Porous Coordination Polymers as Novel Sorption Materials for Heat Transformation Processes

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Abstract: Porous coordination polymers (PCPs)/metal-organic frameworks (MOFs) are inorganic–organic hybrid materials with a permanent three-dimensional porous metal–ligand network. PCPs or MOFs are inorganic–organic analogs of zeolites in terms of porosity and reversible guest exchange properties. Microporous water-stable PCPs with high water uptake capacity are gaining attention for low temperature heat transformation applications in thermally driven adsorption chillers (TDCs) or adsorption heat pumps (AHPs). TDCs or AHPs are an alternative to traditional air conditioners or heat pumps operating on electricity or fossil fuels. By using solar or waste heat as the operating energy TDCs or AHPs can significantly help to minimize primary energy consumption and greenhouse gas emissions generated by industrial or domestic heating and cooling processes. TDCs and AHPs are based on the evaporation and consecutive adsorption of coolant liquids, preferably water, under specific conditions. The process is driven and controlled by the microporosity and hydrophilicity of the employed sorption material. Here we summarize the current investigations, developments and possibilities of PCPs/MOFs for use in low-temperature heat transformation applications as alternative materials for the traditional inorganic porous substances like silica gel, alumino phosphates or zeolites.

Keywords: Adsorption · Coordination polymers · Heat transformation · Metal-organic frameworks · Water sorption

Introduction

Inorganic metal–organic ligand compounds that extend “infinitely” into one-, two- or three dimensions (1D, 2D or 3D, respectively) through the bridging action of the organic ligand are called coordination polymers.[1] The sub-class of 3D coordination polymers which also possesses a usable permanent porosity is termed porous coordination polymers (PCPs)[2] or metal–organic frameworks (MOFs). PCPs/MOFs have attracted tremendous attention over the past years.[3] This is due to their porosity, large inner surface area (typically 1000–4000 m²/g), tunable pore sizes and topologies,[4] which lead to versatile architectures[5] and promising applications,[1,6] such as ion exchange, gas adsorption and storage of, in particular, hydrogen and methane,[7] gas[8] and liquid[9] separation processes,[10] drug delivery,[11] sensor technology,[12] heterogeneous catalysis,[13] hosts for metal colloids or nanoparticles[14] or polymerization reactions,[15] pollutant sequestration,[16] microelectronics,[17] luminescence,[18] non-linear optics[19] and magnetism (Fig. 1).[20] The pore size and sorption properties, including affinity towards different adsorbates of MOFs, can be tuned through a large variety of organic ligands, different from other porous materials like zeolites or active carbon. An additional advantage of MOFs over other porous materials is their identical pore size over the whole framework structure.

Research on thermally driven adsorption chillers (TDCs) or adsorption heat pumps (AHPs) is gaining attention for low-temperature heat transformation applications in view of rising electricity and energy costs.[21,22] Conventional compressor air-conditioner cooling systems use electrical energy, thereby significantly contributing to CO₂ emission. More than 50% of the energy consumption of modern buildings originates from air-conditioning processes.[23] Thus, the demand of electrical energy for air conditioning is expected to increase further in the future due to...
higher living standards as well as building trends. Therefore, energy saving air-conditioning technologies are urgently needed. For this, low-temperature waste heat from industrial processes or even solar energy is an attractive possibility for heating or cooling with alternative technologies in TDCs or AHPs.

**Working Principle of TDCs or AHPs**

From several working principles, the reversible evaporation and subsequent adsorption of a working fluid has proven most promising. The principle method is illustrated in Fig. 2.

In the working, that is the production or adsorption cycle, a dry or empty (hydrophilic) sorption material drives the evaporation of the working fluid, such as water. When the working fluid is evaporated it needs heat of evaporation $Q_{\text{evap}}$ from the environment. Thereby useful cold is produced in the cooling case or heat is extracted from a low-temperature heat source in a heating application. The vapor of the working fluid is adsorbed into a porous material where it generates heat of adsorption $Q_{\text{ads}}$. This heat is released to the environment in the cooling case or utilized in the heat pump application. In the regeneration cycle, the fluid-filled porous material is dried or emptied by applying driving heat $Q_{\text{des}}$ for desorption. This heat of desorption $Q_{\text{des}}$ can come from various external sources like solar energy, industrial waste heat or a gas burner. The adsorbed fluid is released and condenses at a medium temperature level releasing the heat of condensation $Q_{\text{cond}}$. Depending on heat input and output, the operation direction can be chiller or heat pump (see Table).

Water is the working fluid of choice because of its high evaporation enthalpy (2440 kJ/kg at 25 °C) and non-toxicity. Other fluids that can be employed for this process are methanol or ammonia. The adsorbent (solid material)/adsorbate (working fluid) pairs zeolite/water, silica gel/water, active carbon/methanol, active carbon/ammonia have been studied for TDCs or AHPs.[24] The inorganic materials silica gel and zeolites are currently employed in commercial TDC and AHP applications but they have disadvantages.[25] Zeolites have a high affinity to water and already adsorb at low relative pressure of $p/p_r = 0.001$–0.01, but they require high desorption temperatures (typically over 300 °C) and have a low water loading lift (Fig. 4). Silica gels have a lower hydrophilic character than zeolites which leads to lower desorption temperatures (typically ca. 100 °C) but also a low water loading within a desorption cycle (Fig. 4). Therefore new porous materials with improved sorption and cycling properties are attractive. A sorption material for TDCs or AHPs should show a high water uptake capacity at low to medium humidity and desorb the water vapor at low temperature (below 80 °C).[27] Ideally, a porous material should perform in between 0.05 < $p/p_r$ < 0.35 relative pressure range and should have a desorption temperature at or below 80 °C (Fig. 5).[28, 29]

Thermodynamically the water or working fluid exchange between the working (adsorption) cycle and the regeneration (desorption) cycle can be described as a difference between the richest and the weakest isostere of the cycle as illustrated in Fig. 5. In the thermodynamic context, the term **isosteric** denotes a process which occurs at a constant water loading, i.e. without ad- or desorption. An ideal cycle as water loading versus the relative pressure is depicted...
in Fig. 5. This cycle in Fig. 5 consists of two isosteres with load 0.1 (weakest) and 0.4 g/g (richest), respectively, determined by the boundary condition thus leading to a reachable loading lift (as one figure of merit) within the cycle of 0.3 g/g, which is a minimum benchmark.

The cycle is defined by the highest desorption temperature (driving temperature, Point D), the minimum adsorption temperature (Point B), the condenser and evaporator pressure. The maximum desorption temperature at Point D and condenser pressure as well as the minimum adsorption temperature at Point B and at evaporator pressure can be transformed into relative pressures thus giving the working window of the cycle. For typical values this window lies between 0.05 < p/p₀ < 0.32 relative pressure in which a maximum working fluid exchange has to be reached. The evaluation of materials for TDC or AHP application can be realized by measurement of two isotherms, corresponding to the condenser and evaporator temperature.

**Potential of PCPs/MOFs for Water-based Heat Transformation**

The hydrothermal instability of most MOFs limits their application as adsorbents due to the unavoidable presence of moisture on a technical scale. Water stability of MOFs is, of course, a key issue for water-based heat transformation. Well-known MOF-5 and the IRMOF-series have a low moisture stability.[29-31] HKUST-1 (Cu-BTC) is intermediate but eventually decomposes (see below).[32] However MOFs that are synthesized hydrothermally are expected to show higher water stability, though their porosity as well as crystallinity in the absence of water molecule needs to be explored. The research group of Férey has hydrotrophically synthesized a series of porous materials, also known as MILs (MIL stands for Material Institute Lavoisier).[30,31] These materials have high surface areas and large pore volumes. The MIL compounds, including MIL-101[32,33] and ZIF-8[34] are of higher water stability.[35,36] The water stability of ZIF-8 derives, however, from its hydrophobic nature which precludes its utilization as a water sorbent material.

Work on MOFs as water adsorbent is gaining attention since an early report by Aristov[22b] and of water adsorption studies on HKUST-1[22b] and ISE-1[37] from our group.[27] HKUST-1 or Cu-BTC with composition [Cu₆(BTC),(H₂O)]₆ is an easily prepared[38] and widely investigated MOF[39] constructed from a Cu₆ handle coordinated by four benzene-tricarboxylate molecules to a cubic structure (Fig. 6). HKUST-1 shows a water uptake of 0.3–0.55 g/g, albeit at poor hydrothermal stability (Fig. 6).[22b,35]

The mixed-ligand MOF [Ni₆(µ-three-BTRE)(µ-H₂O)]₆ (ISE-1, Fig. 7) (BTRE = 1,2-bis(1,2,4-triazol-4-yl)ethane) is synthesized from water with an initial water content of ca. 30 wt%.[40] This water content can be reversibly desorbed and adsorbed over several cycles (Fig. 7).[37] MIL type materials absorb huge amounts of water (1.0–1.5 g/g for MIL-101Cr, 0.6–0.7 g/g for MIL-100Cr, 0.65–0.75 g/g for MIL-100Fe, 0.5 g/g for MIL-100Al) and have very good water cycle stability.[27] The adsorption of water vapor in the highly porous MIL-101 with the composition [Cr₂O₃(OH)₃(H₂O)],(BDC) of over 1 g/g together with the stability over several cycles makes MIL-101 a promising material for heat transformation applications (Fig. 8). MIL-101Cr has an augmented MTN zeolite topology with two types of inner cages with diameters of 29 Å and 34 Å (Fig. 8) and pore aperture windows diameters of up to 16 Å which give a high surface area (BET surface area up to 4000 m²/g). MIL-101Cr is synthesized in quite harsh reaction conditions (220 °C in water).[32] Thus, a fundamental water stability of this material can be expected and was verified over 40 water sorption cycles.[35]

MIL-101Cr can be functionalized with amino, nitro or other groups on the benzene-1,4-dicarboxylate linker through time-controlled post synthetic modification of the parent material.[42,43] The partially functionalized materials contain about 78 mol% amino or nitro functionalized terephthalate linker (Fig. 9).[44] Hydrophilic nitro or amino functionalities were intro-
duced into MIL-101Cr in order to achieve the water loading at lower p/p₀ values for the possible use in thermally driven adsorption chillers or heat pumps (Fig. 9).[43] Fully and partially aminated MIL-101Cr-(p)NH₂ showed unchanged water loading with respect to parent MIL-101Cr (about 1 g H₂O/gMIL) as well as very high water stability over 40 adsorption-desorption cycles.[44] At high humidity (p/p₀ = 0.8–0.9) the water uptake capacity is not only determined by the available porosity, but also by the hydrophobicity/hydrophilicity of the ligand, the hydrogen-bonding capabilities and directing effects of functional groups, and a possible degradation or structure transition of the adsorbent material, as was discussed for functionalized Zr-based UiO-66 MOFs.[45]

MIL-100 materials have the empirical formulae [M₂O(F,OH)(H₂O)(BTC)] (M = Cr, Al, Fe) and have received attention in literature with respect to their catalytic, gas separation and gas storage properties.[11c,46] The porosity of MIL-100s originates from 25 Å and 29 Å mesopores, which are connected through 5.5 Å and 8.6 Å windows, respectively, to give surface areas of 1500–2000 m²/g (Fig. 10).[46] Again, MIL-100s form under quite harsh synthesis conditions (pH <1, T >150 °C) so that water stability can be anticipated.[46a,d] The adsorption/desorption of 0.5–0.75 g of water vapor per g of the porous MIL-100 materials occurs at small relative pressures of p/p₀ <0.4 and a comparatively small hysteresis. Together with very good cycle stability, these properties render all MIL-100 (Cr, Al and Fe) as very suitable candidates for thermally driven heat pumps or adsorption chillers (Fig. 10).[23,41]

Zeolitic imidazolate frameworks (ZIFs),[47] also termed metal-azolate frameworks (MAFs)[48] are PCPs/MOFs with cubicoctahedral β-cages and often with a sodalite topology. These metal-organic zeolites are built from anionic imidazolate ligands (or its derivatives) bridging between single zinc atoms (Fig. 11). ZIFs are porous but with less open pores than other MOFs due to smaller pore windows. Only smaller molecules can access ZIFs. The pore aperture of ZIF-8, [Zn(2-methylimidazolate)], has a diameter of 3.4 Å allowing it to readily absorb small molecules such as H₂ and CO₂. ZIF-8 is one of the most hydrostably stable PCPs among those studied.[29] However, this water stability can be traced to its hydrophobic nature with only small water uptakes of 26 mg g⁻¹.[48]

When the 2-methylimidazolate ligands in ZIF-8 are partially substituted by 3-methyl-1,2,4-triazolate ligands (mtz), the ZIF-8 structure is retained and the hydrophilicity of the mixed-ligand MAF-network increases. The mtz ligand uses only two of its three N atoms for metal coordination, leaving the third as a hydrogen-bond acceptor. With increasing mtz content not only does the water load increase but the adsorption isotherm starts to rise at much lower p/p₀ values. For the pure [Zn(mtz)₂] MAF the water load is 0.44 gg⁻¹ with a sharp rise of the adsorption isotherm already between p/p₀ = 0.24–0.37.[48]

Conclusions

MOFs are about to substantially broaden the range of potential adsorption materials which can be used for heat transformation (cooling, heat pump) and heat storage applications. MOFs show a very promising potential in this field and surpass traditional materials with their large water uptake capacities. The variabilty in metal and ligand compositions inherent in MOFs allow for the flexibility in the sorption properties needed in heat transformation applications. Water adsorption capacity correlates not only with the available pore volume,
but also with the hydrophobic/hydrophilic nature of the ligand, its hydrogen-bonding capabilities, directing and intergrowth effects of functional groups, metal or ligand site preference and a possible degradation or structure transition of the MOF material. Further research efforts are needed to lower the still relatively high load pressure at which the still relatively high load pressure at which the water content increases only a small loss in the water uptake over 40 sorption cycles.

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PCPs/MOFs. Also, the hydrothermal stability needs to be proven for over 100000 ad- and desorption cycles without significant loss of uptake capacity (aging).

Fig. 11. Section of the crystal packing diagram of ZIF-8. The zinc atoms are bridged by 2-methylimidazolate ligands which span the edges (blue topological lines) of the cuboctahedral β-cage in the sodalite network. The yellow sphere with a diameter of 12 Å highlights the inner pore of the sodalite cage, the orange sphere with a diameter of 3.4 Å the pore aperture window of the 6-membered rings. Both spheres take into account the van-der-Waals radii of the framework atoms.

Fig. 10. Top: The largest mesoporous ‘L cage’ in MIL-100Fe to build up the network.[45] The yellow sphere with a diameter of 29 Å takes into account the van-der-Waals radii of the framework walls (hydrogen atoms and solvent molecules of crystallization are not shown). MIL-100Cr and -Al are isostructural. Middle: Water adsorption and desorption isotherms at 25 °C of the MIL-100Al and -Fe samples in comparison to MIL-100Cr by Akiyama et al.[41] and MIL-100Fe by Kögus et al.[42] MIL-100AI shows an isotherm with a maximum uptake of 0.5 g g⁻¹. Bottom: Temperature profile and load signal of the MIL-100Fe cycling experiment acquired at pₚ₀ = 5.6 kPa, showing only a small loss in the water uptake over 40 sorption cycles.


