Study the effectiveness of V-incorporation in the Al-metal-organic framework MIL-53 with electron-nuclear double resonance spectroscopy

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Introduction
- Metal Organic Frameworks (MOFs) → ‘superzeolites’ or ‘the next generation of porous materials’
- 3D structures are self-assembled by coordination of suitable metal ions/clusters with organic ligands
- Combining different ‘metal nodes’ and organic linkers → tuning the structure, functionality
- Wide range of applications in catalysis, hydrogen storage, optics, ...
- MIL-47 [VO(BDC)] and MIL-53 [Al(OH)(BDC)]
- BDC = terephthalate or 1,4-benzendicarboxylate
- MIL = Matériaux de l’Institut Lavoisier

MIL-47 vs. doped MIL-53
- Recently, we have demonstrated that MIL-47 is an efficient catalyst in the liquid phase oxidation of cyclohexene(1)
- 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 framework?
- V$^{IV}$ (3d$^1$) → a paramagnetic ion
- Electron paramagnetic resonance (EPR) and ENDOR spectroscopy may provide the answer

EPR spectra
- In two figures (left) the powder EPR spectrum in X and Q-band for as-synthesized V-doped MIL-53 at RT is shown
- The spectra are dominated by just one V$^{IV}$ center with rhombic g and $^{51}$V hyperfine (HF) tensors whose principal axes do not coincide

MIL-53 $^1$H, $^{27}$Al and $^{51}$V range
- The ENDOR spectra of V$^{IV}$ in MIL-53 reveal HF interactions with the central $^{51}$V, $^1$H and $^{27}$Al nuclei

MIL-53 ENDOR spectrum in $^{27}$Al range
- Interaction with two nearest $^{27}$Al nuclei → $A_1 = 0.75$ MHz and $A_2 = 2.3$ MHz → $d_{\text{exp}} = 3.4$ Å, $d_{\text{c}} = 3.31$ Å
- Suggesting that the V$^{IV}$ ions are incorporated in the framework

MIL-53 field dependence ENDOR spectra in $^1$H range

References:

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