EPR and ENDOR study of V-doped Al-MOF

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Metal-Organic Frameworks (MOFs) are ordered porous materials constructed of metal ions connected by organic linkers. These materials possess many interesting features, like well-defined pore size, pore shape and ultra-high porosity. A characteristic example of MOFs with one dimensional pores is MIL-53 ([Al(OH)(BDC), BDC = terephthalate or 1,4-benzenedicarboxylate]. The 3D framework of as-synthesized MIL-53 is built up of infinite chains of corner-sharing $AlO_4(OH)_2$ octahedra with BDC connecting these chains. The 1D channels are filled with disordered uncoordinated terephthalic acid molecules and other impurities, which can be removed by calcination or solvent extraction methods, which are referred to as activation procedures. After activation MIL-53 exhibits breathing: the framework can reversibly change from a large pore (lp) to narrow pore (np) structure by changing temperature or pressure.

EPR and ENDOR spectroscopy are excellent tools for characterizing V^{IV}-centers (with a $3d^1$ electron configuration) in MIL-53. The EPR spectra of as-synthesized V-doped MIL-53 show nicely resolved ^{51}V (I=7/2) hyperfine (HF) structure. The spectra at RT are dominated by a center with rhombic g and ^{51}V HF tensors whose principal axes do not coincide. ENDOR spectra reveal interaction with the central ^{51}V, ^{27}Al (I=5/2) and ^{1}H (I=1/2) nuclei, suggesting that vanadyl ions substitute Al-OH in the MIL-53 framework.

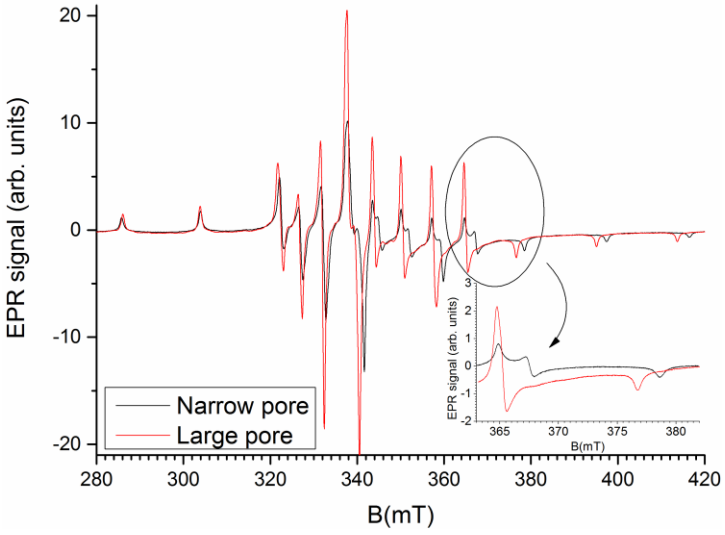

Figure 1 - EPR spectra of V-doped MIL-53 at RT in X-band (9.5 GHz). Black spectrum – narrow pore form, red spectrum – large pore form. Inset shows enlarged part of the spectrum where differences between np and lp form spectra are evident.

The EPR spectra of activated V-doped MIL-53 differ from those of as-synthesized MIL-53. Furthermore, the EPR spectra of V^{IV} in the large and narrow pore forms of MIL-53 can easily be distinguished (Figure 1). ENDOR spectra (10 K, narrow pore) reveal interactions with the same types of nuclei as in as-synthesized V-doped MIL-53 in a slightly different coordination environment.