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Adsorption properties and structure of CO_2 adsorbed on open coordination sites of metal–organic framework Ni_2(dhtp) from gas adsorption, IR spectroscopy and X-ray diffraction†

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The microporous metal–organic framework Ni_2(dhtp) (H_4dhtp = 2,5-dihydroxyterephthalic acid) shows distinct end-on CO_2 coordination to coordinatively unsaturated nickel sites giving rise to high CO_2 adsorption capacity at sub-atmospheric pressures and ambient temperatures.

Separation of CO_2 from flue gases is challenging due to the relatively low concentrations of CO_2, typically from 4 to 12 volume% depending on the fuel used in the process. At present, the most developed technology for flue gas separation is absorption of CO_2 into solvents, often based on aqueous alkanolamines, such processes having high energy demand and potential unwanted environmental consequences due to solvent loss and degradation.[1] A step towards dry processes utilizing either membranes or adsorbents might give both environmental and energetic benefits. However, in the development of adsorption based processes one major challenge is to develop adsorbents having high adsorption capacity for CO_2 at the actual low partial pressures. Most promising low pressure adsorbents reported so far are based on the deposition of nitrogen containing oligomeric or polymeric species onto high surface area silicas,[2] having initial adsorption capacities up to 18 wt% CO_2 at around 0.1 atm CO_2 pressure and 298 K. However, for some of these the capacities drop to below 10 wt% after the first adsorption cycle.[3] For metal–organic framework based adsorbents most focus has been put on the high pressure adsorption capacity of CO_2,[4] and capacities up to 150 wt% CO_2 at 40 bar and ambient temperature have been reported.[5] The low pressure adsorption capacity of CO_2 on MOFs is in most cases below 5 wt% and for some MOFs a high external gas pressure is needed to open up the flexible MOF structure for further adsorption.[6] One important advantage with MOFs as compared to most polymer based adsorbents is that MOFs form crystalline solids. Thus, structural information about the mechanism of adsorption is possible through XRD analyses. From such studies the structure of the adsorption site(s) can be obtained which subsequently can be used for further adsorbent optimization.

In the present communication we report the structure of the adsorbate on the single-site adsorption site in Ni_2(dhtp),[7] based on X-ray diffraction data and IR spectroscopy. Adsorption experiments show that this MOF has an adsorption capacity of CO_2 of 11 wt% even at 0.1 atm CO_2 pressure and 303 K which is among the highest CO_2 adsorption capacity reported for MOFs at these conditions.

$[Ni_2(dhtp)(H_2O)_2]\cdot 8H_2O$ (CPO-27-Ni) was prepared as described previously.[7] Prior to the adsorption experiments the powder was activated by thermal treatment in a vacuum at 383 K overnight. From nitrogen adsorption experiments at 77 K the Langmuir and BET surface areas were determined to be 1312 and 1083 $m^2\ g^{-1}$, respectively. The same sample was used to measure the CO_2 isotherm at temperatures from 303 to 353 K. Fig. 1 shows the isotherms as well as the deduced differential enthalpy of adsorption using the isosteric method from vacuum to a CO_2 pressure of 1 atm. The steepness of the slope in the low pressure part of the isotherms collected at 303 and 313 K indicate strong adsorption, while the isotherm at 353 K is noticeably less steep in this region. At low pressures the differential enthalpy of adsorption is estimated to be around 40 kJ mol^{-1} up to around $p > 0.2$ atm. It subsequently decreases slightly at higher pressures. Theoretically, full coverage of CO_2, *i.e.* one CO_2 bonded to each open nickel coordination site, corresponds to 28.2 wt% CO_2. Consequently, a $\sim$80% coverage is reached at a CO_2 pressure of 1 atm in the isotherm collected at 303 K. Even higher degrees of coverage have recently been obtained in the case of NO,[8] in which a

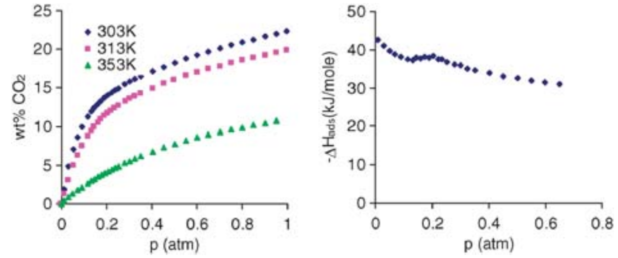

Fig. 1 Adsorption isotherms (left) and differential adsorption enthalpies (right) for the adsorption of CO_2 on CPO-27-Ni at the temperatures indicated.

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strong coordinative bond is found between the NO and the metal cation of the MOF, as indicated by a crystal structure determination of the NO adduct of CPO-27-Co.[9] The difference in adsorption capacities between the isotherms collected at 303 and 353 K indicates a possible temperature swing process cycling between these two temperatures having an effective CO_2 capacity of around 10 wt% for $p > 0.1$ atm.

In order to study the structure of the adsorbate–adsorbent system, a powder sample was prepared in a capillary and flame sealed at a partial pressure of 0.2–0.5 atm, corresponding to 50–65% coverage at room temperature, and measured at 100 K at the Swiss-Norwegian Beamlines at the ESRF using a high resolution powder X-ray diffractometer. The crystal structure of the host–guest compound was then determined by Rietveld refinement.‡

The structure of the dehydrated framework Ni_2(dhtp) was used as a starting model. The atoms of the CO_2 molecule were subsequently localised from difference Fourier maps (full details are given in the ESI†).The structure of the three-dimensional network of CPO-27-M (M = Co, Ni, Zn, Mg),[7,10,11] which is isostructural to MOF-74,[12] resembles a honeycomb. The hydrated compound contains metal atoms which are octahedrally surrounded by oxygen atoms of the organic ligands and a solvent molecule. After removal of the solvent molecule, the metal atoms have a square-pyramidal environment formed by five oxygen atoms of the organic linking molecules and a sixth coordination site available for coordination of adsorbates.[7,10,13]

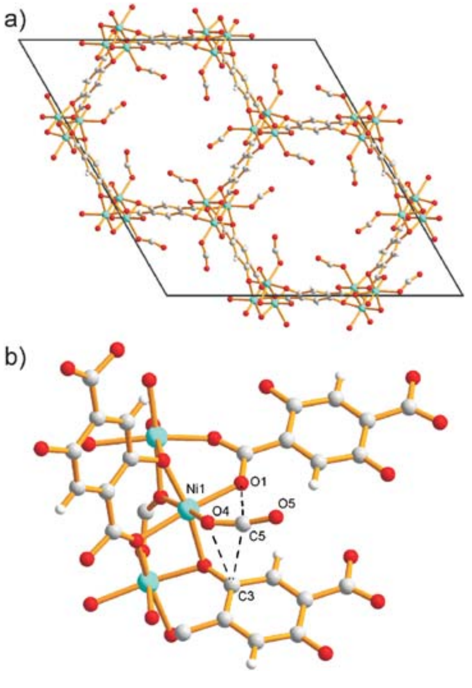

Fig. 2 Crystal structure of CPO-27-Ni with adsorbed CO_2 at the metal atom. (a) Packing along [001] showing the end-on coordination of the CO_2 molecule; (b) local environment of the adsorbed CO_2 molecule. The black dashed lines indicate selected distances longer than covalent bonds and shorter than 3.2 Å (corresponding to the sum of the van der Waals radii of oxygen and carbon) which might influence the structure of the CO_2 molecule through crystal packing effects or back-donation.

In the structure of the CPO-27-Ni/CO_2 complex (Fig. 2), the CO_2 molecule is clearly coordinating the Ni^{2+} atom in the framework in end-on fashion with a Ni–O distance of 2.29(2) Å, a Ni–C distance of 3.04(2) Å, and a Ni–O–C angle of 117(2)°. The Ni–O distance is significantly shorter than the sum of the van der Waals radii of Ni and O of 3.1 Å, and it therefore attests to the strength of interaction between the metal adsorption site of the framework and carbon dioxide. The carbon dioxide molecule appears to be slightly distorted from its usual linear structure with an O–C–O angle of 162(3)°. However, notice that the estimated standard deviations given by Rietveld refinements are underestimated and should be multiplied with a factor of at least 3 to reach a realistic value.[14]

IR spectroscopy is a complementary method which can be used to study the interaction of carbon dioxide with the Lewis acid sites of such material. CO_2 can interact with the cations through one of the oxygen lone pair orbitals with formation of end-on adducts,[15–17] though it is generally weakly bonded at room temperature.

Fig. 3 shows the background subtracted IR spectra obtained by progressive lowering of equilibrium pressure at room temperature, the highest coverage spectrum (grey curve) corresponding to an equilibrium pressure of 0.02 atm. Starting the discussion from low coverage, we observe the growth of the main component at 2341 cm^{-1} with a low frequency shoulder at 2329 cm^{-1}. Both bands quickly go off the scale without reaching saturation. This band can be readily assigned to the ν_3 mode of carbon dioxide forming $Ni^{2+}\cdots O{=}C{=}O$ adducts with end-on configuration. The bands due to the ν_3 mode of CO_2 are slightly red shifted by $\Delta\nu = -8$ cm^{-1} with respect to gas phase (2349 cm^{-1}) as previously observed in case of HKUST-1. On the low frequency side of this main absorption we observe the growth of less intense bands, centred around 2275 cm^{-1}, due to $Ni^{2+}\cdots O{=}^{13}C{=}O$ which is present naturally in $^{12}CO_2$ (1%). The broad and weak band centred at 2408 cm^{-1} can be associated with the combination mode $\nu_3 + \nu_{M-O}$, where ν_{M-O} denotes the $Ni^{2+}\cdots O$ stretching of the $Ni^{2+}\cdots O{=}C{=}O$ adduct. The ν_{M-O} mode would be expected at about 70 cm^{-1}.[18]In the low frequency range, an intense band is expected for doubly degenerate bending mode (ν_2) of CO_2 (gas frequency at 668 cm^{-1}). In this case (see the

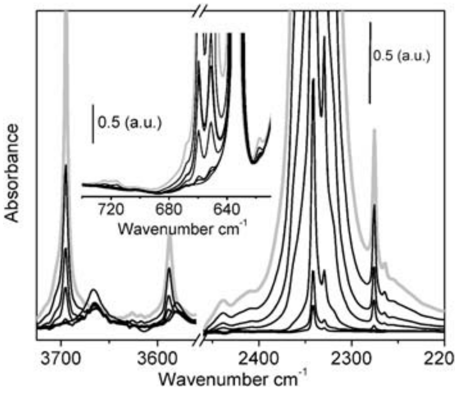

Fig. 3 FTIR spectra (background subtracted) of CO_2 adsorbed on CPO-27-Ni at decreasing equilibrium pressure (higher coverage, grey curve corresponds to 0.02 atm equilibrium pressure). In the inset the CO_2 bending region is reported.

inset in Fig. 3), a doublet at 659 and 651 cm^{-1} is clearly visible, testifying that the molecule is weakly perturbed and also might be slightly distorted.

In the high frequency region (3800–3500 cm^{-1}), two components are observed at 3666 and 3580 cm^{-1}. The nature of these two absorptions is well known and is interpreted on the basis of the combination of ν_1 and ν_3 modes of CO_2. The reason for the presence of a doublet shifted by about ±50 cm^{-1} from the expected frequency for the combination mode ν_1 and ν_3, is due to the fact that the first overtone of the ν_2 mode coincides with the ν_1 mode, causing a strong Fermi resonance effect that induces a band splitting in two components 100 cm^{-1} apart.[19,20]

In contrast to what is observed in the case of metal complexes, where experimental structural evidence for CO_2 coordination *via* η^1(C) (bonded through the C atom) and η^2(C,O) modes has been previously reported,[21,22] coordination of CO_2 *via* η^1(O) to metal ions is reported here for the first time. The spectroscopic data can be explained only with an end-on coordination of CO_2, and a slight bending of the CO_2 molecule as suggested by XRD can be hypothesized. A bending can be explained by considering the steric and electronic environment around the coordinated carbon dioxide: in particular the short $C5\cdots O1$ interaction of 3.00(3) Å may indicate a secondary interaction between the framework O1 atom and the C atom of CO_2 leading to a slight bending in a similar manner as previously suggested to take place in zeolites[23] and in HKUST-1.[19] In the other metal–organic framework for which crystal structural information of the CO_2 coordination is available, MIL-53(Cr), the carbon dioxide interacts with an OH group of the inorganic building block.[24]

In conclusion, we have demonstrated the high CO_2 uptake of coordination polymer CPO-27-Ni at ambient and elevated temperatures, which may make this material applicable in carbon dioxide removal processes. Our adsorption results are consistent with a very recent publication by Matzger *et al.* on the CO_2 adsorption on a series of isostructural M_2(dhtp) materials,[25] which has appeared in press after submission of this manuscript. We have in addition shown that the strong adsorption is caused by a direct interaction between CO_2 and the open Lewis acid site on nickel where CO_2 is end-on coordinated to the nickel cation of the framework. The strong interaction is exemplified by the short Ni–O distance in the adduct. Both, powder X-ray diffraction and IR-spectroscopy indicate that the CO_2 molecule might be distorted slightly from linear shape.

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Notes and references

‡ The powder sample of the CPO-27-Ni/CO_2 was measured at the Swiss-Norwegian Beamlines (BM01B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Rietveld refinement was performed with the WINPOW program. Details of the refinement process are given in the ESI.† $C_4H_1NiO_3\cdot(CO_2)_{0.67}$, M = 185.4 g mol^{-1}, trigonal space group $R\bar{3}$, $a = b = 25.7836(11)$ Å, $c = 6.7474(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 3884.7(5)$ Å^3, $Z = 18$, $\lambda = 0.520054$ Å, $T = 100$ K, 2θ range 1.027–25.499°, step size 0.004°, $R_p = 0.0590$, $R_{wp} = 0.0814$, $R_{exp} = 0.0264$, $R_{Bragg} = 0.0155$, GoF = 3.09.

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