A Step-Growth Model for Molecular Mechanisms of Monolayer Formation in Ordered Nanoporous Channels

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The work describes the direct evidence of a new step-growth mechanism in which the silane molecules are first deposited in the wide region of the mesoporous surface. When the wide pore region is filled, the silane molecules begin to deposit in the narrow pore region. The pore size in the wide region and narrow region change alternatively and discretely in accordance with the step-growth mechanism and the molecular size of the silane.

The technique of self-assembled monolayers (SAMs) has been developed as an excellent method for formation of well-ordered and characterized monolayers on a variety of functional surfaces.[1,2] In practice, one of the most commonly used SAMs is the organosilane monolayer on the hydroxy surfaces of silica.[3,4] The formation of molecular monolayers plays an important role for many applications involving silane molecules of different chain lengths on the smooth surfaces, silica spheres, and gels. Although molecular arrangement and the chain conformation on the flat substrates have been extensively studied by atomic force microscopy (AFM), scanning tunneling microscopy (STM), small angle scattering, and many other techniques,[5–8] the detailed formation process is little known because of the covalent properties of self-assembled monolayer formation.

Hybrid mesoporous materials involve the formation of molecular monolayers in confined spaces with dimensions approaching the sizes of the silane molecules. There have been few reports on the mechanisms in such systems so far. Here we described the formation of molecular monolayers in tailored nanoporous substrates as a function of surface coverage. This work provides a simple, efficient method for self-assembly of alkoxysilanes onto mesoporous substrates, which contain uniform cylindrical pore channels with wide and narrow regions. Such uniform nanoporous materials provide ideal substrates to quantitatively study the monolayer chemistry.

The starting mesoporous silicas were prepared according to a method reported in the literature.[9,10] The synthesized mesoporous silica has the surface areas with up to 900 m^2/g, and the pore sizes with 78 and 65 Å on adsorption and desorption branch, respectively. Typically for the preparation of organosilane-grafted silica, 5.0 g of porous silica was suspended in 60 mL of toluene containing 1.60 mL of deionized water and stirred for 2 h. To the homogeneous silica suspension, 0–4.6 mmole of each organosilane such as aminopropyltrimethoxysilane (APTMS), propyltrimethoxysilane (PTMS), and propyltrichlorosilane (PTCS), was added and heated 120 °C to reflux for 6 h.

The white powder was filtered, washed with toluene, and dried in air and vacuum. Several typical functionalized silanes were selected: APTMS has been frequently used for the functionalization on the substrates, and PTMS and PTCS were used for the comparison of functionality and cross linking with APTMS, respectively.

The transmission electron micrograph (TEM) images of the native 7.8-nm mesoporous substrate were shown in Figure 1a. This material shows a hexagonally ordered array obtained parallel to the direction of the pore channels under slightly under focused conditions. In general, the pore channels are ordered, and the pore sizes are quite uniform. However, a close examination of the pore-wall structure indicates that the pore surface is not atomically smooth. As a result, the pore diameters along the pore channels can change by several nanometers. The surface roughness revealed in the TEM images is consistent with nitrogen adsorption studies, which show wide and narrow pore regions in the channels. The N_2 adsorption and desorption isotherms with different surface coverages of APTMS are shown in Figure 1b. As the silane molecules were deposited on the substrate, the surface area and pore size were reduced. However, it is interesting to point two important observations. First, the pore size does not change continuously with increasing surface coverage . Instead, it only changes in steps. Below 60% (4.6 mmol APTMS/g SiO_2) surface coverage (the percentage of the surface coverage was calculated based on the available silanol groups),[11] the pore diameters from the adsorption branch were reduced from 78 to 65 Å and stayed constant in this range (Figure 1c).

At 80% surface coverage (5.7 mmol APTMS/ g SiO_2), the pore diameter from the adsorption branch was reduced to

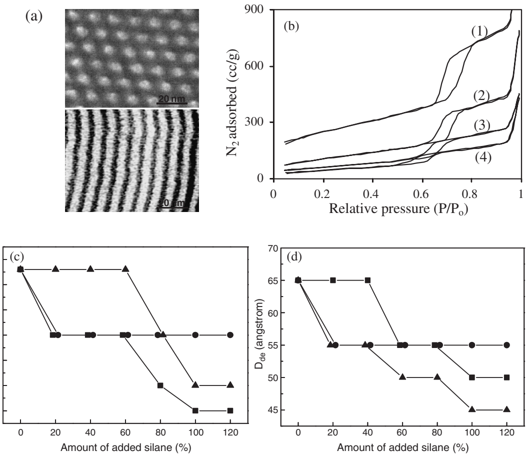

Figure 1. (a) TEM micrographs of 7.8 nm showing the rough wall surface, (b) stepwise change in N_2 adsorption isotherms with different surface coverage of APTMS: (1) 0, (2) 1.6, (3) 3.3, (4) 4.6 mmol APTMS/g silica, (c) adsorption, and (d) desorption pore-size distribution by BET. ((■) APTMS, (▲) PTCS, and (●) PTMS).

55 Å. A surface coverage higher than 100% gave a pore diameter of 50 Å. Second, the change in the pore diameter from the desorption branch also occurs in steps and is always behind the pore diameter change from the adsorption branch (Figure 1d). Below 40% surface coverage (3.3 mmol APTMS/g SiO_2), the pore diameter from the desorption branch was not changed at all. From 40 to 80% (5.7 mmol APTMS/g SiO_2) surface coverage, the desorption pore diameter was reduced to 55 Å. More than 80% surface coverage gave a desorption pore diameter of 50 Å. The implication of the pore sizes change as a function of surface coverage is clear because the adsorption branch gives the pore diameter of the wide pore region, and the desorption branch gives information on the narrow pore region. The most reasonable explanation is that the silane molecules were first deposited in the wide pore region. The pore size in this region would be reduced based on the chain length of the silanes. Before the wide pore region was filled, further deposition of silane molecules did not cause any change in the pore size.

^{29}Si NMR spectra were also obtained to further illustrate the chemical environments of the interfacial region by using a single pulse Bloch-decay method (with proton decoupling) with 5 μs (90°) ^{29}Si pulse, and a 30-s repetition delay. A Lorentzian line broadening of 50 Hz was used for all spectra. The chemical shift was referenced to TMS. Figure 2 shows the spectra for APTMS and CPTMS in 7.8-nm porosity. The peaks from −50 to −80 ppm correspond to the siloxane group indicating the instantaneously completed adsorption of APTMS by the constant stay of siloxane peak. The adsorption density for CPTMS incereases slowly over a long time, causing a gradual increase in packing density. It is interesting that cross-linking ratio Si (cross-link) on silica surface (Q^4) of the two silanes was increased with the reaction time. This ratio inecreased to 0.53, 0.57, 0.60 for 10, 60, 240 min of APTMS, and 0.46, 0.63 for PTCS, respectively. The driving force to form a molecular monolayer includes the intermolecular chain-to-chain interaction and the condensation reaction between the alkylsilane molecules and the substrate. The chain-to-chain interaction is weak for short time; therefore, the molecules are not closely packed. Increased time, the chain-to-chain attraction increases accounting for efficiency of packing and cross-linking. However, a further increase of time reduced the packing efficiency because the steric effect of the alkylsilanes prevents effect packing in the porous channels.

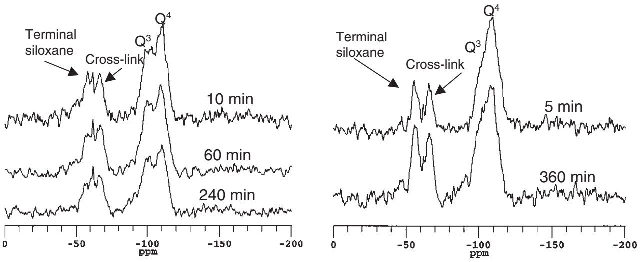

Figure 2. ^{29}Si NMR spectra of APTMS (left), and PTCS (right) in 7.8 nm pores as a function of time.

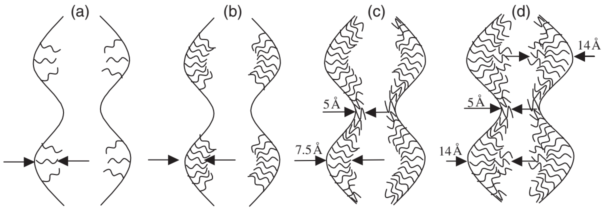

Figure 3. A stepwise growth mechanism for monolayer formation. ((a) 1.6, (b) 3.3, (c) 4.6, and (d) 5.7 mmol/g SiO_2)

A step growth was proposed to explain the step change in pore sizes as shown in Figure 3. Initially, the silane molecules were deposited in the wide pore region and reduced the pore radii in this region by a number corresponding to the chain length (about 7.5 Å). No deposition occurred in the narrow region. After the wide pore region was filled, the molecules began to deposit by about 5 Å. Up to this stage, the pore size in the wide pore region did not decrease further. In this process, the layer thickness in the narrow pore region was less than the expected chain length, indicating that the packing in these regions was not efficient. This result was expected because of the positive surface curvature in these regions. When the surfaces in the narrow pore region were filled, a second layer began to deposit in the wide pore region and reduced the pore radii in this region.

In conclusion, the step-growth model has some implications on the properties of the materials. The wide region in the pore channel is similar to concave defect on the surface. The mechanism suggests that on a rough surface, the silane molecules would be deposited on the concave regions first and spread to the neighboring surfaces. After the first layers are filled, the second layer will start to build up in the concave region again.

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