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Determination and Tailoring the Pore Entrance Size in Ordered Silicas with Cage-like Mesoporous Structures

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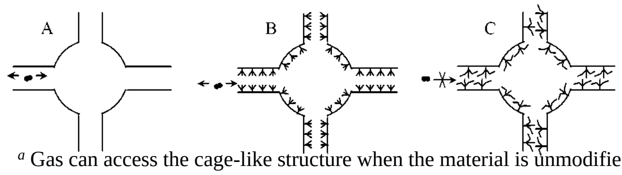
After discovery of ordered silicas with cage-like mesoporous structures (OSCMSs),[1] their synthesis,[2,3] characterization,[4] and application[3c−f] have attracted increasing attention. Currently known OSCMSs include cubic *Pm*3*n* (SBA-1),[1a] 3-dimensional (3-D) hexagonal $P6_3/mmc$ (SBA-2[1b] and SBA-12[2a]), and cubic *Im*3*m* (SBA-16[2a] and FDU-1[2c]) structures, synthesized with alkylammonium, oligomeric, or polymeric templates. Because of their unique 3-D structure and pore connectivity, OSCMSs are promising as catalysts or catalyst supports for processing of large molecules,[3b−d] and hosts or templates for the nanostructures synthesis.[3e,f] From the viewpoint of applications in sorption, catalysis, sensing, molecular sieving, and immobilization of molecules or biomolecules, the elucidation of pore entrance size[4b] and pore connectivity[4a,b] is of crucial importance. To date, the only method used to determine the pore entrance size in OSCMSs is the electron crystallography, and pore entrance dimensions were reported only for single samples of SBA-1, SBA-6 (isostructural to SBA-1), and SBA-16.[4b] This method is powerful, providing the solution of the entire OSCMS structure, but requires extensive high-resolution transmission electron microscopy (TEM) imaging from different directions. The method appears to be restricted to highly ordered samples with appreciable ordered domain sizes, whereas some well-defined silicas with cage-like mesoporous structures exhibit appreciable structural disorder.[5] The local nature of TEM imaging does not allow one to obtain a definite answer about the extent of occurrence of pore entrance structure defects.

Herein, a practical approach to the determination of the pore entrance size in OSCMSs is proposed. Moreover, a fundamental insight into the OSCMS pore connectivity is gained, including the control of the pore entrance size by (i) postsynthesis surface modification, which is capable of bringing the entrance dimension to subnanometer region, and (ii) selection of appropriate synthesis temperature. These findings show new promise for the synthesis of mesoporous solids with molecular size- and shape-selective properties.

The approach to the pore entrance size determination employs the reaction of OSCMS surface with monofunctional organosilane, which is known to result in the introduction of a monolayer of ligands of well-defined structure.[6] OSCMS is modified with a series of ligands of gradually increasing size and the resultant samples are characterized by using a standard gas adsorption method[7] to identify the smallest surface ligand that renders the OSCMS structure inaccessible for gas molecules (Scheme 1). The pore entrance size is then determined from the size of this surface ligand based on its structure, and from the gas molecule size. Our approach was demonstrated for FDU-1 large-pore silica[2c] obtained with use of a poly(ethylene oxide)−poly(butylene oxide)−poly(ethylene oxide) triblock copolymer B50-6600 (DOW; $EO_{39}BO_{47}EO_{39}$) template. The cage diameter of FDU-1 was reported to be 12 nm, whereas the pore entrance size was not determined. Herein, FDU-1 silicas synthesized at room temperature (sample I, cage diameter ∼9 nm), and at room temperature with subsequent heating at 373 K for 6 h (sample II, cage diameter ∼10.5 nm), were reacted with commercially available silanes of gradually increasing alkyl chain length, including trimethyl-, triethyl-, propyldimethyl-, butyldimethyl-, hexyldimethyl-, and octyldimethylchlorosilane. FDU-1 was dispersed in a mixture of silane and pyridine, heated under reflux conditions,[8] and washed to remove unreacted silane and reaction side products. The modification involves reaction of surface silanols (═Si−O−H) with organosilane (R_3Si-Cl), resulting in the formation of a monolayer of surface ligands attached via covalent ═Si−O−SiR_3 bonds.

Scheme 1. Illustration of the Proposed Approach for the Pore Entrance Diameter Determination[a]



[a] Gas can access the cage-like structure when the material is unmodified (A) or modified with smaller surface groups (B), whereas larger groups block access of gas to the pores. The size of the smallest group that causes the pore blockage is related to the pore entrance size.

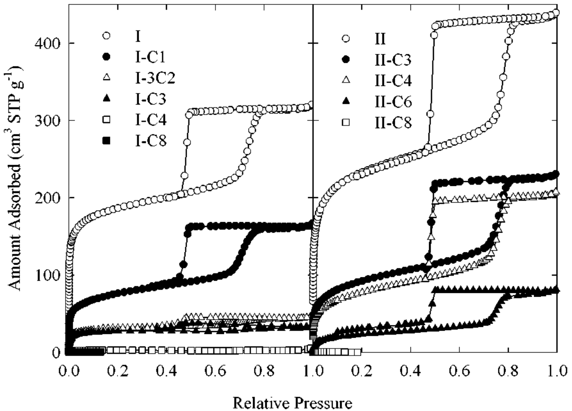


Figure 1. Nitrogen adsorption isotherms at 77 K for FDU-1 samples I and II before and after surface modifications with organosilanes.

Nitrogen adsorption isotherm at 77 K for FDU-1 (Figure 1) features a broad adsorption−desorption hysteresis loop[2c] that provides evidence of delayed capillary evaporation and thus the presence of constrictions in the mesoporous structure.[7] A relatively large uptake of N_2 at low relative pressures is related to adsorption in framework micropores characteristic of block-copolymeric-templated silicas,[8] in addition to adsorption on the surface of the cage-like mesopores. The cage-like structure of sample I modified with the smallest ligand used (−$Si(CH_3)_3$, denoted C1) was accessible to N_2. The decrease in adsorption capacity was only slightly larger than that observed for the channel-like structure of 2-D hexagonal SBA-15 silica[2a] modified with C1 ligands,[8] and thus this decrease is related to the introduction of the surface groups and partial or complete blockage of the micropores.[8] In contrast,

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the modification with slightly larger $-Si(C_2H_5)_3$ ligand (denoted 3C2) resulted in almost complete loss of adsorption capacity. The modification with $-Si(CH_3)_2C_3H_7$ ligands (denoted C3) had a similar effect, whereas the modification with $-Si(CH_3)_2C_4H_9$ ligands (denoted C4) completely shut down N_2 adsorption. A decrease in the diameter of pore entrance caused by introduction of C1 ligands can be estimated as ~0.8 nm, because the group extends ~0.4 nm from the surface.[6a] Because N_2 molecules ~0.35 nm in size were able to essentially fully penetrate the porous structure of the I-C1 sample, the diameter of the pore entrance of sample I has to be above ~1.2 nm. On the other hand, the 3C2 ligands capable of decreasing the pore entrance size by not more than 1.0 nm (the maximum extension of this group is ~0.5 nm) largely blocked the access of N_2 to the mesopore structure, indicating that average entrance size is below 1.4 nm. C4 ligands capable of a pore diameter decrease by not more than 1.5 nm completely blocked the access of N_2, showing that there are essentially no entrances above 1.9 nm. For sample II, the cage-like mesoporous structure was accessible after modification with both C3 and C4 ligands. Somewhat larger $-Si(CH_3)_2C_6H_{13}$ ligands (denoted C6) partially blocked the access of N_2, whereas the introduction of $-Si(CH_3)_2C_8H_{17}$ ligands (denoted C8) shut down N_2 access. The maximum pore diameter decrease related to the intoduction of C6 and C8 ligands is 2.0 and 2.5 nm, respectively. Thus, the pore opening sizes for sample II are above ~1.9 nm, but below 2.9 nm (as inferred from the accessibility and complete blockage of the structure after modification with C4 and C8, respectively).

Most of the silanes used had alkyl groups that may exhibit different configurations and thus their effective size was uncertain. Therefore, the modifications of MCM-41 silicas[6a] with cylindrical pores of uniform size were also performed. In contrast to hitherto unreported organic modifications of OSCMSs, similar modifications of silicas with channel-like pores were extensively studied,[6] but in this case even the introduction of large surface groups usually did not cause any appreciable pore blocking due to the lack of constrictions. We found that C4 ligands did not block access of N_2 to 2.4 nm MCM-41[9a] pores. C6 and C8 ligands completely blocked the 2.4 nm pores, but C8 ligands were too small to block 3.1 and 3.5 nm cylindrical pores.[9b] These results are in accord with the predictions based on the maximum ligand extension. Our FDU-1 pore entrance size estimates are consistent with the electron crystallography estimate of 2.3 nm for SBA-16.[4b]

The proposed method for the pore entrance size determination has many attractive features. It involves easy chemistry, cheap and readily available chemicals, and inexpensive equipment. The pore accessibility can be judged even on the basis of a single-point adsorption run that lasts several hours on a simple adsorption analyzer. This is an advantage when compared to the extensive imaging with HR TEM and subsequent data processing involved in electron crystallography. The present approach can be used for weakly ordered and disordered silicas with cage-like structures.[5] Taking into account commercially available modifiers, the range of pore entrance dimensions that can be studied is from 1.2 to ~5.0 nm. This fills the hitherto existing gap between narrow micropores that can be studied on the basis of molecular size exclusion (without prior surface modification), and mesoporous constrictions that can be characterized on the basis of position of desorption branch of gas isotherms.[5b] The present method is limited to materials whose surface can be modified with groups of well-defined size, but this covers most of the ordered cage-like structures reported to date, that is silicas[1−5] and organosilicas.[10] In any case, one needs to ensure sufficiently high surface coverage of the modifier to be able to make predictions based on the surface layer thickness.

The current study demonstrated several important features of OSCMSs. The size of their pore entrances can be controlled by the modification with organosilanes, allowing them to achieve the molecular dimensions of the entrances. For instance, sample I modified with C1 ligands was fully accessible, whereas the modification with 3C2 ligands that can additionally reduce the pore size by just 0.25 nm made most of the structure inaccessible for N_2. This result holds promise for applications in size- or shape-selective adsorption and catalysis, which are currently largely restricted to crystalline microporous solids and microporous carbons.[11] The pore entrance size can be tailored for the same polymeric template simply by adjusting the synthesis temperature, which is likely to be related to the redistribution of EO_n blocks of the template within the silicate matrix as a result of decrease in their hydrophobicity as temperature increases.[12] The previously known example of tailoring the entrance size for the same structure type required the use of a completely different template[4b] and thus was much less practical. It was also demonstrated herein that the pore entrances in OSCMSs under study are uniform in size throughout the particles of the material, otherwise the degree of blockage would gradually vary with the size of the modifier.

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