Supplementary Material (ESI) for Chemical Communications

Supplementary information for

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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Details of the structure determination of Ni_2(dhtp)/CO_2:

High-resolution X-ray powder diffraction data of the CPO-27-Ni-CO_2 was recorded at the Swiss-Norwegian Beamlines (SNBL/BM01B) at the European Synchrotron Radiation Facility (ESRF) using a two-circle diffractometer equipped with 6 counting chains and a wavelength of 0.520054 Å.

For sample preparation, material CPO-2-Ni in a tube was activated at 383 K in a dynamic vacuum for more than two hours. The activated material was transferred into a capillary of 1 mm diameter in a glove box. The capillary was attached to a vacuum line and exposed to the adsorbate gas. The setup unfortunately only allows an estimate of the partial pressure of adsorbate that the material experiences, which in the present case is in the range 0.2-0.5 atm (at ambient temperature). The capillary was cooled somewhat before it was sealed.

The structure of the CPO-27-Ni-CO_2 sample measured at 100 K was refined using the Rietveld refinement program WINPOW (Ståhl 2008). The starting model for the refinement was based on the previously reported single-crystal solution of the dehydrated CPO-27-Ni (Dietzel 2006). The positions of the atoms in the CO_2 molecule were found by means of difference Fourier calculations. A split pseudo-Voigt function with seven profile parameters was used for the refinements over a 2θ range of 1.027 - 25.499º (with a step size of 0.004º) in order to cope with the asymmetry of the diffraction peaks at low scattering angle. The pattern was corrected for polarization and cylinder absorption. The scale factor, the unit cell parameters, and the 2θ zero-point shift were refined. Eight Chebyshev-background parameters were used to describe the background and nineteen soft distance restraints were used to restrain the distances and angles within the ligand. Two soft distance restraints were applied to the C–O distances within the CO_2 molecule. All the atomic coordinates (except for the H atom) and the occupancy factor of the atoms sites of the CO_2 molecule were refined. The position of the H atom was geometrically constructed. The isotropic atomic temperature factors of the carbon and hydrogen positions and the oxygen positions in the 2,5-dioxidoterephthalate moiety were coupled and subsequently refined, whereas the isotropic atomic temperature factors of the nickel position and the carbon and oxygen positions in the CO_2 molecules were refined individually. The O-O distance in the CO_2 molecule was also tried to be strongly restraint in order to get a linearly CO_2 molecule, but the refinement did not converge.

References

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K. Ståhl, WINPOW, Version 28-FEB-2008, 2008.

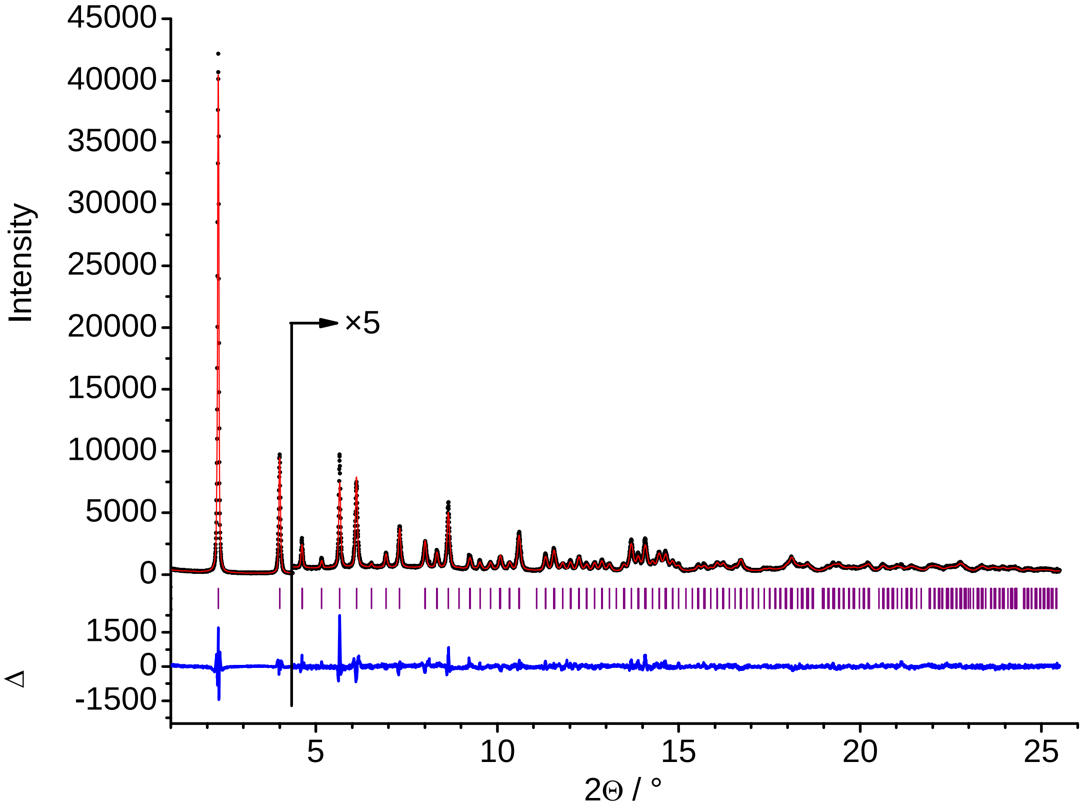

Figure S1. Experimental (black circles), calculated (red line), and difference (blue line) X-ray powder diffraction patterns of Ni_2(dhtp)/CO_2. The tick marks show the positions of the Bragg reflections. Intensities and difference plot of the high-angle part are enlarged by a factor of 5.

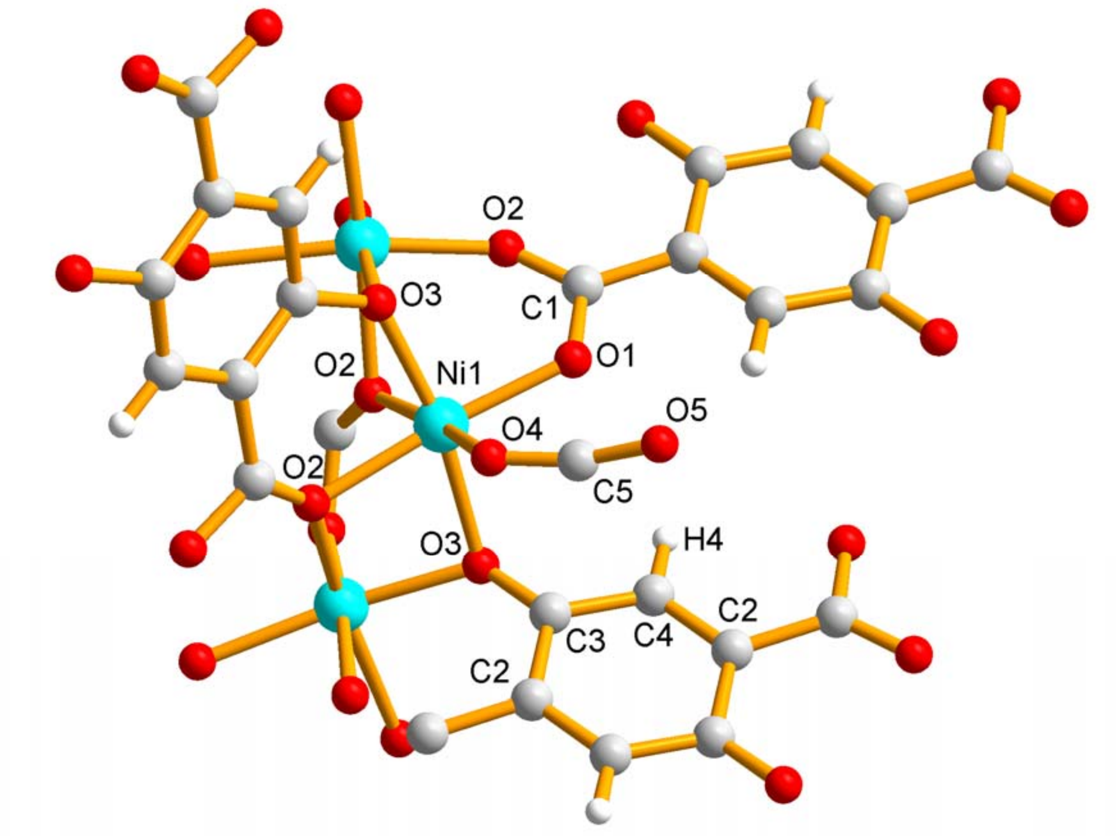

Figure S2. Atom labelling scheme used in the structure determination of $Ni_2(dhtp)/CO_2$.

Table S1. Crystallographic data for the Rietveld refinement of Ni_2(dhtp)/CO_2.

Temperature	100 K
Space group	*R*3;¯
Z	18
A	25.7836(11) Å
C	6.7474(3) Å
V	3884.7(5) Å^3
λ	0.520054 Å
ρ_{cal}	1.425 g/cm^3
2θ range	1.027 - 25.499º
R_p	5.90 %
R_{wp}	8.14 %
R_{exp}	2.64 %
R_{Bragg}	1.56 %
GoF	3.09
No. of observations	6119
No. of reflections	626
No. of parameters	59
No. of soft distance restraints	21

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for Ni_2(dhtp)/CO_2.

Atom	*x* / *a*	*y* / *b*	*z* / *c*	s.o.f	U_{iso}
C1	.4152(7)	.4047(7)	.2551(17)	1.0000	.003(4)
C2	.4593(6)	.4517(6)	.1202(19)	1.0000	.003(4)
C3	.5557(4)	.5478(5)	.0841(18)	1.0000	.003(4)
C4	.5145(6)	.4955(6)	.1970(14)	1.0000	.003(4)
H4	.52573	.49429	.33325	1.0000	.003(4)
Ni1	.61906(13)	.64921(13)	.3531(4)	1.0000	.0102(8)
O1	.4357(4)	.4041(5)	.4355(16)	1.0000	.002(2)
O2	.3663(5)	.3629(5)	.2172(14)	1.0000	.002(2)
O3	.6103(3)	.5825(4)	.1623(17)	1.0000	.002(2)
C5	.1766(9)	.7214(12)	.079(4)	.668(8)	.049(13)
O4	.6807(7)	.5536(9)	.883(2)	.668(8)	.015(8)
O5	.2284(9)	.7493(13)	.025(5)	.668(8)	.26(2)

Some details of the adsorption experiments with Ni_2(dhtp):

Adsorption isotherms up to around 1 atmosphere pressure were recorded on a Quantachrome A1 instrument using either N_2 (5.0) or CO_2 (4.6) as adsorbates. Prior to all measurements the sample was outgassed at 110°C for approx. 16 hrs. Nitrogen adsorption measurements were carried out at 77K (liquid N_2 as coolant) to estimate the specific surface area of Ni_2(dhtp) by using either the Langmuir or BET methods. Carbon dioxide isotherms were recorded at different temperatures keeping the sample at a stable temperature by using a thermostated water bath. The same sample was used in several adsorption experiments by regenerating the adsorbent between each run. Regeneration was carried out by heating the sample to 110°C for 16 hrs. After regeneration the adsorption isotherms were fully reproducible.

Some more details of the IR experiments with Ni_2(dhtp)/CO_2:

At high coverage the band associated with ν_3 and ν_2 modes of $Ni^{2+}\ldots{}^{12}CO_2$ adducts goes rapidly out of scale and spectra evolution can be followed only by monitoring the correspective modes of the $Ni^{2+}\ldots{}^{13}CO_2$ adducts. In particular, as the band at 2275 cm^{-1}, becomes more and more intense without any appreciable shift in frequency, the formation of $Ni^{2+}\ldots(CO_2)_2$ species (observed in some cases of exchanged zeolites)[i] can be excluded.

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 inset in Fig. S3), a doublet at 659 and 651 cm^{-1} is clearly visible, testifying that the molecule is weakly perturbed and also might

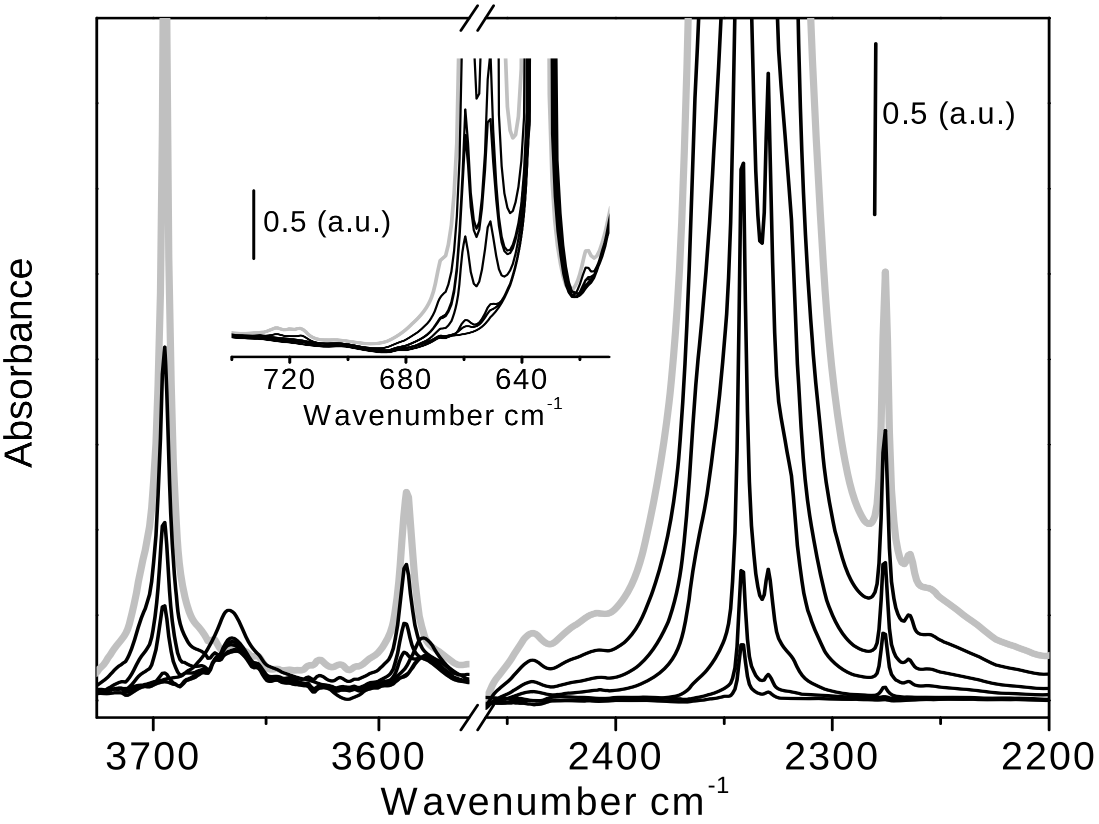

Figure S3: FTIR spectra (background subtracted) of CO_2 adsorbed on CPO-27-Ni at decreasing equilibrium pressure (higher coverage, grey curve corresponds to 0.02 atm equilibrium pressure). In the inset the CO_2 bending region is reported.

be slightly distorted. On the high and low frequency sides of these peaks, very weak bands are growing. In particular a doublet at 725 and 716 cm^{-1} can be assigned to $\nu_2 + \nu_{M\text{-}O}$, and the 617 cm^{-1} band can be explained as ν_2 $^{13}CO_2$.

In case of alkaline and alkaline earth metals exchanged zeolites, e.g. for Mg-ETS-10, the formation of carbonates[ii] has been evinced by the doublet at 1620 and 1380 cm^{-1}. In CPO-27-Ni, the strong absorptions associated to the carboxylate modes avoid any spectral inspection in the range 1600-1300 cm^{-1}, however, as no appreciable change has been observed where the asymmetric mode of the carbonate is expected (1620 cm^{-1}), this allows to exclude the formation of these species.

At high coverage the band associated with ν_3 and ν_2 modes of $Ni^{2+}\cdots{}^{12}CO_2$ adducts goes rapidly out of scale and spectra evolution can be followed only by monitoring the correspective modes of the $Ni^{2+}\cdots{}^{13}CO_2$ adducts. In particular, as the band at 2275 cm^{-1}, becomes more and more intense without any appreciable shift in frequency, the formation of $Ni^{2+}\cdots(CO_2)_2$ species (observed in some cases of exchanged zeolites[iii]) can be excluded.

Upon increasing the equilibrium pressure the bands associated to combination modes of ν_1 and ν_3 become very intense and shift at 3587 cm^{-1} and 3694 cm^{-1} indicating the filling of the cages. The shift in these components and broadening of the ν_3 mode of the $Ni^{2+}\cdots CO_2$ can be associated with the contribution of physisorbed CO_2 which cause a change in dielectric constant.

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[i] B. Bonelli, B. Onida, B. Fubini, C. Otero Areán, E. Garrone *Langmuir* 2000**, 16**, 4976.

[ii] F.X. Llabrés i Xamena and A. Zecchina, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1978.

[iii] B. Bonelli, B. Onida, B. Fubini, C. Otero Areán, E. Garrone *Langmuir* 2000**, 16**, 4976.