

# THE POTENTIAL OF PCPS/MOFS FOR THE USE IN ADSORPTION HEAT PUMP PROCESSES

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## ABSTRACT

Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) are a new emerging class of microporous materials possessing unique features such as huge surface areas, large pore volumes and a tunable composition.

PCPs are inorganic-organic hybrid materials based on metal clusters linked by organic ligands forming a 3-dimensional coordinated network. PCP or MOFs are related to zeolites with their porosity and reversible guest adsorption properties. Similar to zeolites, the Si or Al atom is schematically replaced by a metal atom or metal cluster, the O atom by a bridging organic ligand.

Compared to traditional adsorbents used in heat pump applications like zeolites or aluminophosphates, PCPs/MOFs exhibit a much richer variety in terms of composition, pore structure and topology. The underlying cluster/linker concept allows the tuning of pore structures and chemical functionality over a wide range.

In this work an overview of the current developments and possibilities of PCPs for the use in adsorption heat pumps will be given. Different very promising candidates have been identified and synthesized. The surface area and pore size as well as the water adsorption characteristics have been measured showing an impressive water loading capacity with up to 1 g/g.

In addition, first investigations on the hydrothermal stability for one candidate have been performed with very promising results showing only a slight degradation of approximately 3 % compared to the initial load after 40 cycles.

In summary, the potential of the new family of PCPs or MOFs for the use in adsorption heat pumps is tremendous.

## 1. INTRODUCTION

### 1.1. General overview

The discovery of new microporous materials for the use in adsorption heat pump processes is still a fundamental research topic with exciting improvements and numerous publications. (Aristov, Restuccia, Cacciola, & Parmon, 2002), (Janchen, 2004), (Ng & Mintova, 2008), (S.K. Henninger, Schmidt, & Henning, 2010).

Beside the inorganic materials like zeolites and aluminophosphates a new class of microporous materials known as Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) has emerged (C Janiak, 1997),(Omar M Yaghi et al., 2003), (Gérard Férey, 2008).

In view of the current state, the industrial production of certain MOFs has been launched e.g. by BASF.

With regard to the similarity of the metal-linker bond to concepts in coordination chemistry, these solids were first labeled as coordination polymers. The term metal-organic framework was then introduced by Yaghi et al.(H. Li, M. Eddaoudi, O'keeffe, & O. Yaghi, 1999; O.M. Yaghi, G. Li, & H. Li, 1995).

PCPs or MOFs can also be called metal-organic zeolites with their reversible guest adsorption properties. Compared to zeolites, the Si or Al atom is schematically replaced by a metal atom or metal cluster, the O atom by a bridging organic ligand.

Due to unique features such as huge surface areas and pore volumes accompanied by tunable pore sizes and compositions, MOFs have attracted a still increasing attention over the past years with various applications (see Fig. 1) ranging from ion exchange, separation processes up to drug delivery and sensor technology (Christoph Janiak & Vieth, 2010).

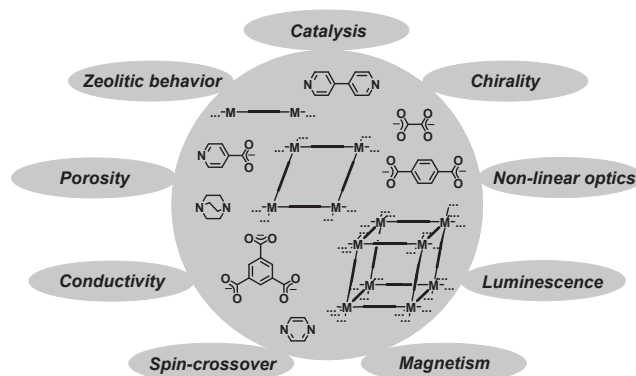


Figure 1 Illustration of application oriented properties of MOFs and prototypical linkers.

Like zeolites and aluminophosphates, metal organic frameworks are crystalline open porous materials with a one, two or three-dimensional framework. In contrast to the zeolites MOFs are not purely inorganic but inorganic-organic hybrid materials based on metal atoms or metal clusters as nodes, which are linked by organic ligands.

Compared to traditional adsorbents used in heat pump applications, MOFs exhibit a much richer variety in composition, pore structure and topology. The cluster/linker concept allows the tunability of pore structures and chemical functionality over a wide range.

Another advantage is the mechanism of synthesis, that the solvent itself acts as the main template in contrast to the templated synthesis of e.g. SAPO-34 where a high temperature activation process is needed.

At the moment it is still difficult to impossible to predict the molecular and crystal structure of MOFs when using new linkers or linker/metal combinations. A notable exception is based on aromatic-dicarboxylate linkers and tetranuclear and tetrahedral  $\{Zn_4O\}$  building units to give a series of cubic so-called *iso-reticular* MOF structures, IR-MOF-*n* (*n* = 1-16) (H. Li, M. Ed-

daoudi, O'keeffe, & O. Yaghi, 1999), (Mohamed Eddaoudi et al., 2002), (Tranchemontagne, Mendoza-Cortés, O'Keeffe, & Omar M Yaghi, 2009).

For some applications the weak comparatively thermal stability of MOFs can be a disadvantage. Because of the organic matter incorporated in the construction of MOFs, the long-time thermal metal-ligand framework stability lies typically between 150-250 °C and seldom surpasses 300 °C. This is much less than what is known for zeolites.

### 1.2. Early steps

First investigations of the suitability of MOFs for the use as an adsorption material for heat transformation applications have shown the high potential, but also some critical issues (Stefan Kai Henninger, 2007). In this work, one of the first 3-dimensional porous MOFs, namely  $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$ , which is also called HKUST-1 or just Cu-btc, has been evaluated. HKUST-1 consists of a basic building unit containing two central  $\text{Cu}^{2+}$ -ions which are coordinated by four carboxylate groups in a way that they form the paddle-wheel-like structure of the copper-acetate  $\text{Cu}_2(\text{H}_3\text{C-COO})_4(\text{H}_2\text{O})_4$ .

With this building unit, a cubic structure can be realised. Although the material shows a water uptake of up to 0.41 g/g the hydrothermal stability is poor (S.K. Henninger, Schmidt, & Henning, 2010). However a synthesis with improved thermal stability has been reported earlier (Schlichte, Kratzke, & Stefan Kaskel, 2004). The adsorption characteristics of different HKUST-1 samples from ISE in comparison with data from Küsgens et al. are shown in Figure 2. Sample 1 shows the best agreement with the calculated data by Küsgens et al. as well as the highest loading spread within the ISE samples. This sample has been synthesized with high purity ethanol whereas samples 2 and 3 have been synthesized with technical ethanol. The maximum water uptake of the HKUST-1 sample by Küsgens is  $0.55 \text{ gg}^{-1}$  for a relative pressure of 0.9  $p/p_0$ .

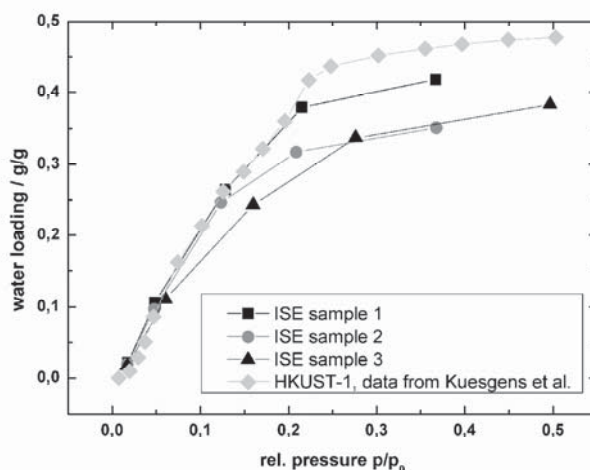


Figure 2 Water adsorption characteristics of different HKUST-1 (Cu-btc) samples. ISE sample 1 has been synthesized with high purity ethanol, whereas sample 2 and 3 have been synthesized with technical ethanol.

Another early example of a MOF evaluated as a potential adsorbent for low temperature heating and cooling applications was  $3\text{D-}\{[\text{Ni}_3(\mu_3\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-H}_2\text{O})_2] \cdot 22\text{H}_2\text{O}\}$  (ISE-1),

which is constructed from the same organic ligands, namely benzene-1,3,5-tricarboxylate (btc) and 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) and filled with ~22 water molecules per formula unit to a potential solvent volume of  $1621 \text{ \AA}^3$  (52%) of the unit cell volume (Figure 3). ISE-1 is water stable over several water de- and adsorption cycles (Stefan K Henninger, Habib, & Christoph Janiak, 2009).

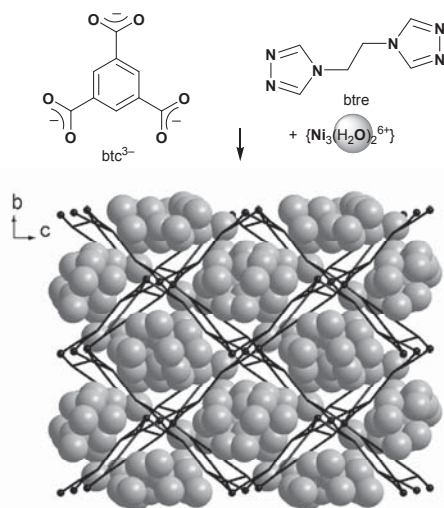


Figure 3 Schematic drawing of the ISE-1 MOF and the organic ligands used in its construction (btc and btre ligand are depicted schematically as black lines only, nickel atoms as black spheres and the oxygen atoms of the guest-solvent water molecules as grey space-filling spheres).

## 2. STRUCTURES

The number of possible structures by combination of the various organic linkers and metal clusters is immense. It is out of the scope of this paper to give a comprehensive overview on the available structures which can be found in extensive reviews like (Kitagawa, Kitaura, & Noro, 2004), (Rowsell & Omar M Yaghi, 2004), (Rosseinsky, 2004), (Gérard Férey, 2008) and (Christoph Janiak & Vieth, 2010).

Therefore in this section a short overview on the structures and properties as well as on current developments with regard to the use in adsorption heat pumps will be given.

### 2.1. Synthesis

The most common way of MOF synthesis is the so called solvothermal way. Here, the required metal salt and a corresponding linker compound are dissolved and heated to a specific temperature which can lie below or above the boiling point of the solvent at standard pressure, but is still comparatively low (<250 °C).

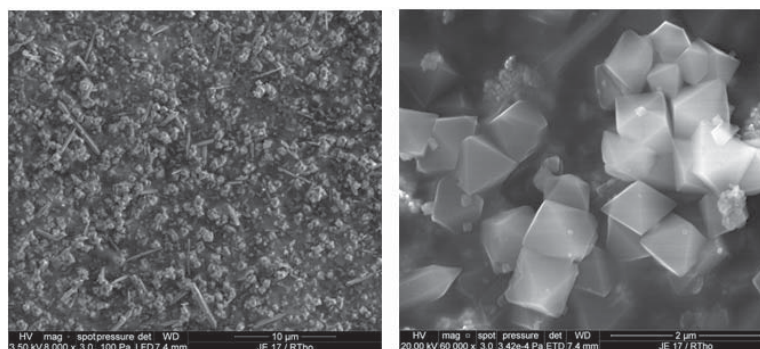
The most commonly used solvents are water and alcohols, however some syntheses require special solvents like dialkyl formamides or pyridine.

*Solvothermal synthesis can also be performed using microwave irradiation. This turned out to be a very promising way for many MOF syntheses, as it shortens reaction and crystallization time and narrows particle size distributions. Furthermore, the size of the achieved MOF crystallites is smaller which is advantageous for the application (see Figure 4).*

In addition to these routes, alternative syntheses have been developed. A further step towards commercial production is the development of electrochemical syntheses, which has been used e.g. for Copper-benzene-1,3,5-tricarboxylate.

Here, the required  $\text{Cu}^{2+}$  ions are generated by anodic dissolution of copper metal sheets. The MOF is then formed from these ions and the linker, the latter being dissolved in the electrolyte.

Some syntheses can even be performed at temperatures below 100°C.



*Figure 4 SEM pictures of synthesized PCP showing crystal size of approximately 1 μm.*

## 2.2. Physical properties

As illustrated above, there exist various useful physical properties depending on the application of MOFs like catalytic, magnetic, conductive and optical properties. With regard to the application in adsorption heat pump processes the main focus lies on the gas adsorption properties and storage capacities, which are strongly connected to the specific pore volume.

In the first years gas storage properties, especially for hydrogen storage has been in focus of the MOF development. With ongoing development the specific pore volumes increased from  $1 \text{ cm}^3 \text{ g}^{-1}$  (MOF-5) up to more than  $2 \text{ cm}^3 \text{ g}^{-1}$  for MIL-101 (S. Kaskel, 2010).

In combination with increasing pore volumes, extremely high surface areas up to  $5000 \text{ m}^2 \text{ g}^{-1}$  have now been reported for several MOFs. This also started a discussion on the applied measurement methods e.g. the determination of the surface area by the BET method (Thommes, 2010).

Another unique feature can be observed when dealing with the adsorption properties of MOFs. Some frameworks show a geometric flexibility, that is a reversible change of the structure and sometimes even physical properties as a response to guest adsorption. This “breathing” effect can be observed for several structures and for all dimensionalities.

This dynamic effect can lead to a stepwise adsorption of water or, even more interesting, to the phenomenon of a switching system. As reported by Tanaka et al (Tanaka et al., 2008) this so-called gate effect occurs during the adsorption process itself, when the MOF structure changes from a “closed” to an “open” structure at a specific gate pressure. The resulting adsorption isotherm shows an S-shape which is advantageous for the application in focus of this work.

However, the repeated expansion and shrinkage of the framework leads to several problems like discontinuities at high relative pressures or large hysteresis. Furthermore, the framework

itself can be destroyed due to the significant stress to the coordinative bonds during the structural transformation.

### **3. POTENTIAL OF PCP/MOFs FOR WATER ADSORPTION PROCESSES**

#### *3.1. Evaluation of promising candidates*

In the early stages of the development, MOFs have been considered as most promising materials for hydrogen storage. Unfortunately the adsorption enthalpy is quite low (5-8 kJ/mol) due to the small polarizability of the hydrogen molecule which means that significant adsorption occurs only at very low temperatures (< 100 K) (S. Kaskel, 2010).

Hence other guest molecules like methane or CO<sub>2</sub> have been investigated, while water adsorption has been treated as an unrequested side-effect of hydrogen or methane adsorption.

Even more problematic, the presence of water often needs to be rigorously avoided as many MOFs, in particular the {Zn<sub>4</sub>O}-IRMOF-*n* series proved unstable in the presence of water impurities over several gas sorption cycles. Consequently water adsorption measurements are now performed in order to investigate structural properties like pore size and pore volume stabilities in the presence of water vapor (Küsgens et al., 2009).

The metal-ligand network of MOFs which are synthesized in water, e.g., under hydrothermal conditions, and which contain water as a solvent template can be considered more stable towards water. Still, the pore stability in the absence of water and the amount of water adsorbed and desorbed needs to be addressed.

Based on the available literature, several promising candidates have been identified and synthesized for the direct investigation of water sorption.

First, the compound MIL-101, developed at and named after the origin at the (Material) Institut Lavoisier (G Férey et al., 2005) has been evaluated, which is by now one of the best known and most cited MOFs.

The crystalline mesoporous material 3D- $\{[\text{Cr}_3(\text{O})(\text{bdc})_3(\text{F})(\text{H}_2\text{O})_2] \cdot \sim 25\text{H}_2\text{O}\}$  is a chromium(III) terephthalate with inner free-cage diameters of up to 34 Å. The framework is similar to the MZN zeolite topology.

Water adsorption isobars and isotherms have been measured using thermogravimetric and volumetric methods. The gravimetric measurements have been performed with a Setaram combined TG/DSC thermobalance under a continuous humidified gas flow using argon as carrier. Details on the measurement principle can be found in (S.K. Henninger, Schmidt, & Henning, 2010).

The volumetric measurements have been performed with a modified Quantachrome Autosorb. Surface area and pore size has been determined using BET and DFT methods. The water adsorption characteristics have also been measured and the results as well as a direct comparison with independent performed measurements at Quantachrome using a Hydrosorb have recently been published (Ehrenmann, Stefan K. Henninger, & Christoph Janiak, 2010). With an impressive water loading spread of 0.939 g g<sup>-1</sup> (see Figure 4) under typical conditions (desorption at 90°C, adsorption at 40°C, vapour pressure 5.6 kPa) this material shows the largest water-loading spread reported so far. Similar water uptake results with a maximum of 1.28 cm<sup>3</sup> g<sup>-1</sup> has been reported by Küsgens (Küsgens et al., 2009).

As illustrated in Figure 5 the isotherm of the compound shows a sigmoidal shape. This is advantageous for the application, as a large loading lift can be achieved within a narrow range of relative pressure. Unfortunately, the usable loading lift in the application is slightly reduced due to the hysteresis between adsorption and desorption. First experiments on the hydrother-



mal stability have been performed with very promising results showing only a slight degradation of approximately 3 % compared to the initial load after 40 cycles.

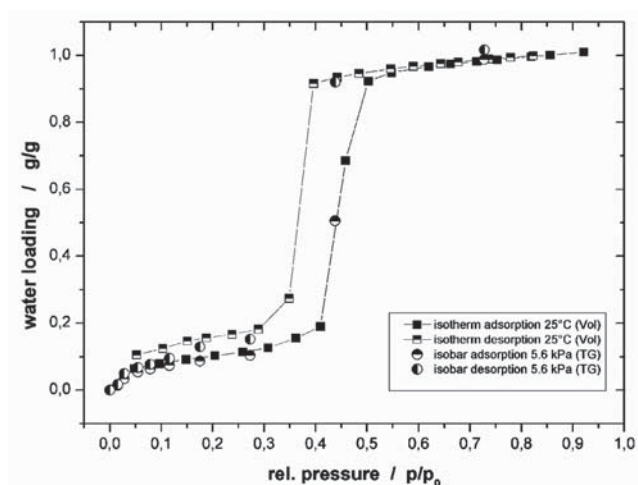


Figure 5 Water adsorption and desorption isotherms/isobars of the Mil-101 sample. This compound shows an uptake of up to  $1\text{ g g}^{-1}$  (Figure modified from. (Ehrenmann, Stefan K. Henninger, & Christoph Janiak, 2010))

As a second candidate, the compound MIL-100 (Volkringer et al., 2009) has been evaluated. This compound of formula  $3\text{D}-\{[\text{Cr}_3(\text{O})(\text{btc})_2(\text{X})] \sim 28\text{H}_2\text{O}\}$  ( $\text{X} = \text{F}, \text{Cl}, 1/2\text{SO}_4$ ) has also attracted attention as a promising adsorbent for water adsorption. As can be seen in Figure 6,

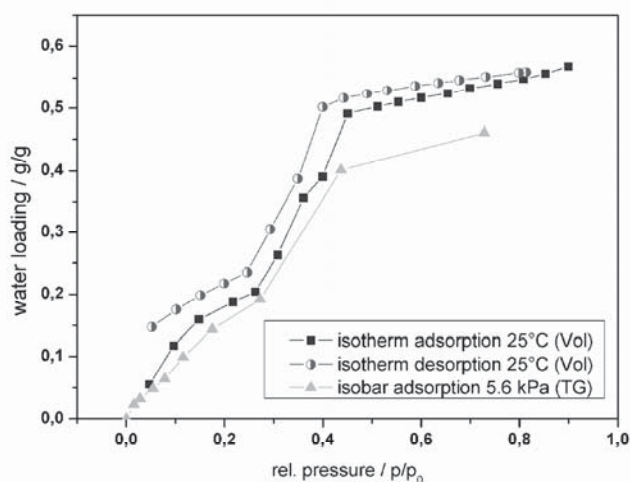


Figure 6 Water adsorption and desorption isotherms/isobars of the MIL-100 sample. This compound shows a different shape of the isotherm with a maximum uptake of  $0.57\text{ g g}^{-1}$ .

this compound shows a different shape of the isotherms with a maximum water uptake of  $0.57 \text{ g g}^{-1}$ .

Similar to the results reported by Akiyama (Akiyama, Matsuda, & Kitagawa, 2010), the adsorption isotherms show several steps. A first step can be observed at a relative pressure of  $p/p_0 = 0.3$ .

Akiyama and co-workers explained this mechanism as a first strong adsorption on the open metal sites of the chromium ions for relative pressures below 0.2. Following water molecules are adsorbed in the smaller cages with 2.5 nm diameter.

Unlike the MIL-101 compound, this material shows only a small hysteresis between the adsorption and the desorption path.

Furthermore, Akiyama et al. performed a stability test on this compound with two thousand cycles. No effect on the adsorption capacity was observed. Hence, this compound is of great interest for the use in adsorption processes, although the feasible water loading spread is in the range of  $0.4 \text{ g g}^{-1}$  for typical application conditions and therefore smaller compared to the first compound MIL-100.

A general overview with an excellent steam stability map of several porous coordination polymers can be found in Low et al. (Low et al., 2009). In agreement with the hydrothermal stability test performed on the MIL-101 sample, the MIL-101 compound has been classified into the high steam stability region with an activation energy for ligand displacement of 43.4 kcal/mol and a structural stability up to 300°C.

### 3.2. Potential of MOFs/PCPs

As a result of this work and in agreement with the literature, the new family of MOFs can be considered as a very promising class of materials for the use in adsorption heat pump processes. Several compounds have been found with a large water uptake. A brief overview on the maximum water adsorption capacities and heat of adsorptions for the most promising candidates is given in Table 1. The achievable water uptake is in the range of  $0.4 \text{ g g}^{-1}$  up to over  $1 \text{ g g}^{-1}$ .

Table 1 - Overview on the maximum water uptake and heats of adsorption (HoA).

Compound	rel. pressure	water uptake	HoA	Source
	--	$\text{g g}^{-1}$	$\text{kJ mol}^{-1}$	
MIL-101 (Cr)	0.921	1.01	46.0 - 47.2	this work
MIL-101	0.9	1.03	45.13	Küsgens et al.
MIL-100 (Al)	0.899	0.568	--	this work
MIL-100(Fe)	0.9	0.651	48.83	Küsgens et al.
MIL-100 (I*Cl)	0.48	0.671	47.6 - 47.9	Akiyama et al.
MIL-100 (I*F)	0.47	0.614	47.7 - 49.0	Akiyama et al.
MIL-100 (I*SO <sub>4</sub> )	0.49	0.611	47.9 - 49.1	Akiyama et al.
HKUST-1	0.367	0.418	50.7	this work
HKUST-1	0.9	0.55	--	Küsgens et al.

Although the adsorption occurs at high relative pressure ( $>0.35 p/p_0$ ) these material are still very promising, as the modular concept allows to tune the physical properties according to the desired application boundary conditions in a wide range. A clear advantage of MOFs over conventional zeolite type sorbents is the fine tuning of the hydrophilicity of the network



through the organic linker. In principle the network can be tuned from hydrophobic to more hydrophilic by attaching either unpolar alkyl or polar amine or nitro groups to the aromatic core of the typical benzene-carboxylate linkers.

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