



Contribution ID: 194

Type: Oral 20 Minutes

Properties of Water Confined in Periodic Mesoporous Organosilicas: Nanoimprinting the Local Structure

Tuesday, 15 May 2018 10:08 (15 minutes)

The confinement of liquids in porous media greatly influences their physical properties, in particular, when the pore size approaches the molecular length scale. Several mechanisms, such as the pure geometrical restriction and the liquid-solid interaction at the interface contribute to the confinement effects, however, their roles for the drastic changes in the thermodynamic and dynamic behaviors of the liquids are not clearly understood. Especially, water molecules adsorbed on the surface and restricted within the pores are interesting in the scope of biochemistry, catalysis, and energy storage. The influence of the pore size on the melting and freezing points of confined water has been studied extensively. In contrast, fewer studies have been made concerning the effects of the surface polarity on the properties of spatially confined water, which may be due to the lack of highly defined porous substances. Periodic mesoporous organosilicas (PMOs) fill this gap perfectly because they combine the highly ordered pore structure of the well-established M41S-phases with the variety of surface chemistry within the pores. PMOs are synthesized using bis-silylated precursors of the form $(R'O)3Si-R-Si(OR')3$ where R is an organic bridging group which can be altered according to the desired surface properties [1]. Furthermore, PMOs with an aromatic bridging group may exhibit a molecular-scale periodicity within the pore walls. This allows a periodically alternating surface chemistry along the pore channel, caused by arrays of silica and aromatic organic groups. It is assumed that water will adsorb differently at the diverse areas of the pore wall surfaces owing to the varying hydrophilic or hydrophobic properties. Because of the endless possibilities for the organic bridging function, the surface chemistry of PMOs can be fine-tuned. For example, when going from a benzene bridging group to a biphenyl bridge, the organic hydrocarbon part becomes larger and thus the overall pore wall becomes more hydrophobic. For a divinylaniline bridge, the amino function offers the possibility of forming hydrogen bonds with water, thus making the material considerably more hydrophilic. Here, we show that the molecular mobility of water confined in periodic mesoporous organosilicas (PMOs) is influenced by the polarity of the organic moiety. Multidimensional solid-state NMR spectroscopy directly probes the spatial arrangement of water inside the pores, showing that water interacts either with only the silicate layer or with both silicate and organic layers depending on the alternating surface polarity. A modulated and a uniform pore filling mode are proposed for different types of PMOs [2]. Our study gives a molecular-level picture of the adsorbate-surface interaction, which helps understanding various confinement effects and provides a new design concept of the pore structures with the desired properties.

References

- [1] F. Hoffmann, M. Cornelius, J. Morell, and M. Fröba, „Silica-Based Mesoporous Organic-Inorganic Hybrid Materials“, *Angew. Chem. Int. Ed.* 2006, 45, 3216-3251.
- [2] J.B. Mietner, F.J. Brieler, Y.J. Lee, and M. Fröba, „Properties of water confined in periodic mesoporous organosilicas - nanoimprinting the local structure“, *Angew. Chem. Int. Ed.* 2017, 56, 12348-12351.

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Session Classification: Parallel 3-E

Track Classification: MS 1.12: Fluids in Nanoporous Media