Assessing the Electronic Structure of Iron Sites in Fe-Substituted MOF-5

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Introduction

Metal-organic frameworks (MOF) are rigid solid-state scaffolds that can be altered in a rational fashion to incorporate redox-active metal sites. Consequently, owing to their large surface area and well controlled porosity, MOFs can be engineered to function as exquisite catalysts for a variety of small molecule transformations.

Experimental

Several Mössbauer and high-field EPR of iron(II/III)-doped MOF-5 samples were investigated using the transmission EPR and Mössbauer instruments of the EMR facility.

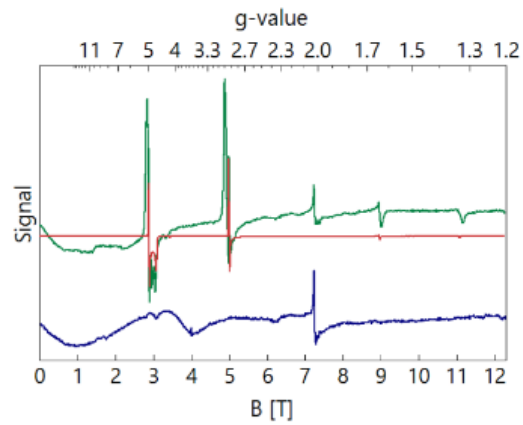

Figure 1. Blue and green traces are high-field EPR spectra recorded for the iron-doped MOF-5 at 5 K and 203.2 GHz.

Results and Discussion

The high-field EPR spectra of Fig. 1 were recorded for an all-ferrous Fe-doped MOF-5 sample. While the green spectrum was recorded before, the blue was collected after evacuating the MOF network. For the green spectrum, the sharp resonances observed at g = 5.1, 2.9, 1.6 and 1.3 can be ascribed to molecular dioxygen species. Interestingly, the features at g = 5.1 and 2.9 clearly show the presence of two distinct O_2 species, namely (1) characterized by narrow resonances which can be ascribed to surface absorbed O_2 (the simulated spectrum of this species is shown in brown) and (2) MOF-coordinated O_2 that exhibits much broader absorption peaks. Interestingly, by pumping at 170 K on a MOF sample that was previously stored at 77 K under LN2 (green trace) the spectroscopic signature of molecular dioxygen is completely removed (blue trace). This result suggests that the MOF-O_2 bonding is weak and reversible.

The Mössbauer spectrum recorded for a parallel sample at 4.2 K, 0 T (Fig. 2) consists of a well-defined quadrupole doublet characterized by parameters typical of high-spin ferrous ions. Analysis of the variable field spectra reveals the presence of two distinct spectral components that exhibit identical zero-field spectra and dissimilar hyperfine coupling tensors. Thus, the solid lines of Fig. 2 are simulations obtained using a standard S = 2 spin-Hamiltonian. The gray traces are obtained from the sum of the blue and red curves that account for the individual spectral components. The two components differ from one another only by about 4.5 T in the magnitude of the hyperfine coupling tensor component along the easy axis of magnetization. The two individual spectral components can be understood as originating from two distinct molecular conformations, e.g. two iron sites populations that exhibit distinct bonding angles. Interestingly, the relative ratios of the two components was found to be time-dependent indicating that even at 77 K there is a slow conformational conversion of the iron sites.

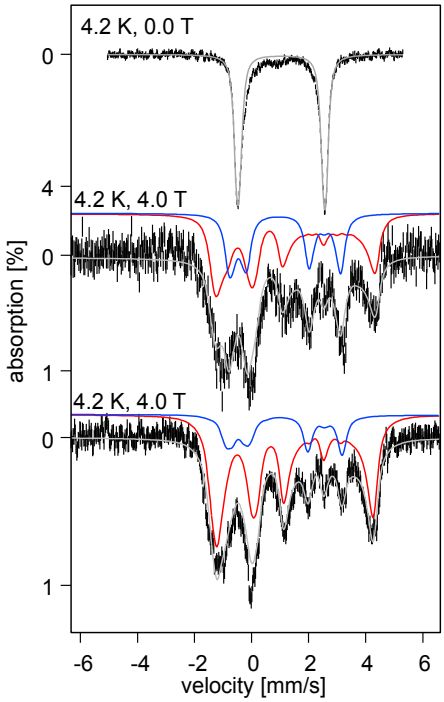

Figure 2. 4.2 K Mössbauer spectra recorded in 0 and 4 T applied field. The two 4T spectra were recorded for the same sample, nearly one month apart, time for which the sample was stored under LN2 at 77 K.

Conclusions

Iron(II)-doped MOF has been found to exhibit a rich spectroscopic behavior.

Acknowledgements

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