Characterizing vanadium dopant sites in an Al-Metal-Organic Framework by Electron Magnetic Resonance spectroscopy

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Introduction

- Metal Organic Frameworks (MOFs) are crystalline porous solids constructed of metal ions or clusters linked by organic ligands to form an infinite network
- Interesting for many applications, structure can easily be tuned to specific chemical functionalities
- Potential use in catalysis, gas storage and purification
- MIL-47(1) [VO(BDC)] and MIL-53(2) [Al(OH)(BDC)]
- BDC = terephthalate or 1,4-BenzeneDiCarboxylate
- MIL = Matériaux de l’Institut Lavoisier

MIL-47 vs. doped MIL-53

- Recently we reported that V-MIL-47 can be a highly selective catalyst in the epoxidation of cyclohexene(3)
- Problem: MIL-47 exhibits limited stability in aqueous environments
- Solution: Doping the highly stable MIL-53 with catalytically active V(IV) ions
- Question: Is vanadium really incorporated in the lattice? → here checked for as-synthesized structures

V(IV) (3d1) → a paramagnetic ion
Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance spectroscopy can reveal the nearest environment of the dopant ions

Analysis

- In two figures (left) the powder EPR spectra at two microwave frequencies for as-synthesized V-doped MIL-53 at RT are shown
- The spectra are dominated by just one V(IV) center with rhombic g and 27Al hyperfine (HF) tensors whose principal axes do not coincide

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A [MHz] =

163 0.9686 0.1361 0.2079
165 0.1392 0.9903 0
493 -0.2059 0.0289 0.9781

EPR spectra at 295 K

- CW-ENDOR spectra at Q-band at 10 K
- CW-ENDOR in 27Al range
- CW-ENDOR at Q-band at 10 K
- Field dependence of ENDOR spectra in 1H range

References:

Acknowledgments:

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