Breathing effect in activated V-doped Al-MOF studied with EPR

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Introduction

- Metal-Organic Frameworks (MOFs) are ordered porous materials constructed of metal ions connected by organic linkers
- Many interesting features 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, MIL = Materials of the Institute Lavoisier)
- The 3D framework of MIL-53 is built up of infinite chains of corner-sharing AlO4(OH)2 octahedra connected by BDC creating one-dimensional rhombically shaped porous channels

EPR spectra of MIL-53as at RT

In the two figures the X and Q-band powder EPR spectra for as-synthesized V-doped MIL-53 at RT are shown

V-doped MIL-53

- Two sample types:
  - As-synthesized (MIL-53as) - channels filled with unreacted linker - non porous structure
  - Activated (MIL-53act) - after activation procedure - channels empty - porous structure
- After activation V-doped MIL-53 exhibits breathing: by changing temperature and pressure, the structure can be changed from a large pore (lp) to a narrow pore structure (np)
- V51(3d1) \(\rightarrow\) paramagnetic ion
- EPR and ENDOR spectroscopy give information about the local coordination environment and the site symmetry of paramagnetic centers

The ENDOR spectra of V51 in as-synthesized MIL-53 reveal HF interactions with the central 51V, 1H and 27Al nuclei (\(B = 1218\) mT)

The two broad resonance lines at 64 and 92 MHz are assigned to the 51V HF interaction
The spectra in the 27Al range can be explained assuming an axial HF tensor \(A_\|\) and \(A_\perp\)
Field dependence ENDOR spectra close to the Larmor frequency of hydrogen are shown in the right figure
The \(g\) and \(A(\perp)\) tensors, and the ENDOR results are compatible with an \(\text{V}^{\text{IV}}\text{=O}\) molecular ion replacing a regular Al

Analysis of MIL-53as

- The EPR spectra are dominated by one low-symmetry \(\text{V}^{\text{IV}}\)-related component
- It exhibits a nicely resolved 8-lines hyperfine (HF) structure due to the interaction between the unpaired 3d\(^{1}\) electron and the \(51\text{V}\) nucleus
- The \(g\) and \(51\text{V}\) hyperfine (HF) tensors have these distinct principal values and their principal axes do not coincide

CW-ENDOR of MIL-53as at Q-band at 10 K

EPR spectra of MIL-53act at RT

Temp. dependence XRD of MIL-53act

LP and NP EPR spectra (MIL-53act)

- In situ XRD measurements on activated sample show that the structure can change reversibly from narrow pore (RT) to large pore (130°C) form at ambient pressure

References:

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