

Confirming vanadium dopant incorporation in an Al-Metal-Organic Framework MIL-53 by EPR and ENDOR spectroscopy

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Metal organic frameworks (MOFs) are often called “superzeolites” or “the next generation of porous materials”. MOFs are compounded of two basic structural units, an inorganic metal centers and connecting organic ligands, forming infinite three-dimensional framework. Possibility of designing MOF to desired functionality, by combining different metal ions and organic linkers, makes these materials very interesting for wide range of applications, from catalysis and gas storage to purification. Two characteristic types of MOFs, exhibiting one-dimensional pores, are MIL-47^[1] [VO(BDC); BDC = terephthalate or 1,4-benzenedicarboxylate, MIL = Materials of the Institute Lavoisier] and MIL-53^[2] [Al(OH)(BDC)], originally synthesized by Ferey's group.

Recently we reported that V-MIL-47 can be a highly selective catalyst in the epoxidation of cyclohexene^[3]. However, water exposure should be avoided, as it causes framework instability. A solution for this problem may be doping the highly stable MIL-53 with catalytically active V^{IV} ions. In order to understand the catalytic activity of such doped framework, it is necessary to verify where dopant ions actually are in the framework. As V^{IV} (3d¹) is a paramagnetic ion, and EPR and ENDOR spectroscopy gives information about local coordination environment and the site symmetry of paramagnetic centers, that characterization method can provide the answer. Due to the dipole-dipole interaction between the magnetic moment of ⁵¹V nucleus and the unpaired V^{IV} electron the EPR spectra shows nicely resolved signal with eight hyperfine (HF) lines (Fig. 1). This signal is dominated by just one V^{IV} center with rhombic g and ⁵¹V HF tensors whose principal axes do not coincide. The ENDOR spectra of V^{IV} in MIL-53 reveal HF interactions with ¹H and ²⁷Al nuclei, whose anisotropy allows reconstructing the nearest environment of the dopant ions, thus yielding direct information on whether and where the dopant is actually incorporated in the MIL-53 lattice.

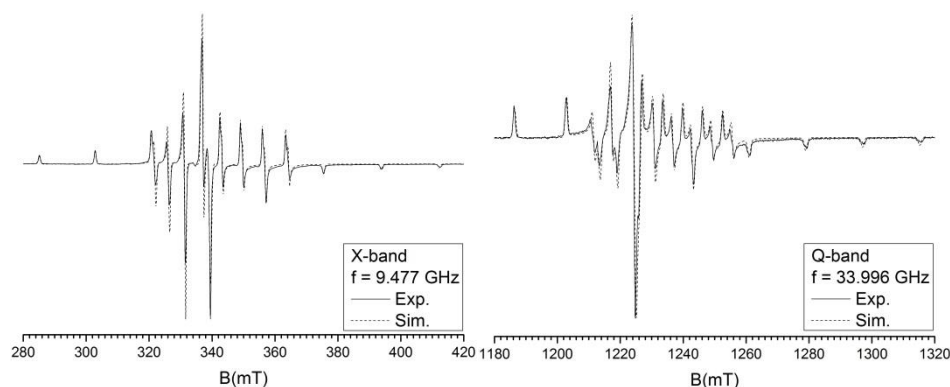


Figure 1 - X and Q-band spectra of V-doped MIL-53 at RT

1. K. Barthelet et al., *Angew. Chem. Int. Ed.* 2002, 41, 281–284
2. C. Serre et al., *J. Am. Chem. Soc.* 2002, 124, 13519–13526
3. K. Leus et al., *J. Catal.* 2012, 285, 196-207