Electronic Supplementary Information for:

Evidence of CO_2 molecule acting as an electron acceptor on a nanoporous Metal-Organic-Framework MIL-53 or $Cr^{3+}(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$

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Experimental

A) Synthesis method

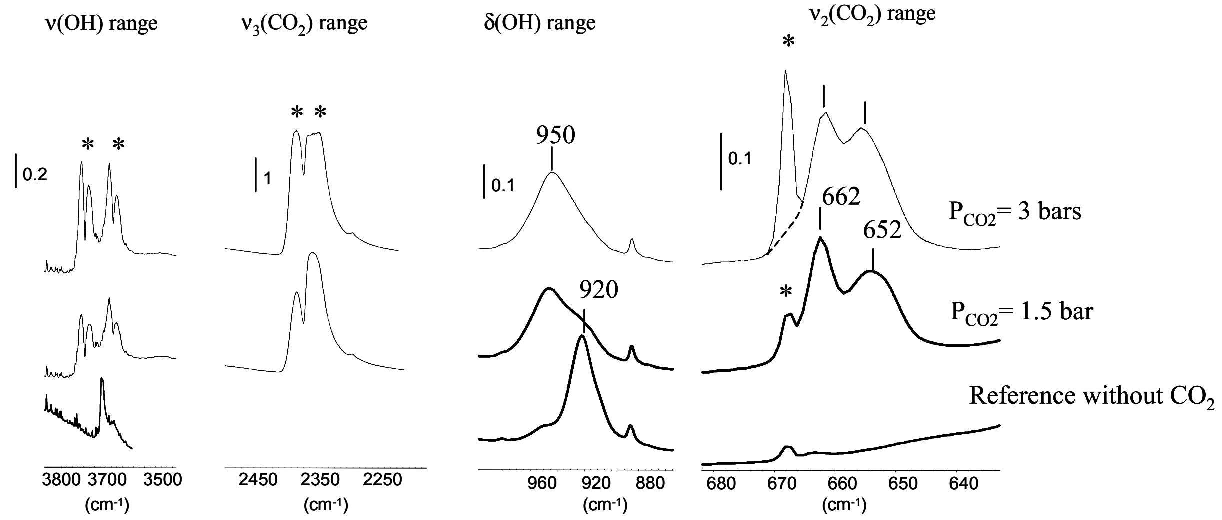
MIL-53as was hydrothermally synthesized as reported before[1] but with a slightly improved recipe. First, chromium(III) nitrate, terephthalic acid , hydrofluoric acid HF and H_2O were mixed in the molar ratio 1: 1.5: 1: 280. Reactants were introduced in a Teflon-lined steel autoclave and the temperature was set at 493 K for four days. A light purple powder was obtained together with traces of terephthalic acid. These traces were first eliminated by dispersion in an excess of DMF (dimethylformamide) during ca. 10 minutes under stirring. Then, the free terephthalic acid, present in the pores of MIL-53as, was evacuated by a solvothermal exchange with DMF (1g of MIL-53as in 25 ml of DMF) using again a Teflon-lined steel autoclave and the temperature set at 423 K overnight. After cooling down to room temperature, the solid MIL-53dmf was calcined overnight at 523 K to evacuate DMF molecules. After cooling under air atmosphere, the resulting solid adsorbed water at room temperature to give **MIL-53lt** or $Cr^{III}(OH).\{O_2C\text{-}C_6H_4\text{-}CO_2\}.H_2O$.

B) Infrared measurements

Samples were pressed (10^7 Pa) into self supported discs (2 cm^2 area, 7 mg cm^{-2}) for CO experiments. Because MIL53 is hardly transparent in the 600-700 cm^{-1}, a small amount of sample (2 mg) was dispersed in deionized water and spread on a silicon wafer for IR measurements during CO_2 adsorption. They were placed in a quartz cell equipped with CaF_2 windows. A movable quartz sample holder permits to adjust the pellet in the infrared beam for spectra acquisition and to displace it into a furnace at the top of the cell for thermal treatments. The cell was connected to a vacuum line for evacuation, calcination steps ($P_{residual} = 10^{-3}$-10^{-4} Pa) and for the introduction of probe molecules into the infrared cell. Spectra were recorded at room temperature. In CO adsorption experiment, the temperature of the pellet was decreased to about 100 K by cooling the sample holder with liquid N_2, after quenching the sample from the thermal treatment temperature. The pressure of CO, CD_3CN or CO_2 probe molecules inside the IR cell was measured by a pressure gauge. Transmission IR spectra were recorded in the 500-5600 cm^{-1} range, at 4 cm^{-1} resolution, on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitting device and a mercury cadmium telluride (MCT) cryodetector.

Results

IR spectra of MIL-53(Cr) under high CO2 pressure



IR spectra of MIL-53(Cr) under high CO_2 pressure
* Indicates the bands due to CO_2 gas phase

1. C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer and G. Ferey, *J. Am. Chem. Soc.*, 2002, **124**, 13519-13526.