Direct Assessment of Transport Properties of Supercritical Fluids Confined to Nanopores

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With two essential properties, that is, liquid-like density providing substantial solubility and gaseous-like diffusivity offering enhanced mass transfer, supercritical (SC) fluids have become a powerful tool in many chemical processes. Because of their easily tunable properties between those of liquids and gases, SC fluids provide an invaluably accurate application-oriented instrument for manipulation of chemical reactions using green solvents. The rational design and full exploitation of the unique processing opportunities of SCF with unprecedented options of performance enhancement in a wide range of applications, such as heterogeneous catalysis, however, are severely limited owing to poor knowledge of their behavior in porous solids making their use rather empirical.

The phase behavior of fluids in pores at near- and supercritical conditions has been the subject of numerous studies. The overwhelming part of these is focused on the fluid densities and their anomalies with varying temperature or pressure under the conditions of confinement inside pores. Transport properties, which are essential not only for reaction operation but also for the understanding of the very nature of their intrinsic dynamics, were, so far, accessed indirectly by model-based analysis of diffusion-related processes (like catalytic conversions) or by theoretical calculations. Here, by using the unique potentials of pulsed field gradient (PFG) NMR for the exploration of molecular diffusion in nanopores we have overcome this ambiguity inherent to such type of procedures by simultaneously determining the fluid densities and diffusivities during transition from subcritical to SC conditions.

Two porous glass materials as host systems have been used: Vycor particles of about 500 μm size having internal mesoporous structure with a mean pore diameter d of about 6 nm and ERM-FD121 (ERM) with particles of 140−200 μm size and d of about 15 nm. The NMR glass tubes with the porous materials have been filled under vacuum with an amount of n-pentane to yield the critical density ρc = 3.22 mol/L at the bulk critical temperature $T_c \approx 470$ K. To calculate the required amount of the liquid, an account of both the free volume between the particles in the tube and the volume of the mesopores has been taken. This amount was sufficient to completely cover the porous particles, that is, during the experiments they were always surrounded by the liquid phase at temperatures below $T_c$.

Figure 1 illustrates typical diffusion spin−echo attenuation functions obtained at different temperatures using the PFG NMR method. A sufficiently large size of the porous particles prevented considerable exchange between molecules in the bulk phase and in the mesopores during the used observation time $t = 3$ ms of the Hahn-echo pulse sequence. In turn, this justified modeling the spin−echo attenuations, in first approximation, as a sum of two terms—exponentials with the respective weights. The thus obtained diffusivities $D_b$ and $D_p$, in the bulk liquid and in the mesopores, respectively, are shown in Figure 2 as a function of temperature. Both diffusivities increase with increasing temperature following an Arrhenius law, with the difference in the absolute values caused by the tortuosity of the porous space. Most importantly, however, around a certain temperature (ca. 438 K for Vycor and ca. 458 for ERM) a remarkable deviation from the Arrhenius pattern in $D_b$ is observed. Noteworthy, in the vicinity of this temperature the diffusivity of the bulk liquid for the sample with Vycor does not show an appreciable deviation from the normal behavior. In the ERM sample, owing to (i) the closeness of $D_b$ and $D_p$ and (ii) the smaller size of the porous particles, the fitting procedure at temperatures above 458 K is ill-posed, especially concerning $D_p$. However, similar as with the Vycor sample, the shape of the spin−echo attenuations in Figure 1b exhibits a well-observable transition around $T \approx 458$ K, manifesting the change in the fluid transport properties.
The signal intensity of the NMR free induction decay (fid) is a sensitive, relaxation-free quantity to probe a density change in the sensitive region of the NMR receiver coil. In our NMR tubes, the liquid height exceeded that of the receiver coil (see Supporting Information), allowing the use of the fid signal as an indicator of the density change. These measurements revealed a jump in the fid signal intensity at the same temperatures, namely 438 K for Vycor and 458 K for ERM.

This complementarity in the measured diffusivities and densities, that is, the coincidence of jumps in both quantities at one and the same temperature $T_{cp}$ below $T_c$ unambiguously indicates the transition into the SC state within the pore space.

The thus calculated diffusivities, with $D_i$ represented by the Knudsen diffusion coefficient,21 are shown by the full lines in Figure 2 and well reproduce the experimentally observed behavior.

Figure 2. Arrhenius plot of the bulk and pore fluid diffusivities for $n$-pentane in Vycor porous glass (a) and ERM (b) as a function of temperature. The solid line is calculated by assuming a transition to the supercritical state at $T = T_{cp}$. The vertical dashed lines show the positions of the bulk (left line) and pore (right line) critical points.

The present studies do not only represent the first concomitant evidence of the shift of the pore critical temperature by directly measuring the fluid transport (diffusivity) properties in the pores. They also do provide directly obtained absolute numbers for the diffusivities of a fluid in the SC state confined in a nanoporous solid. This helps, in particular, to rationalize that around the bulk critical temperature, that is, in the range of the dramatic increase in the bulk diffusivities, pore diffusion can already proceed in the SC state. The diffusivity remains essentially constant, being determined by the mean free path in the pore space according to the Knudsen limit of diffusion. In turn, this gives a tool to vary the diffusivity by a tiny change of the temperature by choosing an appropriate porous material. It is also noteworthy that such type of measurements may directly provide the pore critical temperature $T_{cp}$, which may be different from the hysteresis critical temperature obtained from adsorption isotherms.8,10

Thus, the direct measurements of pore diffusion in the SC state, all previous efforts of modeling and direct manipulation of processes by molecular transportation, can now be based on a sound, quantitative basis.13 The novel option of direct diffusion measurements should be extensively exploited for a better understanding and a rational exploitation of SC fluids for their manifold applications, for example, in extraction, separation, and heterogeneous catalysis.

Acknowledgment. Financial support from DFG and Fonds des chemischen Industrie is gratefully acknowledged.

Supporting Information. Financial support from DFG and Fonds des chemischen Industrie is gratefully acknowledged.

References