Advanced Textural Characterization of Novel Nanoporous Materials with Hierarchical Pore Structure

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Introduction

Most catalysts possess high specific surface areas and are highly microporous. However, the effective diffusivity in microporous molecular sieves (e.g. zeolite crystals) is very low, which hampers the application of zeolites for various applications. Therefore, the targeted introduction of mesoporosity into microporous molecular sieves is highly desirable in order to improve their transport properties. An accurate textural characterization of such micro/mesoporous materials is crucial for optimizing their applications, but is challenging because the pores in such materials have various geometries of different widths which range from narrow micro- to large mesopores. The most popular method to obtain surface area and pore size information from powders and porous solids is gas adsorption. However, despite the recent progress achieved in the understanding of the adsorption mechanism of fluids in highly ordered mesoporous materials with simple pore geometries (e.g., M41S materials), there are still many open questions concerning the phase and sorption behavior of fluids in more complex pore systems. In order to address the problem, we performed (i) systematic adsorption studies of pure fluids on a series of novel micro/mesoporous silica materials with hierarchical pore structures (ii) analyzed the gas adsorption data with novel Non-Local-Density-Functional-Theory (NLDFT) [2, 3] methods, which allows to describe the configuration of the adsorbed phase on a molecular level, and (iii) compared the pore size data from gas adsorption/NLDFT analysis with the results obtained by novel SANS (Small Angle Neutron Scattering)/SAXS (Small Angle X-ray Scattering) techniques and TEM (Transmission Electronic Microscopy).

Materials and Methods

The synthesis of the hierarchically ordered materials used in our study is described in detail in refs [1,2]. High-resolution nitrogen, argon, and krypton adsorption/desorption isotherm measurements (at 77 and 87 K) were performed with an Autosorb-I -MP sorption instrument (Quantachrome Instruments, Boynton Beach, FL). The adsorption data were analyzed using a new NLDFT model applicable to cylindrical and spherical pores with micro/mesoporous amorphous silica walls [2]. Details of the applied SANS/SAXS and TEM techniques are described in [2].

Results and Discussion

We report results of nitrogen and argon adsorption experiments performed at 77.4 K and 87.3 K on novel nanoporous silica materials with hierarchical pore structures. These materials consist of spherical pores (mean pore diameters ranging from 10 nm up to 35 nm)

connected through narrow micro- and mesopores (pore diameter < 5 nm). An example of a nitrogen adsorption/desorption isotherm on a hierarchically ordered silica material (KLE/IL silica) is shown in Figure 1, which reveals a wide hysteresis loop in the region where pore condensation/evaporation occurs. A detailed analysis of our data confirms that pore condensation was delayed due to the existence of metastable adsorption films, thus hindering nucleation of liquid bridges. Evaporation of the condensed pore fluid from the spherical cavities occurs by cavitation if the width of the connecting pores is smaller than a critical value ($\leq$ 5 nm) [2]. However, if the width of the neck is larger than this critical width, evaporation occurs through pore blocking/evaporation; in this case the size of the pore necks (which control the accessibility of the porosity) can be determined from an analysis of the desorption branch [2]. It has been further demonstrated that the use of different probe molecules (e.g. nitrogen and argon) allows for detecting and separating the effects of pore blocking/percolation and cavitation in the course of evaporation [2]
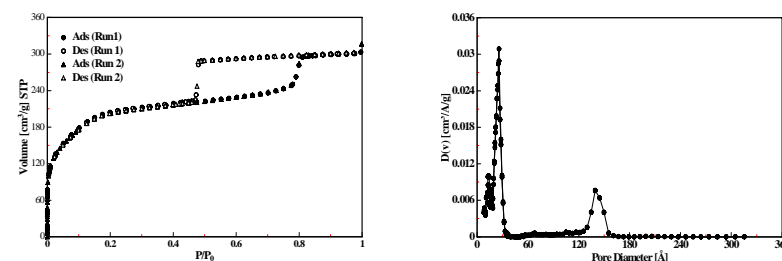
Figure 1 (a) Adsorption of nitrogen (at 77 K) in hierarchical ordered silica (KLE/Il silica) and (b) NLDFT pore size distribution, revealing modes at 1.3 nm, 2.6 nm and 14 nm).

We applied a novel NLDFT method for calculations of pore size distributions from adsorption isotherms in the entire range of micro-and mesopores.This novel NLDFT method takes into account the effect of delayed capillary condensation in pores of different geometries (cylindrical pores for the micro- and narrow mesopore size range, spherical pores in the range where hysteresis occurs [2,3]). The pore size data obtained by the NLDFT method agree with the results of novel SANS/SAXS techniques [2].

Significance

Our results lead to a better understanding of the adsorption and phase behavior of fluids in hierarchical ordered porous materials, which is not only important for an accurate and comprehensive textural characterization of adsorbents consisting of complex micro-mesoporous pore networks, but also for optimizing their use in practical applications.

References

[1]. Sel, O., Kuang, D., Thommes, M; Smarsly, B. *Langmuir* **22**, 2311 (2006)
[2] Thommes, M., Smarsly, B., Groenewolt, M.; Ravikovitch, P.I., Neimark, A.V.
 Langmuir **22**, 756 (2006)
[3]. Neimark, A.V., Ravikovitch, P.I., Vishnyakov, A., *Phys. Rev. E* **62**, (2000) R1493