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Molecular interactions of CO_2 with the CuBTC metal organic framework: An FTIR study based on two-dimensional correlation spectroscopy

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ABSTRACT

The sorption of Carbon dioxide in the prototype metal-organic framework CuBTC was examined in detail by FTIR spectroscopy. The spectra were collected *in-situ* under isothermal equilibrium conditions at two different temperatures (308 and 273 K). The results were analyzed by difference spectroscopy (DS) and 2D correlation spectroscopy (2D-COS). In particular, 2D-COS was employed to improve the resolution of the spectral profiles and to verify the occurrence of multiple molecular species. The spectroscopic monitoring of the sorption process provided precise quantitative data as well as relevant molecular-level information. Distinct interaction sites were identified in the framework structure, in agreement with first-principles simulations. A minor fraction of probe molecules characterized by a gas-like behavior was identified by analysis of the ν_2 frequency range.

1. Introduction

Metal organic frameworks (MOFs), also known as coordination polymers, are a recently developed class of hybrid crystalline materials. They are composed of transition-metal ions joined together by organic ligands (often polycarboxylic acids) via strong coordinative bonds. The perfectly ordered molecular structure realized in these systems offers important advantages such as a high surface area and a stable nanoporous network. These structures display a relatively high thermal stability that allows one to perform activation cycles. Numerous applications for MOFs have been devised, for instance as storage media [1], adsorbents for separation processes, drug delivery carriers and catalysts [2–8]. For an intelligent design of MOFs with improved properties, it is essential to understand the nature of the interactions between the absorbed molecule and the host framework. Such understanding can be gained either through theory, employing *first-principle* simulations [9,10] or through experimental approaches, notably Infrared and/or Raman spectroscopy [11,12]. In ideal situations, combining theory and experiment can provide complementary information for a deeper molecular characterization [11]. We have employed FTIR spectroscopy to measure CO_2 sorption isotherms at different temperatures using a suitably developed experimental setup capable of working in a pressure range 0.1–200 Torr and in a Temperature range 83–623 K. This experimental approach, coupled with Two-dimensional correlation spectroscopy (2D-COS), has allowed us to gather molecular information on the host/guest system. The material we have investigated is one of the few commercially produced MOF structures, known as CuBTC: it is formed by a 3D network of Copper cations bridging benzene tricarboxylate ligands. It was shown that the absorbed guest molecules interact with acceptor sites in the framework, which were identified as the Cu^{++} cations. Multiple, spectroscopically discernible sites in the CuBTC cage were identified with the aid of 2D-COS spectroscopy. A small fraction of non-interacting CO_2 molecules residing in the framework's cavities was detected.

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2. Experimental

2.1. Materials

Commercial Basolite® C300 [Copper benzene-1,3,5-tricarboxylate (CuBTC, see Scheme S1, and Fig. S1, Supplementary data)], in powder form, was purchased from Sigma-Aldrich (Milano, Italy). Structurally, this MOF has a $Cu_3(BTC)_2$ stoichiometry and is a copper dimer with a Cu−Cu distance of 2.63 Å, coordinated to the oxygen atoms of the benzene-1,3,5-tricarboxylate linkers in a paddlewheel arrangement. The pore structure consists of two types of cages: a large central cavity of 9 Å in diameter, surrounded by small cavities of 5 Å in diameter. The two cavities are connected by triangular-shaped apertures 4.6 Å wide [13,14] (see Fig. S1, Supplementary data). According to the supplier the specific surface area was in the range of 1500−2100 m^2/g, the bulk density was 0.35 g/cm^{-3} and the average particle size of the crystalline powder was 15.96 μm. Carbon dioxide, 99.99% purity, was supplied by SOL S.p.A. (Monza, Italy). Chloroform 99.8% purity and Potassium Bromide (KBr) windows 2.0 mm thick with a diameter of 13 mm were supplied by Sigma-Aldrich (Milano, Italy).

A CuBTC dispersion was prepared from a 5.0 wt % mixture of CuBTC in chloroform stirred for 2 h and further sonicated for 30 min. Samples for spectroscopy measurements were prepared by casting few drops of the CuBTC dispersion on a KBr window allowing solvent evaporation for 2 h at room temperature. Afterwards, the window was slightly pressed at 5.0 bar for compacting the MOF layer, thus optimizing the FTIR transmission measurement.

2.2. FTIR experiments

The FTIR measurements were performed under gas flowing using a modified Linkam cell, THMS350V (Surrey, UK), equipped with temperature control (83−623 K) and a vacuum system. The cell was connected through service lines to a mass-flow-controller [MKS Type GM50A (Andover, MA)] to set the CO_2 flux, while a solenoid valve regulated the downstream pressure. The system was equipped with a Pirani vacuometer and a MKS Baratron 121 pressure transducer (full scale 1000 Torr, resolution 0.01 Torr, accuracy ± 0.5% of the reading) (Andover, MA). The experimental apparatus is represented in Scheme 1. The equipment allowed the *in-situ* activation of the sample at 423 K for 30 min, under vacuum, and the collection of isothermal data at different temperatures. The measurements were performed at 308 and 273 K, in the pressure range from 35 to 150 Torr by 5 Torr step. The diffusion cell was coupled to a Spectrum-100 FTIR spectrometer (Perkin-Elmer, Norwalk, CT, USA), equipped with a beam splitter made of a thin Ge film supported on KBr plates and a wide-band DTGS detector. Instrumental parameters were set as follows: resolution = 2 cm^{-1}; Optical Path Difference (OPD) velocity = 0.20 cm/s; number of co-added scans = 16. Full absorbance spectra (i.e., CuBTC + sorbed CO_2) were obtained using a background collected on the cell containing a plain KBr window, at the test conditions.

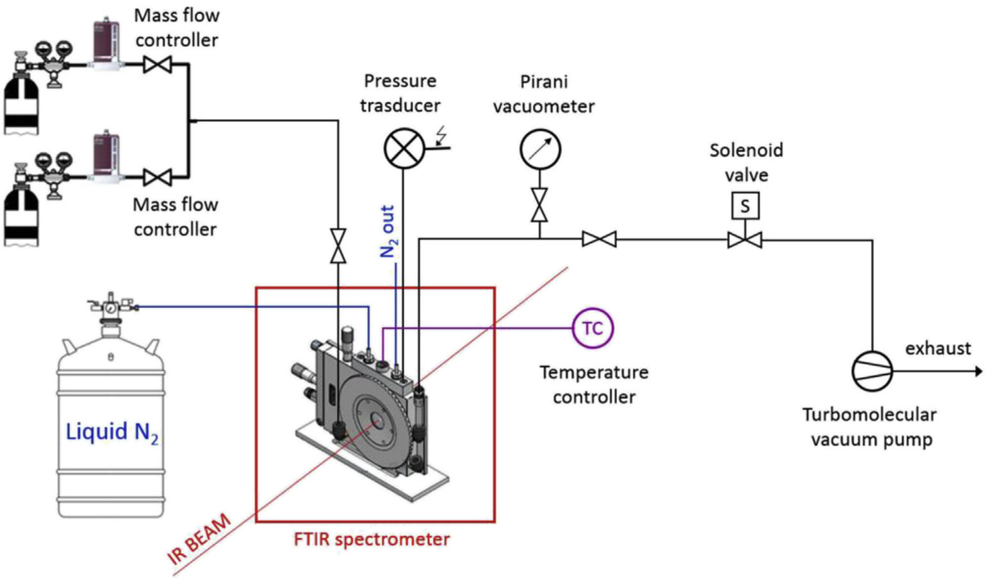
The spectra representative of CO_2 sorbed at equilibrium were obtained by Difference Spectroscopy (DS) eliminating the interference of the substrate, i.e.:

$$A_d = A_s - A_r$$

where A_d, A_s *and* A_r represent, respectively, the difference spectrum (sorbed CO_2), the sample spectrum (CuBTC equilibrated at the test pressure) and the reference spectrum (CuBTC immediately after activation). The data gathered by the instrument were pre-processed (linear baseline correction, offset to zero absorbance) to prevent artefacts due to baseline instabilities. The spectra were converted into ASCII format and transferred to the MATLAB (Mathworks, Natick, MA) computational platform for 2D-COS analysis.

2.3. Volumetric measurements

The CO_2 isotherm at 308 K and with pressures up to 200 torr was obtained using a Micromeritics ASAP 2020 volumetric instrument. It has to be observed that, since ASAP-series devices were mainly designed to work at the boiling temperatures of noble/inert gases, the Dewar flask in which the sample tube is usually immersed was substituted by an *ad hoc* container, whose outer shell was filled with flowing thermostatted water [15,16]. Prior to the adsorption experiment, CuBTC was degassed under high vacuum at 423 K for 30 min.



Scheme 1. Schematic representation of the apparatus for FTIR measurements.