value is 9 to 9.5. When Surf/TEOS ratio decreases to lower than 0.05, the obtained solid would be amorphous. When strong base NaOH was used instead of NH₄OH, the products were often thermally unstable though the XRD patterns of the as-synthesized samples showed one main diffraction peak around 28 Å of d spacing. If the final mixtures were crystallized at the temperature of 40 to 90 °C for 3 d, the pore sizes of the calcined solids could increase with the crystalline temperatures and can be tuned controllably in the range of 15 to 22 Å.

Summary, microporous silicas with uniform pore size of about 12.2 Å have been synthesized in the presence of dodecyl-dimethylbenzylammonium chloride surfactant by both acidic S⁺X⁻I⁺ and basic S⁺I⁻ assembly pathways. The channels of these materials are disordered. Such microporous materials might be useful in the potential applications of catalysis, adsorption and separation.

This work is financially supported by the National Natural Science Foundation of China (NSFC).

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