Structural properties of the F4_MIL-140A(Ce) MOF by solid-state NMR spectroscopy

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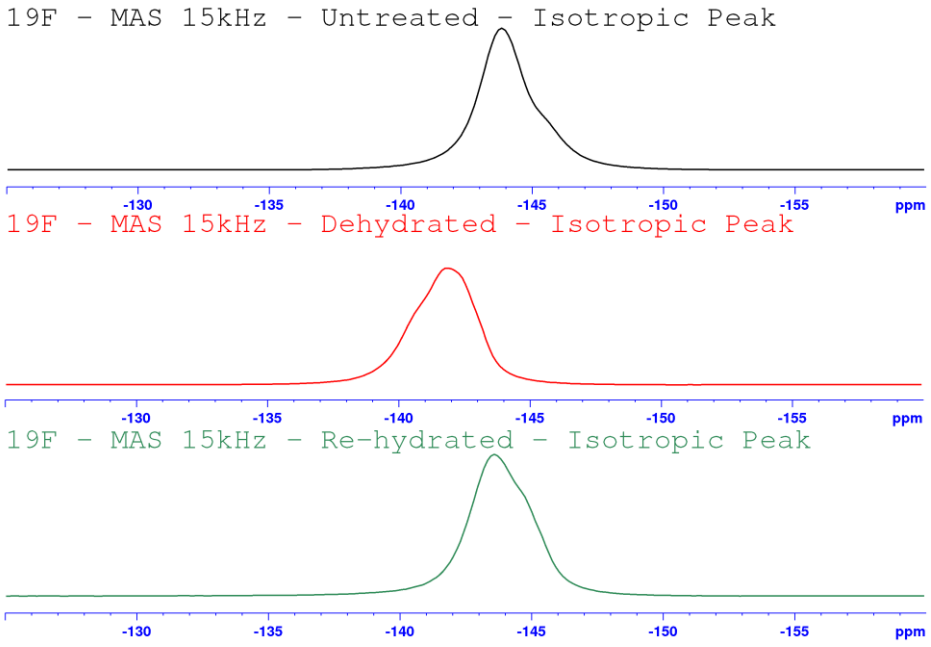
Introduction

Metal-Organic Frameworks (MOFs) are a class of crystalline compounds whose scaffolding derives from metal clusters or ions that are interconnected by organic linkers. Properties of MOFs are highly tunable and thus they can be employed in a wide range of fields of application. Solid State NMR has been employed to gain an in-depth knowledge of a MOF belonging to the MIL class, precisely F4_MIL_140A(Ce).

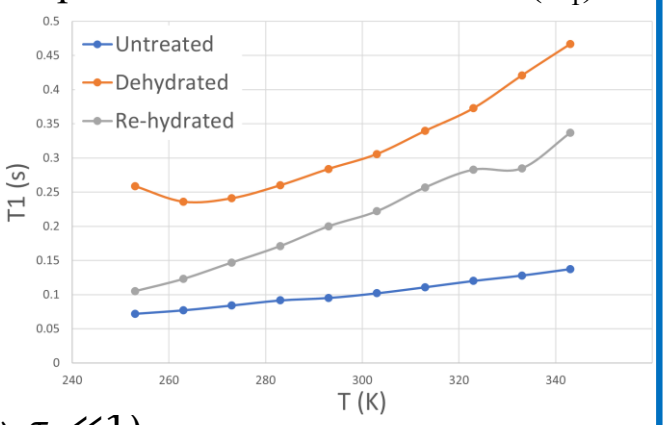
^{19}F MAS Spectra

^{19}F chemical shift is dependent on the presence of water.



^{19}F T_1 Relaxation Times

A dynamic process involving the TFBDC ligands has been detected by the trend of ^{19}F spin-lattice relaxation times (T_1) vs temperature. In the dehydrated sample the dynamic process is slower, and relaxation times are close to a minimum ($\omega_L\tau_s \simeq 1$), whilst in the other two samples dynamics is in the fast-motion regime ($\omega_L\tau_s \ll 1$).

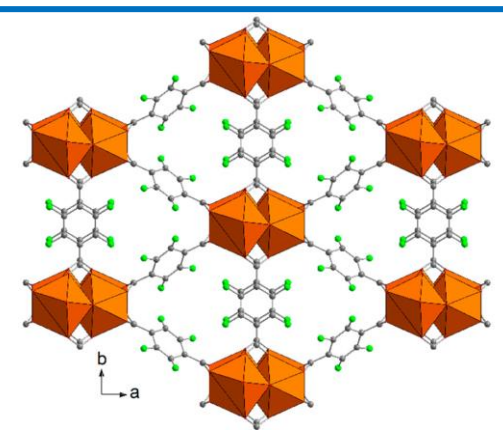


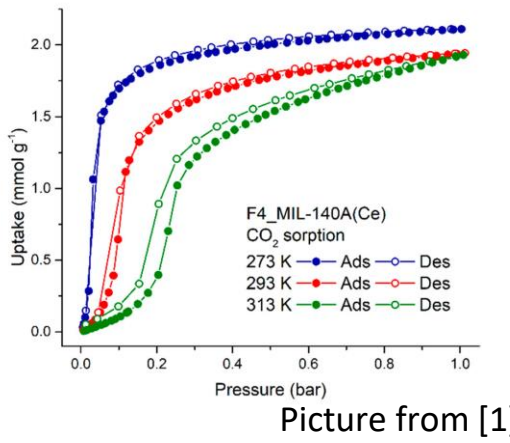
Experimentals

All spectra were recorded on a 3-channel Bruker Advance NEO 500 Solid State NMR spectrometer using a 4mm CP/MAS probe. Frequency Switched Lee Goldburg (FSLG) has been used in HETCOR experiments to remove homonuclear dipolar coupling. ^{1}H-^{13}C and ^{19}F-^{13}C heteronuclear dipolar couplings have been always removed by a SPINAL-64 scheme. ^{19}F T_1's were measured by Inversion-Recovery.

Acknowledgements

CISUP (Centre for Instrument Sharing – University of Pisa) is acknowledged for the use of the Bruker Advance Neo 500 Solid State NMR spectrometer)





Picture from [1]

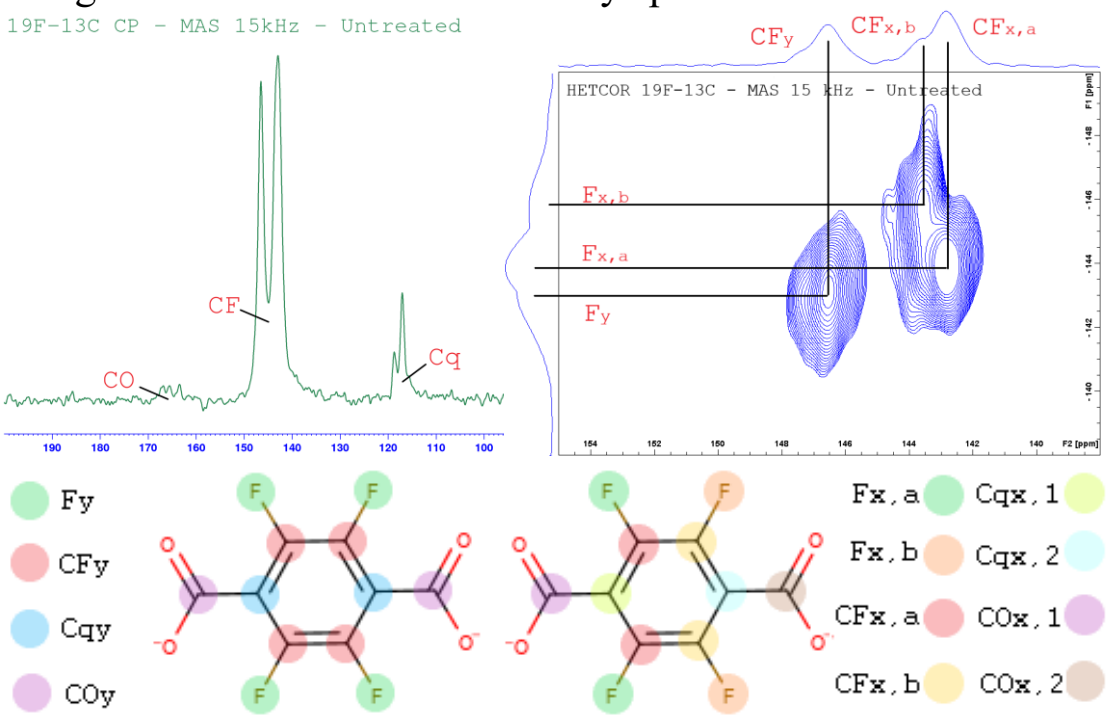
F4_MIL_140A(Ce)

F4_MIL_140A(Ce) is a relatively new MOF in which inorganic building units of Cerium^{IV} are interconnected by tetrafluoroterephtalates (TFBDC) ligands. This MOF is extremely promising for possible applications, in particular as a sorbent for gas separation, because of its water-based synthesis and its step-shaped CO_2 adsorption isotherm [1]. The Solid State NMR study has been carried out on three different samples:

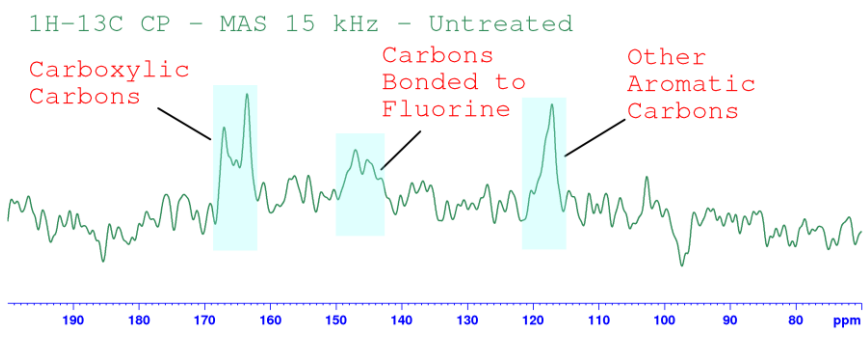
- Untreated;
- After a dehydration process;
- After a partial re-hydration.

^{13}C MAS Spectra

Using a combination of ^{19}F-^{13}C CP/MAS (Cross Polarization/Magic Angle Spinning) and HETCOR (HETeronuclear CORrelation) experiments, two different chemical environments in the solid have been observed. This is in agreement with data from X-Ray spectra.



Moreover ^{1}H-^{13}C CP has been employed to show that water molecules in the sample mainly interact with carboxylic moieties.



References: [1] *ACS Sustainable Chem. Eng.* 2019, 7, 1, 394–402