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

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Introduction

For more than a decade, metal-organic frameworks (MOFs) have been the foci of attention of the scientific community due to their textual properties and ease of assembly. Although there are reports about MOF post synthesis functionalization methods to enhance surface selectivity toward particular guest molecules and tailor the materials thermal properties, many cannot be applied to a broad range of MOFs to avoid compromising crystallinity and stability. Recently, Hernández-Maldonado and co-workers 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 of the material by means of a combined organic solvent mediated impregnation and thermal spontaneous dispersion process.[1] Here we report about the short-range changes that a Zn(*bdc*)(*ted*)$_{0.5}$ (*bdc*: 1,4-benzenedicarboxylate; *ted*: triethylenediamine) MOF experiences upon dispersion of LiCl in an attempt to elucidate the underlying mechanism behind the changes in adsorption properties, particularly during the *irreversible* uptake of CO_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

The ^{13}C MAS NMR spectrum (Fig. 1a) showed four unique resonances consistent with the different environments present in the Zn(*bdc*)(*ted*)$_{0.5}$ structure.[1-3] Upon dispersion of LiCl, the data revealed changes in the intensities of the resonances and displacement toward the low field region for peaks corresponding originally to C_1 and C_4 (Fig. 1b). The resonance of the latter, which corresponds to the carbons of the *ted* linker, is a doublet and its shift could be a product of the interaction the linker with LiCl. This would correlate with an interplanar distance reduction in (002) as estimated from XRD data also associated to the *ted* linker.[1] Such contraction should also produce an increase in distance between the crystallographic planes associated to the *bdc* linker, which are probably associated to the NMR shift and decrease in intensity observed for C_1. Upon adsorption of CO_2 onto the LiCl based MOF (*ex situ*), the NMR spectrum shows changes also asssociated with the environments of C_1 and C_4 (Fig. 1c). These carbon atoms are closer in proximity to the LiCl, which suggests that the CO_2 is interacting with the metal salt and at the same time inducing changes that affect the linker positions. Further, the data shown in Fig. 1d evidences that the interaction of CO_2 with the material is quite strong since the carbon atom environments remained unchanged upon an attempt of desorption via vacuum (ex situ). This is a plausible explanation for the hysteretic CO_2 adsorption-desorption behavior observed from volumetric adsorption data.[1]

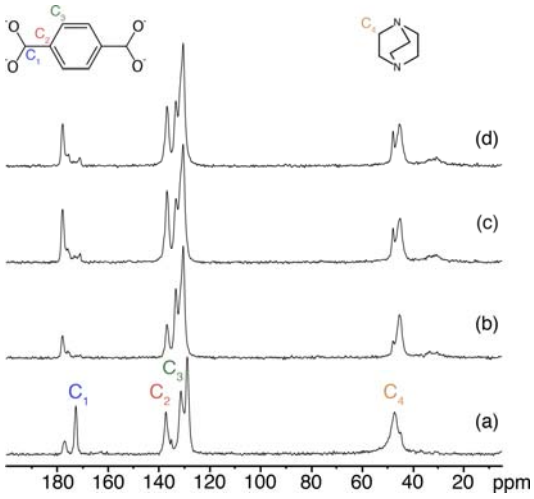

Fig. 1 ^{13}C MAS NMR spectra of (a) Zn(bdc)(ted)$_{0.5}$, (b) (LiCl)[Zn(bdc)(ted)$_{0.5}$], (c) (LiCl)[Zn(bdc)(ted)$_{0.5}$] after CO_2 adsorption, and (d) (LiCl)[Zn(bdc)(ted)$_{0.5}$] after CO_2 adsorption-desorption.

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References

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