Evidence of CO_2 molecule acting as an electron acceptor on a nanoporous metal–organic-framework MIL-53 or $Cr^{3+}(OH)(O_2C–C_6H_4–CO_2)$†

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The adsorption mode of CO_2 at low coverage in the nanoporous metal benzenedicarboxylate MIL-53(Cr) or $Cr^{3+}(OH)(O_2C–C_6H_4–CO_2)$ has been identified using IR spectroscopy; the red shift of the v_3 band and the splitting of the v_2 mode of CO_2 in addition to the shifts of the $v(OH)$ and $\delta(OH)$ bands of the MIL-53(Cr) hydroxyl groups provide evidence that CO_2 interacts with the oxygen atoms of framework OH groups as an electron-acceptor *via* its carbon atom; this is the first example of such an interaction between CO_2 and bridged OH groups in a solid.

Carbon dioxide is a strategic gas in many industrial processes. As both a product of combustion and a significant greenhouse gas, its recovery and elimination/reuse is a major problem facing today's society.[1] One solution to recover carbon dioxide is to employ an adsorption process. Among the potential adsorbent nanoporous candidates (*i.e.* activated carbons, zeolites, clays, silicas…), metal organic frameworks (MOF) could be a serious alternative. These "metal organic frameworks"[2,3] or "metal coordination polymers"[4] are built up from inorganic sub-networks (clusters, chains or layers) and organic complexing molecules (phosphonates, carboxylates, sulfonates). These sub-networks often contain divalent (Zn^{2+}, Cu^{2+}…) or trivalent cations (Cr^{3+}, Al^{3+}…) connected to each other *via* organic moieties such as carboxylates. The structures present tunnels or cavities with pore sizes between 3 and 35 Å. This could lead to highly porous solids with record surface areas and pore volumes.[5,6]

Several studies have examined the adsorption of carbon dioxide by MOF materials. Very large capacities at room temperature have been reached at pressures between 10 and 70 bar.[7,8]

The structure of MIL-53$_{HT}$(Cr) (HT: high temperature form) or $Cr(OH)(O_2C–C_6H_4–CO_2)$ is built up from infinite chains of corner-sharing $CrO_4(OH)_2$ octahedra interconnected by the dicarboxylate groups.[9] This results in a 3D metal–organic framework containing 1D diamond-shaped channels with pores of free diameter close to 0.85 nm (Fig. 1) and an average surface area (Langmuir) of about 1500 m^2 g^{-1}. It was shown previously that MIL-53 is a highly breathing solid which contracts or expands reversibly upon adsorption–desorption of water or polar solvents such as dimethylformamide. It was also observed that adsorption of gaseous CO_2 in the latter solid at 304 K resulted both in a high capacity (*ca.* 10 mmol g^{-1}) and an unusual adsorption isotherm with the presence of a step at around 6 bar. It was assumed that this phenomenon could be due to specific interactions between the gas and the framework which would cause a shrinkage of the structure for low uptake values (<6 bar); at higher pressure, a reopening of the total porosity and total pore filling of the pores would occur.[7]

This communication is related to CO_2 adsorption in MIL-53(Cr) at low coverage. We report evidence that CO_2 is adsorbed molecularly in MIL-53(Cr) as an electron acceptor. To our knowledge, this is the first evidence of such an interaction within a MOF or any other porous material having large CO_2 sorption capacity.

The spectrum of MIL-53(Cr) after outgassing at 473 K is shown in Fig. 2(a, c). It exhibits strong bands between 800 and 1700 cm^{-1} assigned to the vibration modes of the organic moieties. In particular, those at 1550 and 1400 cm^{-1} characterize the $v(COO)$ vibrations of carboxylate groups. The hydroxyl groups of the *trans* corner sharing octahedra $CrO_4(OH)_2$ chains give rise to a $v(OH)$ band at 3655 cm^{-1} with a shoulder near 3610 cm^{-1}. H/D exchange experiments with D_2O at room temperature followed by evacuation at 373 K show that the corresponding $\delta(OH)$ band is situated at 920 cm^{-1}.

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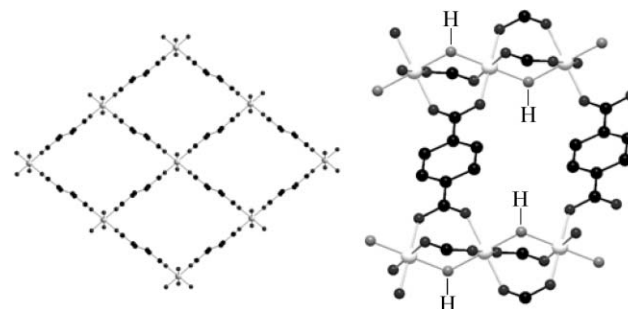
Fig. 1 Left: view of the structure of MIL-53$_{HT}$(Cr) along the pore axis; right: view of the chains of MIL-53(Cr) (Cr: white, O: grey, C: black).
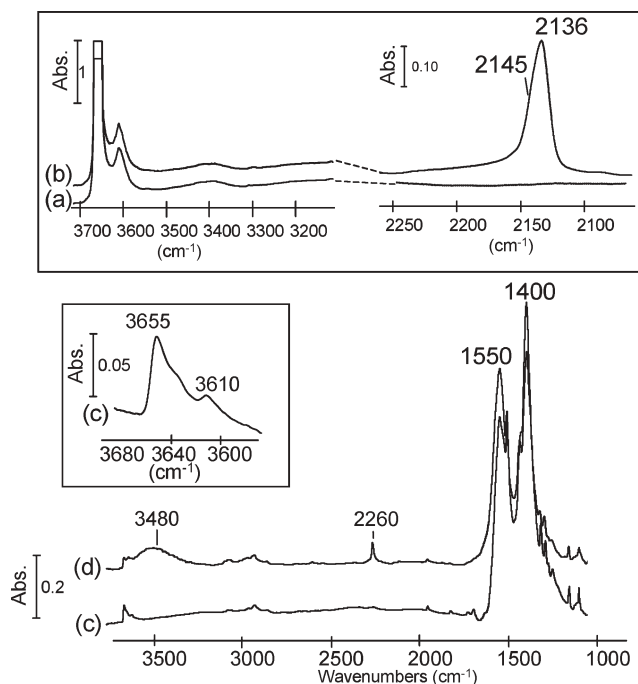
Fig. 2 IR spectra of MIL-53(Cr) activated at 473 K under vacuum (10^{-3} Pa) before and after introduction of 133 Pa of CO at 100 K (spectra (a, b)), before and after introduction of 3300 Pa of CD_3CN at 298 K (spectra (c, d)). Spectra (a, b): self-supported wafer (15 mg); spectra (c, d): sample (2 mg) previously dispersed in deionised water and spread on a silicon plate.
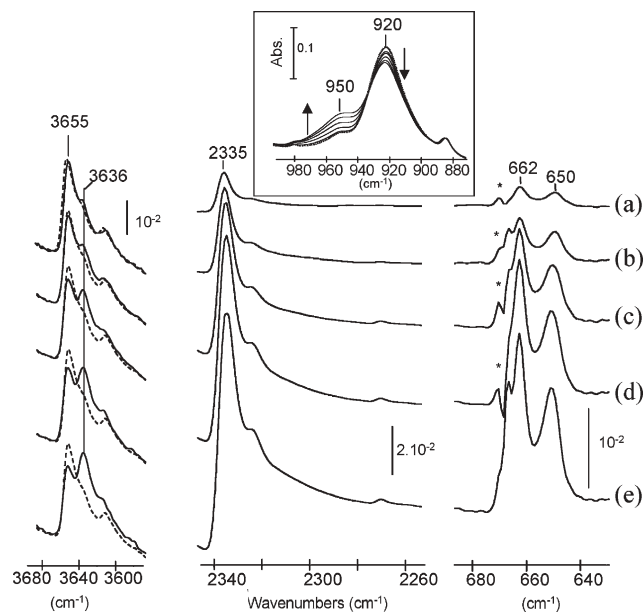

Fig. 3 CO_2 introduction on MIL-53(Cr) activated at 473 K. Spectra of activated MIL-53(Cr) deposited on silicon wafer (dotted lines) and then after introduction of increasing CO_2 equilibrium pressures into the cell (full lines): (a) 1066 Pa, (b) 2400 Pa, (c) 3850 Pa, (d) 5000 Pa, (e) 5850 Pa. Inset: perturbation of the $\delta(OH)$ mode upon CO_2 adsorption. * indicates a residual contribution of the v_2 band of CO_2 gas in the spectra.

In a first step, the acidic properties of MIL-53(Cr) activated at 473 K have been probed using CO adsorption at 100 K and CD_3CN adsorption at 298 K. The spectrum in the $v(CO)$ range after introduction of 133 Pa of CO into the cell (Fig. 2(b)) displays a strong band at 2136 cm^{-1} with a shoulder at about 2145 cm^{-1}. Such low-frequency bands characterize liquid-like species. The lack of any band above 2150 cm^{-1} indicates the absence of coordinatively unsaturated Cr^{3+} sites which would lead to bands in the 2180–2200 cm^{-1} range.[10] Besides, no CO interaction with the hydroxyl groups could be evidenced: neither perturbation of the $v(OH)$ band, nor the appearance of H-bonded CO (2150–2170 cm^{-1} range) is observed. This indicates that acidity of OH groups is very weak in MIL-53(Cr). CD_3CN adsorption at 298 K leads to a perturbation of the OH groups by hydrogen bonding, giving rise to a $v(CN)$ band at 2260 cm^{-1} and a downward shift of the $v(OH)$ band by about 180 cm^{-1} (Fig. 2(d)). These frequencies are close to those reported for acetonitrile H-bonded with weakly acidic alcohols such as methanol.[11] Thus, both CO and CD_3CN adsorptions show that OH groups of MIL-53(Cr) do not present a pronounced acid character.

CO_2 introduction (equilibrium pressure from 133 to 3×10^5 Pa) on MIL-53(Cr) activated at 473 K has been performed at room temperature. The spectra recorded after introduction of CO_2 (0–5850 Pa) are shown in Fig. 3. In the 2350–2300 cm^{-1} range, a strong band at 2335 cm^{-1} with a shoulder at 2325 cm^{-1} are detected. They are assigned to the CO_2 asymmetric stretching mode (v_3) and to the $v_3 + v_2 - v_2$ combination mode (hot band), respectively. The v_3 band frequency is clearly lower than that observed in the gas phase (2349 cm^{-1}). Thus, this rules out the

interaction of CO_2 in MIL-53 as an electron-donor molecule through one of its oxygen atoms since it implies usually an upward shift of the v_3 frequency with respect to that of the gas phase.[12] This is in agreement with the very weak acidity of OH groups of MIL-53(Cr), too low to form H-bonds with CO_2 molecules.

In the v_2 range (CO_2 bending mode), two bands at 662 and 650 cm^{-1} are observed. Their intensity increases at the same rate with the CO_2 pressure, strongly suggesting that both bands correspond to only one type of adsorbed species. Accordingly, only one v_3 band is detected (2335 cm^{-1}). It is worthwhile mentioning that similar spectra are obtained at higher pressure (1.5–3 bar), which are relevant to practical applications. However, the contribution of the gaseous CO_2 spectrum is then important, preventing the v_3 and $v(OH)$ domains to be investigated (see ESI†). In any case, no band due to the v_1 mode (expected near 1385 cm^{-1}) can be observed because of strong carboxylate bands in this spectral range.

The presence of a double band for the doubly degenerated v_2 stretching mode of gaseous CO_2, indicates a lowering of the symmetry upon adsorption, which lifts the degeneracy of the v_2 mode. Confinement effect due to the micropores of the material could be involved. However no v_2 splitting has been observed when CO_2 is adsorbed in micro- and mesoporous compounds such as silicalite,[13] X-zeolite and mesoporous MCM-41 silica.[14] By contrast, similar splittings have been reported previously in the case of electron donor–acceptor (EDA) complexes of CO_2 with molecules such as pyridine,[15] alcohols[16] or functional groups of polymers[17] and was due to the interaction *via* the carbon atom of CO_2 as an electron acceptor. In this case, the high and low v_2 frequency bands are assigned to the out-of plane and in-plane bending modes, respectively.[17] This leads to a v_3 frequency (2335 cm^{-1}) clearly lower than that observed in the gas phase

(2349 cm^{-1}), which is also expected in the case of EDA complexes involving CO_2 as an electron acceptor.[18]

In the case of MIL-53(Cr), two electron donors can be considered: terephthalate moieties and hydroxyl groups. It has been reported that CO_2 incorporation in poly(ethylene terephthalate) provokes the splitting of the ν_2 band, with a doublet at 659 and 655 cm^{-1}.[17] This splitting is significantly smaller than that observed in the present study. Moreover significant perturbations of both $\nu(OH)$ and $\delta(OH)$ bands arise: adsorption of increasing amounts of CO_2 leads to the appearance of two new bands at 3636 cm^{-1} and 950 cm^{-1} at the expense of those at 3655 and 920 cm^{-1} (Fig. 3). The shift of the $\nu(OH)$ band (19 cm^{-1}) is similar to that observed in the case of CO_2-alcohol EDA complexes, whereas that of the corresponding $\delta(OH)$ band (30 cm^{-1}) is much more important than predicted by *ab initio* calculations for a CO_2–CH_3OH EDA complex (30 *vs.* 2–3 cm^{-1}).[16] To explain such a shift, it is worthwhile noticing that the OH groups in MIL-53 are bridged. CO_2 interaction with the oxygen atom of μ_2-OH groups might significantly change the conformation of the OH group with respect to the Cr–O–Cr plane, thus leading to a significant perturbation of the $\delta(OH)$ bending mode (Scheme 1). Preliminary periodic DFT calculations support this result.
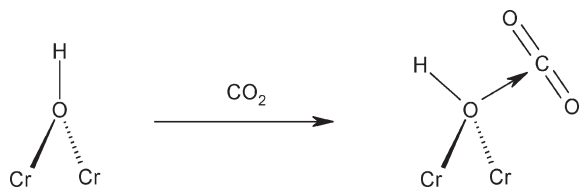
Scheme 1 CO_2 interaction with MIL-53 OH group.

In conclusion, we have observed spectroscopic evidence for the formation of EDA complex between CO_2 and hydroxyl groups in the nanoporous hybrid solid MIL-53(Cr) material, a compound having high sorption CO_2 capacities. This is the first evidence of such an interaction between CO_2 and bridged OH groups in a solid. Work is in progress to understand how such an interaction could provoke the shrinkage of the structure.

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