

Diffusion of methane in nano-porous carbon aerogel probed by quasielastic neutron scattering

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The diffusion of methane confined in nano-porous carbon aerogel with the average pore size of 4.8 nm and a porosity of about 60 % was investigated as a function of pressure at room temperature using high-resolution quasielastic neutron scattering [1]. The diffusivity of methane shows a clear effect of confinement; it is about two orders of magnitude lower than in the bulk at the same thermodynamic conditions and is close to the diffusivity of liquid methane at 100 K. Furthermore, we observe a non-monotonic pressure dependence of the diffusivity of the confined methane. The diffusion coefficient initially increases with pressure, from $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 0.482 MPa to $8.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 2.75 MPa. At higher pressures, the diffusion coefficient starts to decrease. Our explanation of this unusual behavior is based on the results of the small-angle neutron scattering experiment carried out on the same system. The initial increase of the diffusion coefficient with pressure is due to progressive filling of bigger pores, in which overall molecular mobility in the internal pore volume is less affected by the slow mobility in the adsorbed phase. Subsequent decrease of the diffusion coefficient is associated with the increasing intermolecular collisions; such a dependence on pressure is also observed in bulk methane. We compare our results with the data available in the literature on the methane diffusivity in zeolites, metal organic frameworks, and porous silica, as well as with the molecular dynamics simulations of methane in nano-porous carbons and silica zeolites.

Another important observation is that the absolute values as well as the non-monotonic pressure dependence of the diffusivity appear to be similar for the methane confined in the dried and water-containing (due to exposure to atmosphere) aerogels. This finding may be important for understanding the mobility of methane in real coals, most of which contain certain amounts of adsorbed water at natural underground conditions.

[1] Chathoth *et al.* (2010) *Micro Mesopor. Mater.*, in press.

Pico- to nano-second dynamics of water on mineral surfaces

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Chemisorbed and physisorbed water is invariably present on mineral surfaces under ambient conditions. Our recent studies [1-3] present a coherent picture of surface water behavior. The nature of the host surface affects some properties of the adsorbed water, yet there are many universal features shared by surface water species on all minerals.

One of our important findings is the layered structure of the inner molecules of adsorbed water, which is greatly influenced by the surface of the host mineral. The dynamics of such water molecules are limited to the localized motions and layer-exchange jumps. The lateral mobility is greatly suppressed. On the other hand, the outermost layer of the adsorbed water is in many aspects reminiscent of bulk water and exhibits very significant lateral mobility. One important feature of the outermost water layer is the unsaturated number of hydrogen bonds per water molecule. We propose that the reduced number of hydrogen bonds is responsible for the fast dynamics observed on the pico-second time scale.

In general, the number and character of the hydrogen bonds for the molecules of a particular water layer appear to define their dynamical behavior, especially as a function of temperature. The nano-second dynamics of the adsorbed water can be traced down to below 200 K using high-energy-resolution techniques such as neutron backscattering spectroscopy. Combined with molecular dynamics simulations, neutron scattering provides very detailed picture of the adsorbed water dynamics over the temperature range of more than 100 degrees.

[1] Mamontov *et al.* (2007) *J. Phys. Chem. C* **111**, 4328–4341.

[2] Mamontov *et al.* (2008) *J. Phys. Chem. C* **112**, 12334–12341. [3] Mamontov *et al.* (2009) *Phys. Rev. E* **79**, 051504.