Local Range Changes in a (LiCl)[Zn(*bdc*)(*ted*)$_{0.5}$] Metal Organic Framework Upon Hysteretic Adsorption-Desorption of CO_2 Studied Via ^{13}C MAS NMR

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Introduction

Recent approaches developed to functionalize metal organic frameworks (MOFs) include dispersion of metal nanoparticles and cation exchange. The former, however, may result in complete obstruction of the micropores while the latter would be suitable for anionic MOFs. Furthermore, these modifications can be detrimental to both chemical and thermal stability properties. We have demonstrated that it is possible to disperse a metal salt onto a neutral MOF and tailor its adsorption properties without affecting the long-range order by means of a combined organic solvent mediated impregnation and thermal dispersion process.[1] Here we report progress on the analysis related to the changes that *M*(*bdc*)(*ted*)$_{0.5}$ (*M*: Ni or Cu); bdc: 1,4-benzenedicarboxylate; *ted*: triethylenediamine) MOFs experience upon dispersion of LiCl and uptake of CO_2.[2]

Experimental

^{13}C MAS NMR experiments were performed on a Bruker DMX300 NMR spectrometer where the ^{13}C frequency is 75.5 MHz. Samples were spun at 10 kHz, controlled within ±2 Hz by a Bruker pneumatic MAS unit. The ^{13}C signals were enhanced by cross polarization achieved through a Hartmann-Hahn match condition (50 kHz RF spinlock fields on both ^{13}C and ^{1}H channel, 1 ms contact time). The ^{13}C chemical shift was referenced to the carbonyl carbon of alanine at 176.2 ppm.

Results and Discussion

Fig. 1 shows stacks of ^{13}C CPMAS NMR spectra for *M*(bdc)(ted)$_{0.5}$ gathered prior to and after the addition of LiCl.[2] A comparison between the spectra gathered for Zn(bdc)(ted)$_{0.5}$ and Ni(bdc)(ted)$_{0.5}$ revealed considerable signal broadening in the latter, which should be associated to the effect of para-magnetism brought by the presence of nickel(II). The data also show that this resulted in occlusion of resonances that were expected for the carbons of the *bdc* linker. However, the addition of LiCl apparently reduced the said effect as evidenced by the re-appearance of the missing resonances. It also resulted in a significant decrease in intensity in the resonance corresponding to the C_4 carbon from the *ted*. These results suggest that the LiCl might be interacting with the metal paddle wheel secondary building units (SBUs) in a strong fashion. NMR spectra gathered for Cu(bdc)(ted)$_{0.5}$ show that the resonance of the C_4 carbon disappeared upon incorporation of LiCl and this should be related to the expansion observed between crystallographic planes associated to the *ted*. In addition, the resonances of the C_1 and C_2 carbons were displaced to the low field and the intensity of the C_1 carbon resonance decreased significantly. Furthermore, the C_3 carbon resulted in two resonances (C_3 and C_3') upon the inclusion of LiCl and could be the result of the presence of a new environment for the CH bond of the aromatic ring. C_1 is the carbon nearest to the metal in the paddle wheel, so the intensity decrease might be due to a possible interaction between LiCl and copper(II). Upon CO_2 adsorption/desorption, the NMR data gathered for (LiCl)[Ni(bdc)(ted)$_{0.5}$] presented few changes, which contrasts with the observations resported before for the Zn-MOF variant. For (LiCl)[Cu(bdc)(ted)$_{0.5}$], which is almost non-crystalline according to XRD, the spectra showed changes in the intensities of the resonances upon the uptake of CO_2, with results comparable to those gathered prior to the uptake.

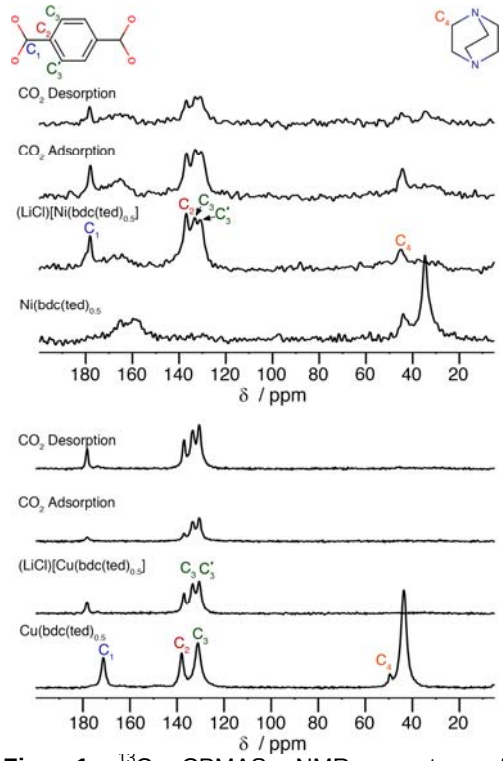

Fig. 1 ^{13}C CPMAS NMR spectra of Ni(bdc)(ted)$_{0.5}$ (*top*) and Cu(bdc)(ted)$_{0.5}$ (*bottom*) prior and after loading of LiCl. Spectra stacks also include data gathered upon adsorption and desorption of CO_2 in the LiCl containing MOFs.

Acknowledgements

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References [1] Hernández-Maldonado, A.J., *et al.,* J. Mater. Chem. A, **1**, 2343-2350 (2013).
[2] Hernández-Maldonado, A.J., *et al.,* RSC Adv., Revision Submitted (2014).