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

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Introduction

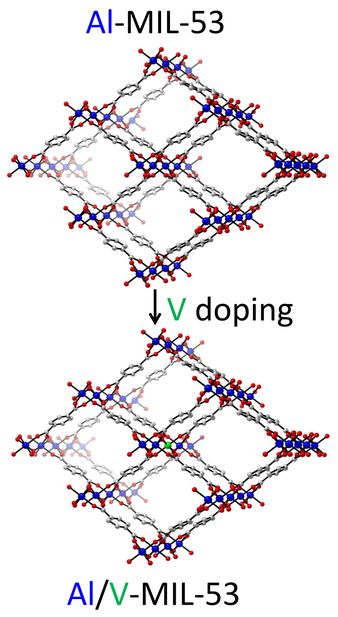
- Metal-Organic Frameworks (MOFs) are ordered porous materials constructed of metal ions connected by organic linkers
- Many interesting features → well-defined pore size, pore shape and ultra-high porosity
- A characteristic example of MOFs with one dimensional pores is MIL-53[1] [Al(OH)(BDC), BDC = 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 $AlO_4(OH)_2$ octahedra connected by BDC creating one-dimensional rhombically shaped porous channels

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 conditions, the structure can be changed from a large pore (lp) to a narrow pore structure (np)

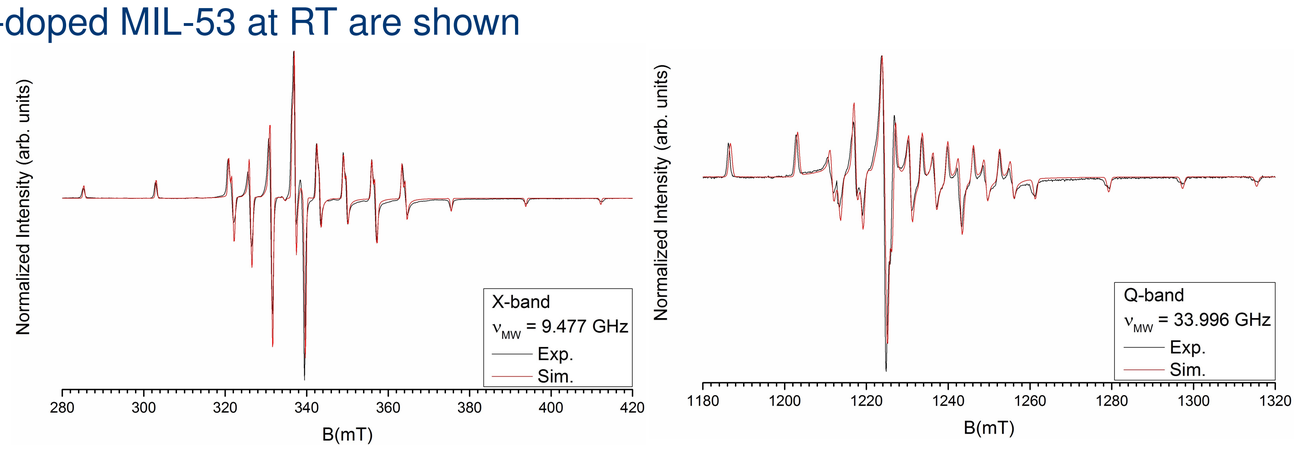
- V^{IV} ($3d^1$) → paramagnetic ion
- EPR and ENDOR spectroscopy give information about the local coordination environment and the site symmetry of paramagnetic centers

- Question: Whether and where dopant ions actually are in the framework?
- Question: Is it possible to monitor breathing effects with vanadium ions?



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



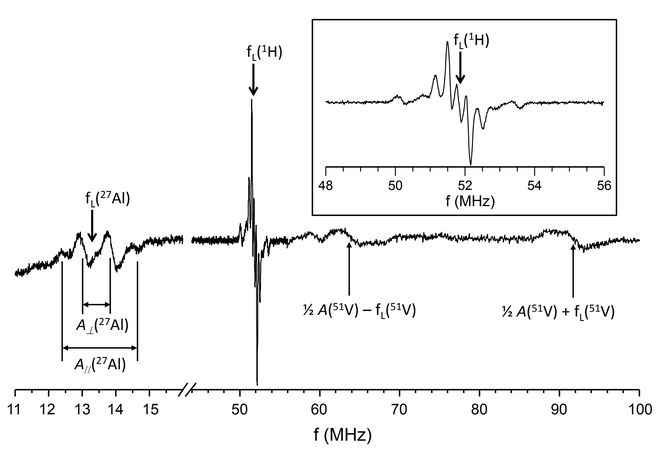
Analysis of MIL-53as

- The EPR spectra are dominated by one low-symmetry V^{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}V nucleus
  - The ***g*** and ^{51}V hyperfine (HF) tensors have these distinct principal values and their principal axes do not coincide

g	x	y	z
1.9725	1	0	0
1.9669	0	1	0
1.9391	0	0	1
A [MHz]	**x**	**y**	**z**
163	0.9686	-0.1361	0.2079
165	0.1392	0.9903	0
492	-0.2059	0.0289	0.9781

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

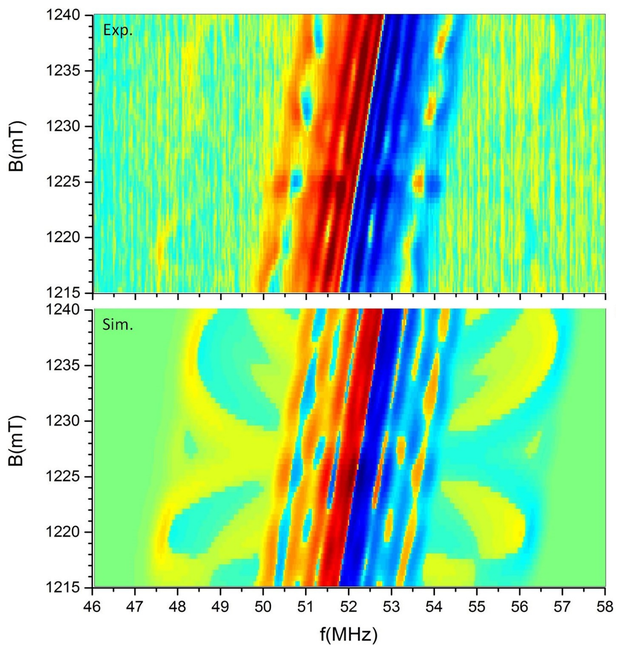
- The ENDOR spectra of V^{IV} in as-synthesized MIL-53 reveal HF interactions with the central ^{51}V, ^{1}H and ^{27}Al nuclei (B = 1218 mT)



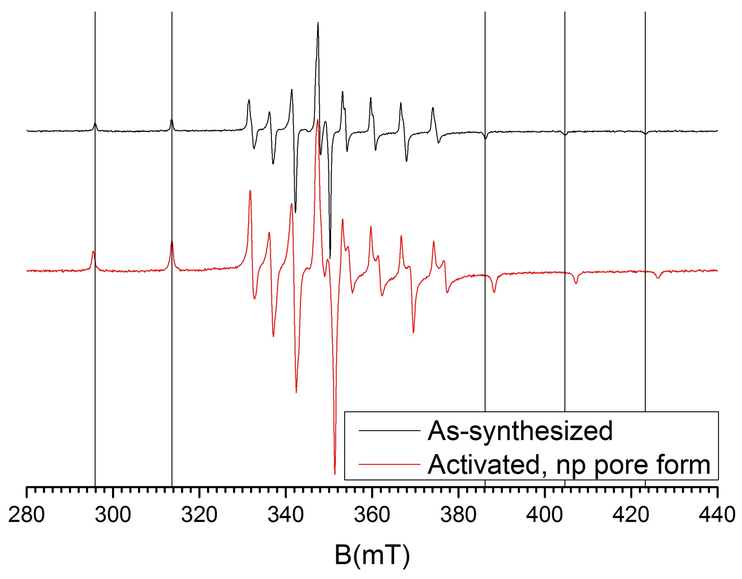
- The two broad resonance lines at 64 and 92 MHz are assigned to the ^{51}V HF interaction
- The spectra in the ^{27}Al range can be explained assuming an axial HF tensor $A_{||}$ and $A_\perp$

- Field dependence ENDOR spectra close to the Larmor frequency of hydrogen are shown in the right figure

- The ***g*** and ***A***(^{51}V) tensors, and the ENDOR results are compatible with an V^{IV}=O molecular ion replacing a regular Al^{III}-OH unit in the MIL-53 framework

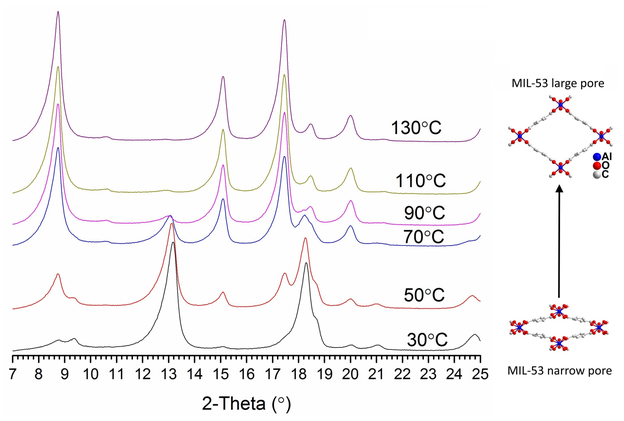


EPR spectra of MIL-53act at RT

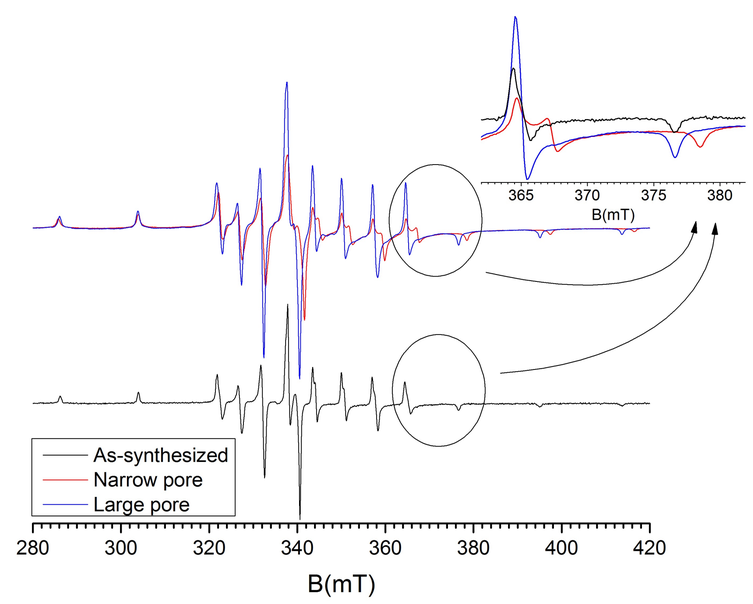


Temp. dependence XRD of MIL-53act

- 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



LP and NP EPR spectra (MIL-53act)



References :

[1] C. Serre et al., J. Am. Chem. Soc. 2002, 124, 13519-13526

Acknowledgments :
Prof. Detavernier and Geert Rampelberg from UGent for XRD measurements
FWO for !

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