Adsorptive Heat Transformation toward Heating and Cooling Applications: Computer Modeling and Experimental Studies of Water Sorbed in Metalorganic Frameworks

Panagiotis D. Kolokathis[a] Evangelia Pantatosaki[a] Tobias Splith[b], Christian Chmelik[b], Frank Stallmach[b], Stefan K. Henninger[c], Gerrit Fueldner[c], and George K. Papadopoulos[a]

[a] *School of Chemical Engineering, National Technical University of Athens, Athens, Greece*
[b] *Institut für Experimentelle Physik I, Universität Leipzig, Leipzig, Germany*
[c] *Fraunhofer-Institut für Solare Energiesysteme ISE, Freiburg, Germany*

Adsorptive heat transformation can be used for energy storage, heat pumps and chillers. For these applications a liquid (usually water) is evaporated from a reservoir at low temperatures and then adsorbed in a porous solid adsorbent (usually zeolites or silica gel). Then the heat of adsorption at moderate temperature levels, or the cooling from desorption is utilized. When saturated, the adsorbent needs to be regenerated with heat at higher temperatures. The efficiency of this cyclic process is limited both by the sorption equilibria as well as by the heat and mass transfer rates. In thin adsorbent coatings on adsorbent heat exchangers, heat transfer is not dominating the dynamics anymore, while diffusion processes can play a rate limiting role.

Here we are examining the adsorption and diffusion properties of water in selected new promising for energy storage metalorganic frameworks (MOFs) such as the Materials Institute Lavoisier, MIL-100, and the Aluminium Fumarate. Our study combines experimental investigations of water diffusion by pulsed field gradient nuclear magnetic resonance (PFG-NMR), time-resolved infrared (IR) microscopy, and adsorption characterization, with molecular dynamics (MD) simulations. The investigations aim at a better understanding of the water transport processes and thermodynamics, and also at the identification of transport resistances within the micropores of the crystalline material as well as within the coatings produced from these materials, all with particular focus on application for the production of efficient heat exchangers. The MOF crystals and their coatings on glass rods and aluminium supports were prepared and characterized by adsorption techniques at the Fraunhofer Institute of Solar Energy Systems.

The selfdiffusivity of water in the beds of crystals and coatings were investigated by PFG NMR. The time resolved IR microscopy was utilized for the measurement of the so-called transport diffusivity and its applicability was tested successfully on silicon aluminon phosphates PFG-NMR and IR-microscopy experiments were carried out at the Physics Department of the Leipzig University.

The sorption thermodynamics of water at room temperature was computed by means of molecular dynamics computer experiments in a digitized MIL-100(Fe) through post processing the MD trajectories by means of the Widom averaging method; our modeling work provided explanation of the experimentally observed isotherm's step. The Henry constant, as well as the isosteric heat of adsorption as a function of loading, were in good agreement with the measured values. The self-diffusivity coefficients of water in the MIL-100 were also predicted by MD simulations for various water loadings; at maximum capacity the self-diffusivity was found to be five times lower than in the bulk liquid water at room temperature. We found that altering the distribution of the anions in the dodecahedral cavities may increase the isosteric heat of sorption of water in the MIL-100 at low pressures prior to the isotherm step, a result that favors the efficient design of adsorptive enthalpy transformation processes.