Hydrogen adsorption in a nickel based coordination polymer with open metal sites in the cylindrical cavities of the desolvated framework†

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The solvent contained within the cylindrical one-dimensional pores of the novel three-dimensional metal organic framework $Ni_2(dhtp)(H_2O)_2 \cdot 8H_2O$ can be removed without decomposition of the network, allowing gas storage within the cavities.

Coordination polymers have a number of promising applications in catalysis, ion exchange, gas separation, or as sensors.[1–4] Because of their low density, large surface area and void volume, coordination polymers may be especially suitable as materials for gas storage. Accordingly, these crystalline materials have recently attracted a lot of interest as potential hydrogen storage media based on physisorption.[5–7] Especially those structures possessing open metal sites, i.e. sites with coordinative unsaturation after solvent removal, show exceptional characteristics for hydrogen physisorption, like high storage capacities at low pressures and temperatures and high heats of adsorption.[7–9] Inspired by these promising properties, we synthesised, characterised and investigated the hydrogen adsorption in a novel three-dimensional coordination polymer with Ni^{2+} as the metal component.

Nickel(II) acetate and 2,5-dihydroxyterephthalic acid (H_4dhtp) react in a THF–water mixture to yield a yellow–green substance, $Ni_2(dhtp)(H_2O)_2 \cdot 8H_2O$ **1**. The size of the crystallites was too small for single-crystal structure determination. We noticed, however, that the powder diffraction pattern of **1** was very similar to the pattern of $Co_2(dhtp)(H_2O)_2 \cdot 8H_2O$.[10] Using the latter as a structural model, we were able to determine the structure of **1** by Rietveld refinement (Fig. 1a). Indeed, both compounds are isostructural with a three-dimensional honeycomb-like network (Fig. 2a). At the intersections of the honeycomb are helical chains of *cis*-edge connected nickel oxygen octahedra. Nearest neighbour helices are of opposite handedness. The chains are connected by the organic ligand with three adjacent chains which results in the honeycomb motif. The channels in the honeycomb have a diameter of ~ 11 Å, and they are filled with solvent. In addition to the carboxylic acid group, the hydroxyl group of the linker has also been deprotonated during the synthesis. This is more easily possible for the more acidic phenolic groups than for aliphatic alcohols. In effect, all of the oxygen atoms of the ligand are involved in the coordination of nickel atoms. These account for five of the oxygen atoms coordinating each nickel atom, while the sixth coordinative bond is to a water molecule which points towards the cavity.

On heating, **1** immediately starts to lose its solvent water. Subsequent behaviour of the sample depends on the type of atmosphere the measurement is conducted in. In nitrogen (Fig. 3a), the sample weight stays constant until 350 °C. Above this temperature, decomposition occurs. In contrast, this final decomposition occurs rapidly already between 240–250 °C in air (Fig. 3b). It yields nickel oxide as a crystalline product, while the only reflection observed below 50° 2θ for the decomposition product in nitrogen fits with nickel carbide NiC.

Complementary thermodiffraction experiments (Fig. 4) reveal that the long-range order of the framework remains intact in the inert atmosphere of nitrogen until the intensities of the reflections start to decrease at 267 °C and finally disappear at 310 °C. In air,
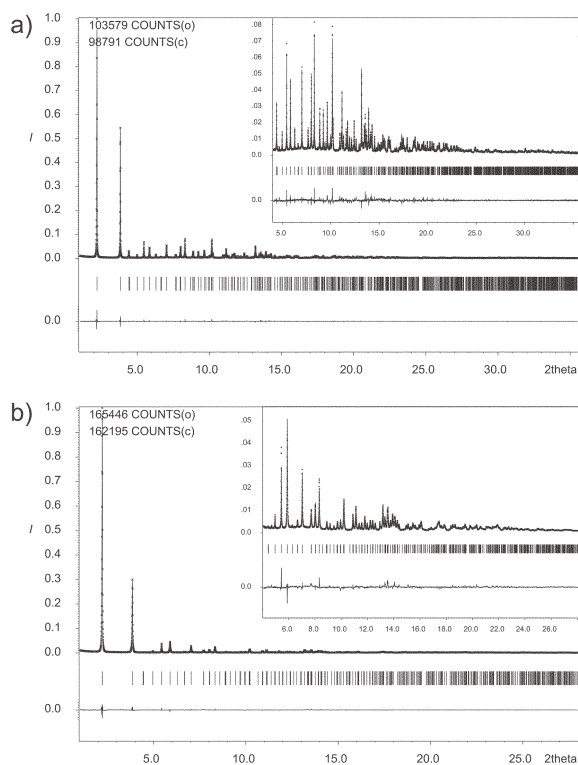

Fig. 1 Rietveld refinement plots of the hydrated (a) and dehydrated (b) form of **1** (crosses: observed pattern, line: calculated pattern, bottom line: difference plot, all plotted on the same scale. Bragg peaks are indicated by tick marks. Insets: enlarged view of the high angle range).

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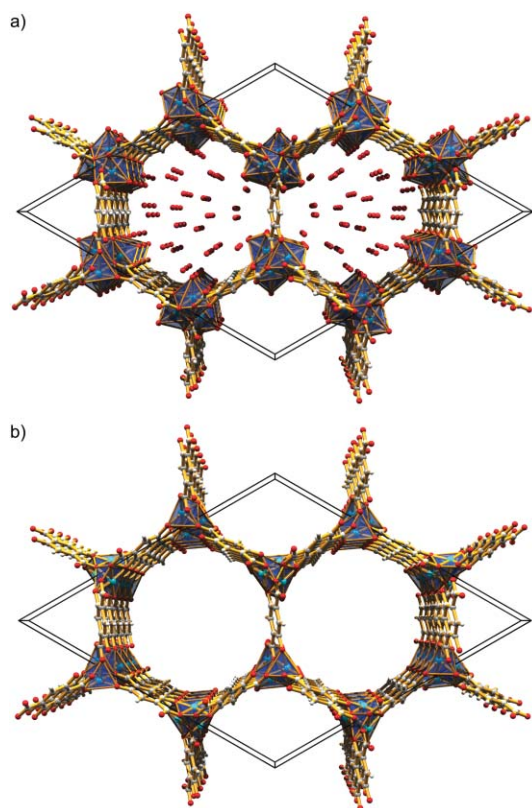
Fig. 2 Crystal structures of **1** in the hydrated (a) and dehydrated form (b). In (b), notice the absence of the vertices of the metal coordination octahedra which point towards the cavities in (a).
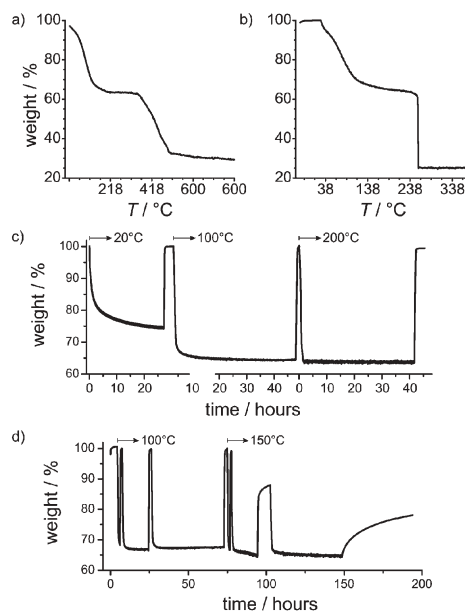

Fig. 3 Thermogravimetric measurements of **1**: a) weight loss in nitrogen, b) weight loss in air, c) dehydration/hydration in nitrogen, d) dehydration/ hydration in air (the sample was intermittently cooled down for the hydration).

the degradation of the crystallinity of **1** occurs already in the range of 140–190 °C. In general, the thermal behaviour of **1** is similar to that of the cobalt compound. The nickel coordination polymer is,
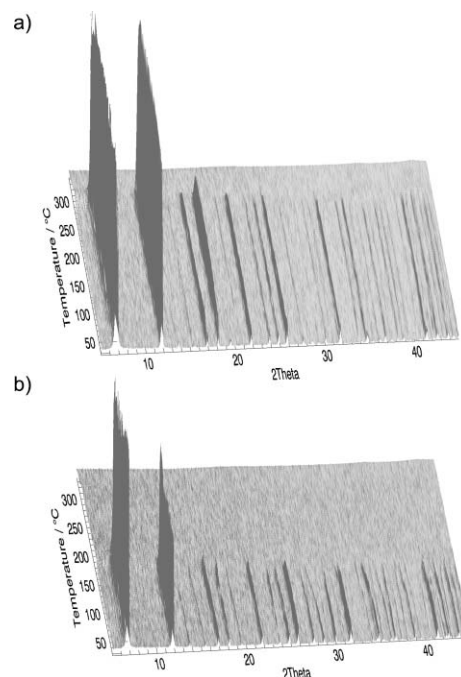

Fig. 4 Variable temperature powder X-ray measurements of **1** in nitrogen atmosphere (a) and in air (b).[11]

however, slightly more stable than the isostructural cobalt compound. The onset of degradation is shifted by $\sim$50 °C in nitrogen and 25 °C in air to higher temperatures, and the final weight loss step begins 30 °C later in nitrogen, while it occurs just $\sim$6 °C later in air than for $Co_2(dhtp)(H_2O)_2 \cdot 8H_2O$.

The stability range of the framework is reflected directly in the ability of **1** to absorb water again after dehydration. Even after heating for prolonged periods of time at temperatures up to 200 °C in nitrogen, it is possible to completely rehydrate the sample to its initial level (Fig. 3c). In contrast, while full reversibility of the dehydration–hydration process in air is possible after thermal treatments at 100 °C, this is no longer the case when the sample is heated at 150 °C. The amount of water that is taken up by the sample again decreases with the time the sample was kept at 150 °C (Fig. 3d). This corresponds to the ongoing degradation of the framework that is observed in the thermodiffraction experiment at this temperature in air.

The amount of weight loss in the TG and the thermodiffraction experiment indicate that the framework of the Ni-coordination polymer is stable in an inert atmosphere even after complete dehydration which includes the removal of the water molecules coordinating the metal. The Rietveld refinement on a sample of **1** that was dehydrated at 100 °C in a dynamic vacuum confirms this conclusion (Fig. 1b). In the absence of all the water molecules, the nickel atom remains in a coordinatively unsaturated square pyramidal coordination (Fig. 2b). The volume of the empty channels accounts for 58% of the total volume of the structure. The permanent porosity of **1** is demonstrated by the reversible uptake of nitrogen at 77 K (Fig. 5). The nitrogen adsorption isotherm yields a Langmuir surface area of 1083 m^2 g^{-1} and a pore volume of 0.41 cm^3 g^{-1}. The calculated Connolly surface resembles a cylinder with walls that slightly undulate along the c axis.
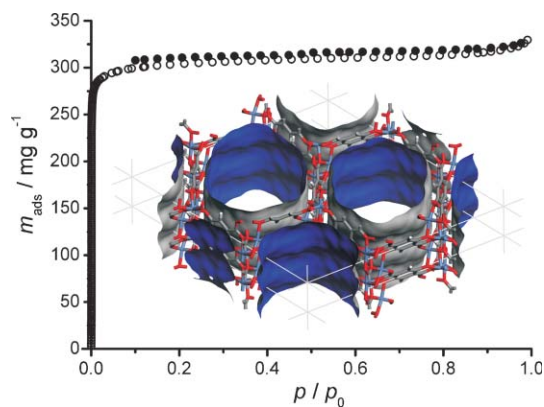
Fig. 5 Nitrogen adsorption isotherm of **1** performed at 77 K (open circles: adsorption, closed circles: desorption, inset: calculated Connolly surface).
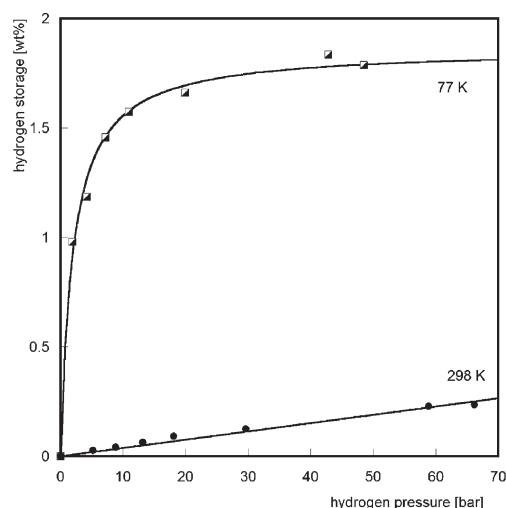

Fig. 6 Hydrogen adsorption isotherm of **1** at 77 K (squares) and 298 K (circles).

Apart from the high specific surface area another important factor for hydrogen adsorption in metal–organic frameworks is the presence of strong adsorption sites like the open metal sites in **1**. While Cu-based metal–organic frameworks possessing unsaturated metal sites have shown promising properties for hydrogen physisorption,[12,13] only a few Ni-based coordination polymers with a high specific surface area have been investigated up to now.[9,14,15] The hydrogen adsorption isotherms of **1** measured at 77 K and room temperature are shown in Fig. 6. At 77 K, the adsorption isotherm has a type I profile, fitted here with a Langmuir equation which yields a saturation value of 1.8 wt%. The shape of the isotherm is typical for microporous materials as the small pore size limits the adsorption to one or a few molecular layers.[1] The adsorbed hydrogen per Langmuir specific surface area corresponds to a value of 1.7×10^{-3} wt% m^{-2} g, which is similar to the value reported recently for the metal organic framework Cu-BTC.[12] At room temperature and approximately 65 bar the storage capacity is less than 0.3 wt% as is usual for physical adsorption at ambient conditions. The shape of the isotherms is independent of the number of adsorption cycles indicating that the hydrogen uptake of **1** is completely reversible as expected for physisorption.

In summary, we have presented a novel Ni-based coordination polymer with large one-dimensional channels that are filled with water. It is possible to desolvate the compound at elevated temperatures with conservation of the porosity which yields an accessible, high specific surface area. It also contains unsaturated metal sites which may enhance the interaction with the adsorbed species. The compound showed a hydrogen storage capacity of up to 1.8 wt% at 77 K.‡§

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