

POROUS COORDINATION POLYMERS AND ALUMINOPHOSPHATES, TRANSFORM WATER ADSORPTIVE HEAT TO DRIVE SOLAR COOLING AND HEATING

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ABSTRACT

We present a recent work ^[1-4] on novel aluminum-based sorbent porous materials for solar thermally driven cooling and heating processes. Such applications constitute an efficient system for adsorptive heat transformation of clean and renewable sorbates (e.g. water) within these materials. The regeneration part of the thermodynamic cycle of the system requires desorption of the sorbate at elevated temperatures, utilizing solar energy thereby minimizing primary energy consumption and carbon emissions. Our studies comprise a combination of experimental and computational techniques; hydrothermal cycle experiments, in-situ powder X-ray diffraction analysis, in-situ second harmonic generation microscopy experiments, pulsed field gradient NMR measurements, density-functional theory computations, Monte Carlo and molecular dynamics simulations, and a Widom-type scheme. The studied Al-frameworks exhibit high uptake capacity and fast kinetics for water sorbate, and the ability to withstand the harsh conditions imposed during repeated water sorption/desorption cycles in heat-pumping and cooling applications with no loss of crystallinity or porosity and no degradation of the framework. Our studies highlight the aluminum-based sorbents coded as CAU-10-H, MIL-100 and SAPO-34 among the most promising next-generation adsorbents for thermally driven cooling and heating applications.

INTRODUCTION

A promising application of aluminum-based metalorganic frameworks (MOF), also known as porous coordination polymers (PCP), and aluminophosphate structures is their use as adsorbents in adsorption heat transformation, i.e., adsorption heat pumps and adsorption chillers ^[1]. The choice of aluminum as the PCP's metal center, has proved to provide stable porous materials, yet its light weight furnishes low density sorbents that along with its natural abundance allow for low-cost production on industrial basis. In our recent work ^[1-4] three aluminum-based sorbents have been highlighted as promising candidates for their use in the aforementioned applications:

(a) The aluminium isophthalate, coded as CAU-10-H, is a recently synthesized porous coordination polymer (PCP) that shows a small reversible structural change during adsorption and no loss in crystallinity or porosity after repeated water vapour adsorption/desorption cycles ^[1].

(b) The aluminum MIL-100, an aluminum benzene tricarboxylate MOF ^[2], is considered as one of the most interesting structures due to the presence of Al active sites, which make its network of interconnected mesoporous cages capable of hosting large amounts of various sorbate guests.

(c) The silicon-aluminum-phosphate SAPO-34 is a microporous structure with a three-dimensional pore network of ellipsoidal cavities; a low silicon content SAPO-34 sample (Si/Al = 0.16) exhibits

structural stability in water vapor atmosphere as revealed by in-situ X-ray diffraction analysis^[5]. The performance of the PCP materials for the aforementioned applications is vastly influenced by the transport rates of guest (water) sorbates inside the pores of the host matrix. The general objective of our studies is the interpretation of the water sorption thermodynamics and kinetics in view of the influence of porosity and chemical interior of these selected aluminum-based structures that have the ability to withstand the harsh conditions imposed during repeated water sorption/desorption cycles.

EXPERIMENTS

Experimental procedures and simulation methodology are described below in brief. For details the reader is referred to our recent publications [Ref. 1-4].

Hydrothermal cycle stability. Hydrothermal cycle stability of the CAU-10-H material was investigated by short cycle experiments under isobaric conditions (5.6 kPa H₂O vapour) between 140 °C and 40 °C within the Rubotherm thermobalance. Advanced long term hydrothermal stability to 10 000 full cycles was acquired within a custom-made closed cycle apparatus, consisting of a vacuum chamber under a pure water vapour atmosphere of 1.2 kPa.

Powder X-ray diffraction (PXRD) analysis. PXRD analysis was performed on a Bruker D8 Advance diffractometer with DaVinci™ design, using Cu-Kα radiation from a Cu anode tube at 40 kV/40 mA with a Ni filter in Bragg Brentano geometry.

In situ second harmonic generation (SHG) microscopy. For the SHG microscopy experiments a customized inverted wide-field Olympus microscope coupled to a femtosecond pulsed InSight DeepSee laser operating at a wavelength of 800 nm was used.

Pulsed field gradient (PFG) NMR experiments. The mobility of the water sorbed phase in the crystals was studied by means of PFG NMR experiments. Also, the water longitudinal relaxation time, T_1 , and the transverse relaxation time, T_2 , were measured via inversion recovery and CPMG (Carr–Purcell–Meiboom–Gill) pulse sequences, respectively. The in-house (Leipzig University) built FEGRIS NT NMR spectrometer operating at the ¹H-resonance frequency of 125 MHz was used for these experiments. For the PFG NMR diffusion studies this spectrometer is equipped with a z-gradient system capable of delivering gradient pulses up to 37 Tm⁻¹.

Computer modeling. Atomistic digitization of the crystals was performed using an in-house code^[1-4]. For the calculation of the partial charges on the frameworks atoms we followed either a hybrid scheme combining density-functional theory (DFT) in small atomic clusters of the host framework and electronegativity equalization method, or pure periodic DFT calculations. Crystal frameworks were modeled as rigid (MIL-100) or flexible (CAU-10-H, SAPO-34) based on the relative size of their apertures with respect to the kinetic diameter of the water molecule, and also in view of our previous studies where adsorbate molecules experience tight fitting in pores^[6,7]. Molecular dynamics (MD) simulations were performed for the extraction of diffusion coefficients for various water loadings. Water sorption isotherms were computed by employing two different computational methodologies: either via Monte Carlo simulations in the Grand Canonical ensemble or a combination of the sorbed-bulk phase coexistence with properly adapting a Widom averaging scheme along the trajectory of the system as produced by MD simulations^[2,3]. A complementary computational scheme to the thermodynamics of the sorbent-water system is the calculation of the differential enthalpy of sorption, which can be evaluated following a Widom averaging procedure^[2,3].

RESULTS AND DISCUSSION

CAU-10-H porous coordination polymer. The total water capacity loss for CAU-10-H upon water sorption/desorption cycles amounts to 0.003 g g⁻¹, 2.3%. The sample passed 10 000 cycles in the custom-made cycle test rig; the uptake capacity was measured after 1000, 5000 and 10 000 cycles

within the thermobalance. No loss of uptake capacity, within the measurement error, was observed (Fig. 1, left). In addition, the powder X-ray diffractogram before and after 10 000 adsorption/desorption cycles showed that all reflections are preserved and no change in crystallinity is visible (Fig. 1, right).

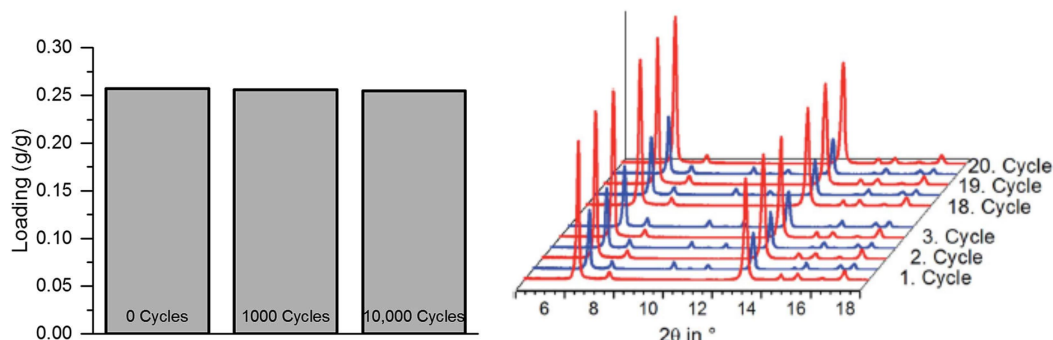


Figure 1. (Left) Comparison of the uptake capacity prior to cycle treatment, after 1000 and after 10 000 adsorption/desorption cycle; (Right) 20 adsorption (blue)/desorption (red) cycles of CAU-10-H with in situ XRD observation. For clarity, only the first 3 cycles and last 3 cycles are shown.

The PXRD analysis and in-situ SHG measurements for the CAU-10-H crystal at different relative humidity values unambiguously prove a phase transition between the known non-centrosymmetric form of CAU-10-H and a not yet reported dry, centrosymmetric conformation. Upon dehydration/rehydration, no bonds are broken and the observed phase transition can be attributed to conformational changes which result from coordination of water molecules.

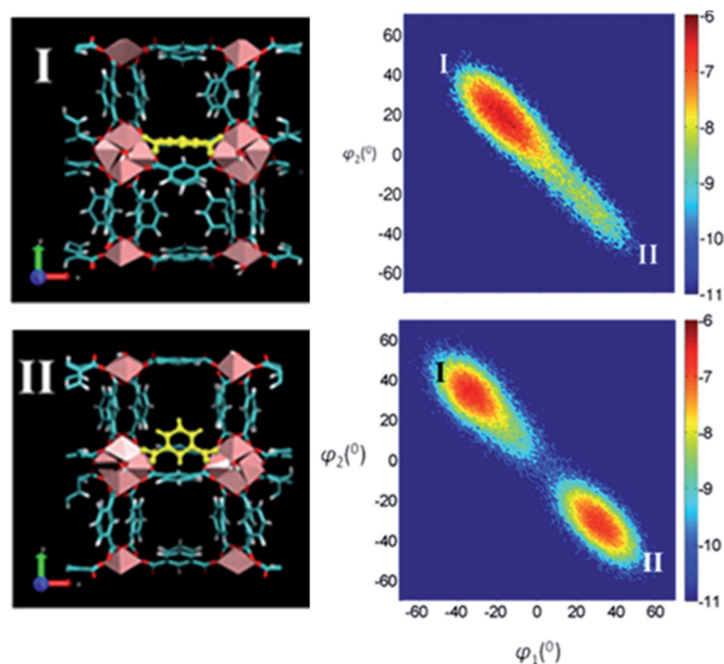


Figure 2. MD calculations: correlation probabilities of the dihedral angles φ_1 and φ_2 for the CAU-10-H ligands attaining two conformation extrema I and II (left), for the dry (right top), and the water-loaded material at 0.303 g g^{-1} (right bottom).

The above conformational changes upon CAU-10-H water hydration were investigated via molecular dynamics simulations. The molecular dynamics revealed that the organic linker in the CAU structure can take conformations between two extrema (Fig. 2) with the one being almost parallel (state I) and the other being vertical (state II) to the channel axis, so that conformations of the linkers approaching the state I or II can widen or narrow, respectively, the effective path-width

of the channels. In Fig. 2, the correlation probabilities between the dihedral angles φ_1 and φ_2 denoting the motion of the linker's carboxylate group relative to the aromatic ring are presented, over the total number of linkers, for both the bare and water-loaded materials at 0.303 g g⁻¹. It is shown that in the dry material the most probable conformations are achieved when the aromatic rings tend to lie almost parallel along the z-direction. The above situation changes gradually upon water adsorption, in the sense that the increasing guest concentration gives rise to two distinct sets of conformations between the vicinity of states I and II separated by a lower probability region, thus forming a free energy barrier of about $3k_B T$, where $k_B = 1.3806 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant; presumably this is a consequence of steric hindrance phenomena at higher loadings up to saturation.

The MD predicted isosteric heats of water in the CAU sorbent were calculated after developing a Widom type scheme and are reported to be in the range of 50-55 kJ mol⁻¹ along the whole occupancy range ^[1].

MIL-100 porous coordination polymer. The mobility of the water sorbed phase in the MIL was studied by means of PFG NMR experiments and molecular dynamics simulations ^[2]. The PFG NMR experiment measured an effective observation time-dependent diffusion coefficient, representing the guests' motion within the intracrystalline mesopore network up to times they have either reflected or left the surrounding surface barriers in various beds of MIL-100(Al) crystallites. To extract the pure intracrystalline self-diffusivity from the measured spin echo attenuation curves, a theoretical expression of random walkers' diffusivity as a function of the NMR observation time was utilized, assuming spherical interfaces, and reflecting boundary conditions for the solution of the diffusion equation following Mitra et al. ^[8].

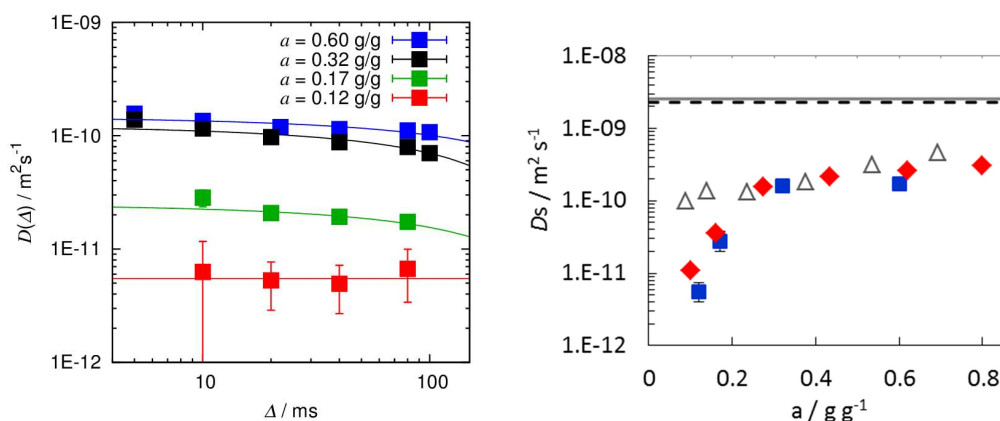


Figure 3. (Left) Effective intra-crystalline diffusivity, $D(\Delta)$, of water in aluminum MIL-100 as a function of the observation time, measured via PFG NMR for various loadings at 298 K; lines represent fit of Eq. (1) thereby the pure intra-crystalline diffusivity, D_s , was evaluated. (Right) Intra-crystalline water self-diffusivity as a function of loading in the aluminium MIL-100, extracted from PFG NMR (blue squares), and predicted by MD simulations (red diamonds); simulation data from the iron MIL-100 homologue (triangles) ^[3] are also present for comparison; measured (dashed line), and computed using the SPC/E model (solid line) liquid water self-diffusivities at 300 K are also shown.

Since our data analysis procedure only takes into account water molecules that stay inside the MIL crystallites over the entire observation time, the case of reflective boundary conditions applies leading to the expression

$$D(\Delta) = D_s \left[1 - \frac{4}{3r} \sqrt{\frac{D_s \Delta}{\pi}} - \frac{D_s \Delta}{2r^2} \right] \quad (1)$$

where r represents the crystallite radius (assuming spherical crystals) and D_s is the unrestricted (true) self-diffusion coefficient of molecules, namely, not being subject to the influence of the particle boundaries; it is the quantity that molecular dynamics simulation directly computes by elaborating the guest trajectories.

Figure 3 (left) presents a measured time-dependent effective (restricted by the mesopores and particle boundaries) diffusivity of water in the bed of particles as a function of the observation time at various loadings. Fit of Eq. (1) to experimental data provides the pure (restricted by the particle pore network) intra-crystalline diffusivity, and the MIL-100(Al) average crystal radius, r . The intracrystalline self-diffusivities computed via MD for a series of water concentrations were found to be in reasonable agreement with the ones extracted from PFG NMR taking into consideration the convenient hypothesis of spherical crystallites; they are presented in Figure 3 (right) over the whole occupancy range.

The measured activation energies for diffusion were in agreement with the predicted trend in the evolution of the water adsorbed phase probability density profile (being analogous to free energy profile) with increasing loading^[2], verifying also the progressive filling of the small and large pore systems first proposed in the iron MIL-100 homologue^[3].

Aluminophosphates. The diffusion of water in SAPO-34 was investigated experimentally by means of PFG NMR in the temperature and loading range relevant for adsorptive heat transformation applications^[4]. We also report the first molecular dynamics simulation of the actual SAPO-34 material containing silicon atoms substituting for P atoms in the ideal alimino-phosphate crystal lattice^[4]. The absence of such simulations in the scientific literature can be attributed to the fact that commercial or academic packages have not included SAPO-34 (no such a force-field yet), and also, because there is no trivial way for adding Si atoms.

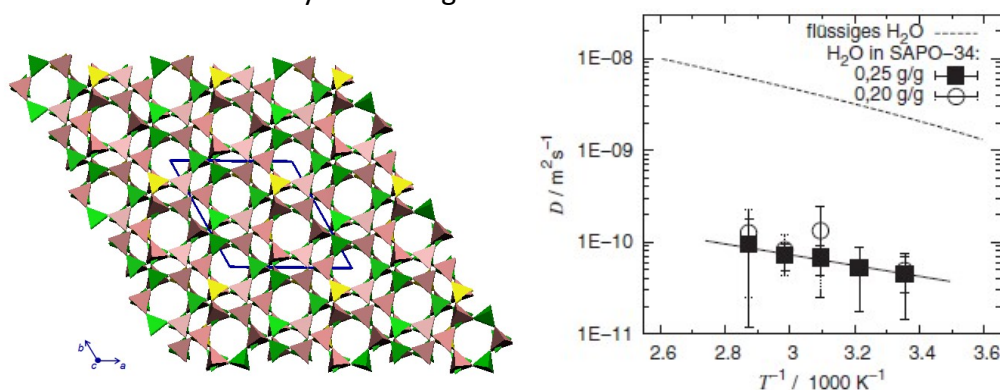


Figure 4. (Left) Representation of the hexagonal unit cell of the SAPO-34 as a projection onto the plane of the 6-membered ring windows between the cavities of the chabazite (CHA) structure. The TO_4 tetrahedral units are shown (AlO_4 : pink, PO_4 : green, SiO_4 : yellow) are shown; hydrogen atoms are omitted. (Right) Arrhenius representation of temperature dependency of the intracrystalline self-diffusion $D(T)$ of water in SAPO-34 at 0.20 and 0.25 $g\ g^{-1}$ water loadings; the experimental self-diffusivity of liquid water (dashed line) is also shown for comparison. The solid line represents the result of the exponential adjustment for determining the activation energy and the pre-exponential factor of diffusion.

Self-diffusion coefficients derived from NMR diffusion studies in thermodynamic equilibrium are found to be two orders of magnitude smaller than the diffusivity of liquid water at the same temperature (Fig. 4). This is a direct consequence of the obstruction of molecular motion in the narrow micropores of the SAPO-34 and the sorbate-sorbent interaction. The temperature dependence of the water diffusion may be well described by an activation energy of (11 ± 2) kJ mol⁻¹.

CONCLUSIONS

Several experimental and simulation techniques were invoked to investigate the water sorption thermodynamics and kinetics in novel crystalline aluminum-based materials in view of the influence of porosity and chemical interior of these selected structures that have the ability to withstand the harsh conditions imposed during repeated water sorption/desorption cycles. All structures exhibited hydrothermal stability with no loss of crystallinity or porosity and no degradation of the framework. Diffusion rates of water in the temperature and loading range relevant for adsorptive heat transformation applications showed that the thermal mobility of water in the pores with a self-diffusion coefficient of about 10^{-11} to 10^{-10} m^2s^{-1} is still large enough to meet the prerequisites for a fast compensation of intra-crystalline concentration gradients during adsorption and desorption. Our studies highlight the Al-based CAU-10-H, MIL-100 and SAPO-34 among the most promising next-generation adsorbents for thermally driven cooling and heating applications.

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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

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