



Characterization of Metal-Organic Frameworks by ^{17}O SSNMR Spectroscopy at 35.2 T

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Introduction

Metal-organic frameworks (MOFs) are a fascinating family of hybrid organic-inorganic porous materials with many practical applications. We report here ^{17}O solid-state NMR (SSNMR) spectroscopic characterization of MOFs using a 1.5 GHz SCH magnet. Oxygen is an important target for MOF characterization due to its presence in many different forms in various MOFs, along with the key roles of oxygen species in applications such as guest adsorption, sensing and catalysis. ^{17}O ($I = 5/2$) is a quadrupolar nucleus, which exhibits a large chemical shift range and is also sensitive to both the EFG and the CSA. However, ^{17}O SSNMR work on MOFs has been rare due to its low sensitivity and quadrupolar broadening which often limits the spectral resolution. Using α -magnesium formate, $\alpha\text{-Mg}_3(\text{HCOO})_6$ as an example, we demonstrated that at 35.2 T, both sensitivity and resolution of ^{17}O spectra can be enhanced dramatically, allowing separation of crystallographically inequivalent oxygen sites with very similar local environments.

Experimental

Both 1D MAS and 2D 3QMAS spectra were acquired on the 1.5 GHz SCH magnet at the NHMFL.

Results and Discussion

Figure 1 shows the ^{17}O spectra acquired previously using the 900 MHz NMR facility in Canada and the recent spectra acquired using the 35.2 T SCH magnet. $\alpha\text{-Mg}_3(\text{HCOO})_6$ MOF represents an extremely challenging system for ^{17}O SSNMR as the crystal structure indicates that there are 12 inequivalent oxygen sites that can be divided into two groups based on their bonding modes. Six independent oxygens adopt $\mu_2\text{-O}$ bonding mode (where one of the oxygen in carboxylate group is bonded to two metal ions), whereas the other six crystallographically inequivalent O sites adopt $\mu_1\text{-O}$ mode (where the other oxygen in the same carboxylate group is bound to only one metal center). The ^{17}O MAS spectrum of the as-synthesized $\alpha\text{-Mg}_3(\text{HCOO})_6$ acquired at 21.1 T (Figure 1) exhibits two separate resonances, corresponding to two groups of chemically inequivalent oxygens from the formate ligands. The six unique oxygen sites in each of the $\mu_1\text{-O}$ and $\mu_2\text{-O}$ are so alike and the MAS spectrum shows no sign of resolution. Insufficient sensitivity even at 21.1 T prevents the acquisition of 2D MQMAS experiment for further resolution.

The 1D ^{17}O MAS spectrum acquired at 35.2 T in Figure 1 shows more spectral features than that of the 900 MHz spectrum. The gain in sensitivity at the high field of 35.2 T now permits the 3QMAS experiments to be carried out. As illustrated in Figure 1, the 3QMAS spectrum at 35.2 T allows separation of all 12 crystallographically inequivalent O sites. The complete spectral assignments were achieved via the DFT calculation. We are currently preparing a manuscript based on the data acquired at 35.2 T.

Conclusions

Our work demonstrates that at 35.2 T, we can push the spectral resolution of ^{17}O SSNMR to its limit.

Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida. The NSERC of Canada is acknowledged for a Discovery Grant.

