## Microporous semicrystalline silica materials

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A new family of microporous semicrystalline silica materials (MSSMs) were developed at room temperature from acidic mixtures of alkyl-substituted silane and tetramethylalkoxysilane. Hydrolyzed alkyl-substituted silica precursors, having hydrophilic silanol groups and hydrophobic alkyl groups, presumably act not only as templates but also as sol stabilizers for continuous pore engineering of silica materials in the micropore region. Depending on the substituted alkyl (SUA) groups in initial sols, MSSMs have distinct broad x-ray diffraction peaks in low 2θ range of 2° to 12°, distinguishable thermal behavior of SUA groups, highly flexible processability, and discrete micropore size with good thermal stability of micropores after the removal of SUA groups. These designer microporous silicas are expected to be useful for molecular sieving applications.

Precise pore-size control in processed silicas has been a great challenge. Although various silica materials were developed with a wide range of morphologies, crystallinities, and pore-size properties, there is still a great need for the development of new and cost-effective silica materials. Especially important is the development of microporous processed materials that can be used for molecular sieving in various technologies such as gas separation, catalysis, membrane reactors, sensors, and adsorbents.<sup>1-4</sup> Recently, precise pore-size control was achieved in the mesoporous range (2-50 nm) by the syntheses of the M41S family of porous materials through the sol-gel technique.<sup>5–8</sup> However, precise control is still not accomplished for silica gels or films in the microporous range (<2.0 nm), although a few microporous silicas with narrow pore-size distribution and zeolites have been investigated for use as membranes.<sup>2,3,9–11</sup> Here, we report the synthesis of microporous semicrystalline silica materials (MSSM) with different pore sizes in the microporous regime.

Common strategies for the pore-size control of silica materials are the manipulation of various process parameters such as sol composition, pH, temperature, aging time and drying method during preparation, and posttreatment.<sup>1,12,13</sup> However, complex origins of porosity and structure evolution greatly limit the efficiency of pore-size control. Another recent strategy is the template approach in which templates direct pore sizes and shapes by interacting with frameworks.<sup>1–7</sup> The combination of the template approach with a sol-gel method allow one to design and fabricate the exact pore size and shape in processed silicas. There are a few synthesis studies of amorphous silicas that used the template approach;<sup>2,3</sup> the exact role of templates is unclear. Unfortunately, liquid-crystal templating,<sup>5–8,14</sup> which was used for mesoporous materials, could not be applied to tailor pore size (<1.5 nm) in the microporous range.

It is interesting that hydrolyzed alkyl-substituted silica precursors have hydrophilic silanol groups as well as hydrophobic alkyl groups. This unique nature led to the recent synthesis of layered inorganic–organic hybrid silica materials from long-chain alkyl-substituted silica precursors.<sup>15</sup> These hydrophilic and hydrophobic properties suggest that substitute alkyl (SUA) silica precursor can act not only as a template but also as a sol stabilizer, and that SUA groups can form micelles of microporous dimension under certain conditions. Using this approach, we have developed a new family of MSSM with highly flexible processability and these materials may be useful in molecular sieving.

A series of MSSMs were synthesized at room temperature by the sol-gel method from acidic mixtures of tetramethylorthosilicate (TMOS) and an alkyl-substituted silane. The alkyl-substituted silanes used were propyltrimethoxysilane, phenyltrimethoxysilane, hexyltrichlorosilane, and octyltriethoxysilane. (Hereafter the resultant sols and xerogels are referred to as PRO-, PHE-, HEX-, and OCT-sol or xerogel, respectively.) A molar ratio of 1.0 silica precursor: 3.0 methanol:  $32 \text{ H}_2\text{O}$  :  $1.4 \times 10^{-2} \text{ HNO}_3$  was used for PRO-,

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PHE-, and OCT-sol and 1.0 silica precursor: 12.0 methanol: 10 H<sub>2</sub>O for HEX-sol. Silica precursors in all sols except OCT-sol consisted of a molar ratio of 3 TMOS to 1 alkyltrialkoxysilane (for OCT-sol, a ratio of 4 to 1 was used). Also tripropylamine (T1) and tripentylamine (T2) were tested as template molecules for PHE- and HEXsols, respectively. (For PHE-sol, acid amount equimolar to tripropylamine was also added.) All sols except OCTsol (biphase) were transparent and homogeneous for a certain duration before they became opaque. Sol stability based on visual transparency depended on the type of SUA group and solvent ratio. PRO-sol showed precipitation after 30 h and PHE-sol after 12 h, whereas HEXsol became opaque within 1 h. Sols were cast either as thin sheets in a petri dish to quickly obtain xerogels at various time intervals or continued to be stirred until precipitates formed. Xerogels, transparent films, and white soft lumps were prepared by drying sols or precipitates at room temperature (hereafter referred to as as-synthesized xerogels). The processing of these silicas into films is useful for membrane applications. The SUA groups were removed by calcination in air (3 h at 250 °C for PRO-xerogels, 10 h at 400 °C for PHE-, HEX-, and OCT-xerogels with a heating rate of 2.5 °C/min). As-synthesized xerogels from HEX-sol and the HEX-sol with the addition of guest template were washed with an aqueous ethanol solution containing 70% ethanol on a volume basis and dried at room temperature before calcination.

All the as-synthesized xerogels showed a distinct broad x-ray diffraction (XRD) (hump) in low  $2\theta$  range of  $2^{\circ}$  to  $12^{\circ}$  [Fig. 1 (a)] unlike amorphous silicas that show a hump around 20° two theta. To the best of the authors' knowledge, such semicrystalline nature was not previously reported for silicas. The d spacings (based on the apex of the hump) and intensities were systematically affected by SUA groups. Intensity and d values increased with an increase in the bulk size of SUA groups, although they were also slightly affected by sol-aging time. Slight increases in d value (about 0.1 nm) and intensity of the XRD hump were observed by extended sol aging time. The as-prepared PRO-, PHE-, and HEX-xerogels showed d values of 1.1, 1.2, and 1.5 nm, respectively. The addition of guest templates (T1 and T2) caused an increase in d values. Distinct XRD humps persisted after the removal of SUA groups by calcination [Fig. 1 (b)]. The XRD humps became broad and d values increased in all the PRO-, PHE- and HEX-xerogels [Fig. 1 (b)] after calcination. In the PRO-xerogel, XRD peak intensity decreased upon calcination. However, these changes were not observed in OCT-xerogels (Fig. 1), which exhibited somewhat stronger XRD peaks after calcination.

Differential thermal analysis clearly showed much higher thermal stability of SUA groups in the present as-synthesized PHE xerogels compared to normal organically modified silicas (ORMOSILs) (see exotherms



FIG.1. Representative XRD of (a) as-synthesized and (b) calcined xerogels. A: PRO-, B: PHE-, C: HEX-, D: OCT-xerogel

caused by oxidation of SUA groups in Fig. 2). This report is the first to show a distinguishable thermal behavior of SUA groups in inorganic–organic silica hybrid materials. It has been shown in normal ORMOSILs that SUA groups are mainly distributed over the surface of primary pure silica particles.<sup>16,17</sup> However, Fig. 2 strongly suggests that SUA groups are encapsulated by silica matrix in these as-synthesized xerogels as indicated by a very high temperature (~600 °C) of their decomposition.

All the as-synthesized xerogels were completely nonporous; that is, no surface areas were detected by  $N_2$ adsorption. On the other hand, all calcined xerogels including both films and lumps exhibited a highly microporous property as indicated by the type I  $N_2$  isotherm with no hysteresis loop (Fig. 3). None of these xerogels showed mesopores and this behavior is similar to that of zeolites.  $N_2$  adsorption patterns at low relative pressure (below 0.1 P/Po) indicated that the pore size systematically increased with an increase in bulk size of SUA groups as well as the addition of guest template. From a comparison of these isotherms to those of zeolites, the pore size of PRO- and PHE-xerogels appears to be about 0.5 nm (pore size of zeolite 5A is 0.5 nm; this sample was supplied by Linde division, Union Carbide Company) and those of PHE + T1, HEX-, HEX + T2, and OCT-xerogels to be slightly higher (Fig. 4). Transmission electron microscopy (TEM) revealed uniformly distributed micropores (Fig. 5).

Thermal stability of micropores depended on the nature of SUA groups (Table I), as indicated by the change of surface areas and/or  $N_2$  isotherms upon thermal treat-



Temperature (°C)

FIG. 2 Thermal analysis of as-synthesized PHE-xerogel and PHEcontaining ORMOSIL.



FIG. 3. Representative N2 isotherms of calcined xerogels.

ment. Larger alkyl group (leading to larger pore size) and extended sol-aging time enhanced thermal stability. Surface area was also affected by the size of SUA groups. However, no significant effect of sol-aging time was



FIG. 4. Pore-size distribution by Horvath-Kawazoe method of calcined ( $\bigcirc$ ) octyl, ( $\blacksquare$ ) hexyl xerogels, and ( $\bigcirc$ ) zeolite 5A.



FIG. 5. TEM of as-synthesized HEX-MSSM.

observed on the surface areas of the xerogels. When PRO-xerogels were treated at high temperatures (>600 °C), nonporous amorphous silica resulted with no XRD hump. The intensity of the XRD hump related closely to surface area, which strongly suggested that XRD hump resulted from the silica matrix surrounding regularly packed SUA groups.

Based on the above-observed results, we suggest that hydrophobic SUA groups of partially hydrolyzed and poorly polymerized alkylalkoxylsilanes came together and were loosely bonded by hydrophobic interaction to form quasi-micelles (seemingly, micelles) under acid and highly hydrophilic environment (Fig. 6). Under acid environment below isoelectric point of silica, silica precursors are rapidly hydrolyzed to form monomers or oligomers. However, polymerization by their condensa-

TABLE I. Textural property of MSSMs.

MSSM	Surface area (m <sup>2</sup> /g)	Thermal stability <sup>a</sup>
PRO	400	230
PHE	440	350
PHE+T1	485	400
HEX	500	400
HEX+T2	525	400
OCT	560	500

<sup>a</sup>Based on the change in surface area and  $N_2$  isotherm after thermal treatment for 1 day at each temperature.



FIG. 6. Schematic (not to scale) representation of quasi-micelle formation.

tion takes place slowly and irreversibly to lead to weakly branched polymers. In the presence of unhydrolyzable alkyl groups, the polymerization is further inhibited by steric hindrance.<sup>12</sup> Quasi-micelle formation seemed to be reversible and metastable, as indicated by the observations that initial opaque sols became transparent by increasing solvent ratio, and that ORMOSILs were obtained by the addition of alkali catalysts and/or by an increase in preparation temperature. Even in the case where high solvent ratio was used for preparation of the transparent film, MSSMs could be synthesized by drying sols at room temperature because rapid volatilization of organic solvent led to highly hydrophilic environment. Quasi-micelle became stable by irreversible formation of dense wall with further polymerization. Silica matrix of their walls may lead to distinct XRD hump, although exact morphology of pore is not known.

Like the synthesis of M41S family,<sup>5</sup> MSSM family could be synthesized with various reagents, pH (less than isoelectric point of silica), and sol compositions. Furthermore, MSSM family could be obtained in various shapes like films, gels, and opaque lumps because of highly flexible processability.

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