Structural modifications occurring during the water sorption processes on a potential material for autonomous indoor humidity control

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The supramolecular compound catena-$\{[Co(amp)_3][Cr(C_2O_4)_3]\cdot6H_2O\}$ (**I**) was synthetized as reported earlier [1,2]. To get insight into the structural modifications of its architecture within the water sorption processes (see Fig.1 (a)), in situ powder X-Ray Diffraction (PXRD) measurements were performed on a Bruker D8 Advance Diffractometer in a Bragg−Brentano geometry, using Cu(Kα_1) radiation. The humidity was controlled by exposing the sample to a nitrogen flow heated at 40°C and having humidity rates ranging from 0 to 90% relative humidity (r.H.) and then from 90 to 0% r.H. The PXRD carpet plot diagram ((see Fig.1 (b)) and the refinements of the PXRD patterns coupled with the single crystal diffraction results were used. During the adsorption and desorption processes, only two phases are involved, that of the dehydrated phase ($[Co(amp)_3][Cr(C_2O_4)_3]$ (**I'**), P $2_1/n$, a= 12.0542, b=16.0920, c = 13.8841, β = 99.8013) and the hydrated phase (**I**, P $2_1/n$; a= 13.2330, b=18.2611, c = 14.1396, β = 100.5016). For the adsorption process, during the first step (from 0 to 30% r.H) corresponding to an adsorption of ∼ 1 mol H_2O / mol of **I'**, only phase **I'** is involved and the volume of its unit cell does not change significantly. During the second step (from 30 to 35% r.H.) corresponding to an abrupt adsorption of ∼5.6 mol H_2O / mol of **I'**, both phases are involved with different percentages (deduced from Rietveld refinements) progressing to the complete conversion of **I'** to **I**. During the third phase where the quantity of water adsorbed shows a plateau (from 35 to 90 % r.H.), only phase **I** is present and the volume of its unit cell does not change significantly with the humidity. For the desorption process, the same observations apply. During the first step (from 90 to 20 % r.H.) only **I** is present and its volume decreases just slightly. During the deep desorption process (from 20 to 14 % r.H.), both phases are involved with different percentages and during the last step (from 14 to 0% r.H) at the contrary to the adsorption process, both phases are still present while the sorption isotherm in this region looks like a type-I isotherm in the IUPAC classification [4]. These results suggest a quick capillary condensation followed by a pore filling process that produces a type-V isotherm profile [4], in relation with the first order structural transition followed by insignificant changes of the unit cell volume. The adsorption and desorption branches in the S- shaped isotherms of H_2O-vapor for this compound occur at the values of relative humidity at which these phase transitions start. The conversion of **I** to **I'** and vis-versa is followed by the cleavage and formation of the hydrogen bonds in the architectures of these materials.
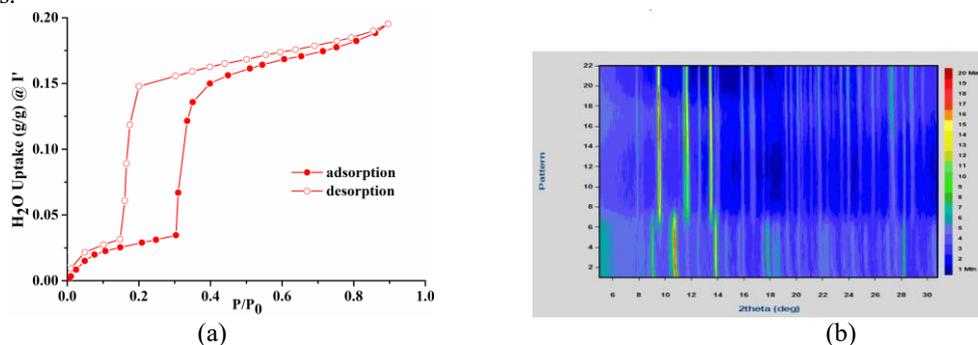

Figure 1. Diagrams showing: (a) the H_2O sorption isotherm of **I'** and (b) its Powder X-ray diffraction (PXRD) carpet plot upon water ad- and desorption.

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