**Quantitative Assessment of Hydrophilicity/Hydrophobicity in Nanoporous Materials**

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We have developed a comprehensive strategy for assessing the surface chemistry of nanoporous materials by combining advanced adsorption studies, novel liquid intrusion techniques and solid-state NMR spectroscopy. The methodology was established on a well-defined system of model materials, the highly ordered mesoporous silica SBA-15, both pristine and functionalized with different amounts of trimethylsilyl (TMS) groups. The surface density of trimethylsilyl groups, was determined by quantitative 1H solid-state NMR spectroscopy under Magic Angle Spinning (MAS). 1H two-dimensional single quantum double quantum MAS NMR spectra reveal an intimate mixture of TMS and residual silanol groups on the surface. A full textural characterization of the materials was obtained by high-resolution argon at 87 K adsorption, coupled with the application of dedicated methods based on non-local-density functional theory. We further present a methodology to determine the effective contact angle of water adsorbed on the pore surfaces, which constitutes a powerful parameter for the characterization of the surface chemistry inside porous materials. The surface chemistry was found to vary from hydrophilic to a hydrophobic as the TMS functionalization content was increased, leading to contact angles from 0 ° (complete wetting) to 120 ° (non-wetting). For wetting and partial wetting surfaces, the contact angle was determined from the water sorption isotherms by applying the modified Kelvin equation on the desorption branch of the observed hysteresis loop, reflecting the thermodynamic liquid-vapour transition. On non-wetting surfaces, we investigated the pore filling of water by the application of a novel liquid water intrusion/extrusion experiment, applying the Washburn equation on the water intrusion branch which reflects the thermodynamic equilibrium vapor-liquid transition for a non-wetting fluid. Molecular simulations provide density profiles of water on pristine and TMS-grafted silica surfaces, which agree with the obtained experimental data.

The methodology presented here can in principle be used for assessing the hydrophilicity/hydrophobicity of a wide range of nanoporous materials for optimizing their properties towards applications in chromatographic separation or heterogeneous catalysis.