

Electron paramagnetic resonance characterization of vanadium dopant sites in DUT-5(Al)

K. Maes^a, Karen Leus^b, Pascal Van Der Voort^b, Henk Vrielinck^a and Freddy Callens^a

^aDepartment of Solid State Sciences, Ghent University, Krijgslaan 281-S1, B-9000 Gent, Belgium

^bDepartment of Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Gent, Belgium

Kwinten.Maes@ugent.be

Electron paramagnetic resonance (EPR) has been used to study the structural environment of V^{IV} ions doped in the metal-organic framework (MOF) DUT-5(Al) ((Al^{III}OH)BPDC). At least three different vanadyl components are observed in the EPR spectrum, two of them are present at low V^{IV} concentrations: a broad-line component, a narrow-line component linked to a large pore state of the structure. At higher V^{IV} concentrations a third vanadyl component linked to the narrow pore state of the structure appears. By recording the EPR spectra at X- and Q-band, spin-Hamiltonian parameters were derived for all three components. Similarities with a related MOF, MIL-53(Al) ((Al^{III}OH)BDC), are discussed.

Introduction

Metal-Organic Frameworks (MOFs) are ordered porous crystalline materials constructed of metal ions connected by organic linkers. Because of their many interesting properties, a diverse scale of applications are being explored (e.g., catalysis, gas adsorption, separation and storage). For the research presented here we use DUT-5(Al), which consists of Al(OH) chains linked by biphenyl-4,4'-dicarboxylate (BPDC), creating a rigid lattice with large one-dimensional pores. In (V^{IV}=O)BPDC, i.e. COMOC-2(V), part of the framework exhibits the breathing phenomenon: the framework can reversibly change from an open (large pore) to a closed (narrow pore) structure. In general breathing can be induced by various external triggers like temperature, mechanical pressure or exposure to (and the presence of) certain gasses. In the case of COMOC-2(V), exposure to CO₂ triggers the transitions [1].

Recent work showed that EPR spectroscopy using V(IV) as a paramagnetic probe is able to distinguish between the large pore and the narrow pore state of a closely related MOF, V-doped MIL-53(Al) ((Al^{III}OH)BDC, BDC: 1,4-benzenedicarboxylate). The g and ⁵¹V A tensors for these dopant ions were determined in both states and the transition between both framework states was investigated using EPR and XRD measurements [2-4]. In mixed (Al^{III}OH)_x(V^{IV}=O)_{1-x}BPDC MOFs, an EPR spectral component was observed that showed similar characteristics as V^{IV}=O in large pore MIL-53(Al), but also other components were found [5].

Results

In the present study we further explore the EPR spectrum of the mixed-metal MOFs. Spin-Hamiltonian parameters were derived from X- (9.5 GHz) and Q-band (34 GHz) spectra. Doping DUT-5(Al) with low (1% - 7%) concentrations of V^{IV} reveals two

components in the EPR spectrum measured in vacuum: a narrow-line and a broad-line component. Both have a spectrum typical for well dispersed vanadyl ions. The narrow-line component, which becomes visible by subtracting the spectrum measured at ambient air pressure from the spectrum at low pressure, has spin-Hamiltonian parameters nearly identical to the parameters of the large pore state of V-doped MIL-53(Al) and also exhibits the same EPR linewidth broadening with oxygen pressure. The spin-Hamiltonian parameters of the broad-line component, dominant at ambient air pressure, have characteristics of both narrow pore and large pore state parameters of V-doped MIL-53(Al). As such it is not possible to easily determine its origin. Additional research will be needed to identify this component. Going to higher (9%+) concentrations of V^{IV} reveals two additional spectral components. First, the z-component hyperfine pattern of an additional isolated vanadyl center is observed, with spin-Hamiltonian parameters comparable to the parameters of the narrow pore state of V-doped MIL-53(Al). Secondly, a broad single line without hyperfine structure, similar to the spectrum of COMOC-2(V), steadily grows with increasing V^{IV} concentration until the structure from other components is no more visible at high (66%+) V^{IV} concentrations.

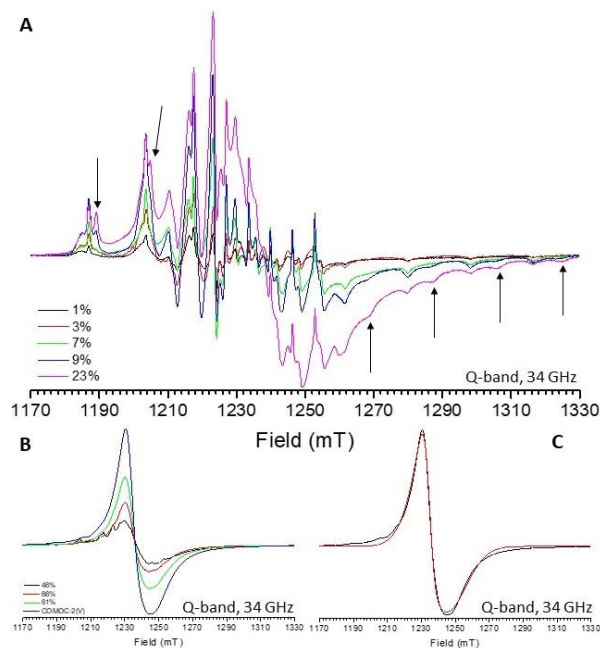


Figure 1: Experimental Q-band (34 GHz) room temperature powder EPR spectra of A: DUT-5(Al), doped with increasing (1% to 23%) concentrations of V^{IV} . Arrows indicate the additional features attributed to $V^{IV}=\text{O}$ in the narrow pore framework state. B: DUT-5(Al), doped with increasing (46% to 81%) concentrations of V^{IV} and COMOC-2(V) C: COMOC-2(V). Black - experiment, red - simulation with $g_{\parallel} = 1.957$ and $g_{\perp} = 1.968$. The spectra are normalized in height.

References

- [1] Liu, Y.-Y., et al., *New V^{IV} -Based Metal–Organic Framework Having Framework Flexibility and High CO_2 Adsorption Capacity*. *Inorganic Chemistry*, 2013. **52**(1): p. 113-120.
- [2] Nevjestic, I., et al., *Multi-frequency (S, X, Q and W-band) EPR and ENDOR Study of Vanadium(IV) Incorporation in the Aluminium Metal–Organic Framework MIL-53*. *Chemphyschem*, 2015. **16**(14): p. 2968-73.
- [3] Nevjestic, I., et al., *In Situ Electron Paramagnetic Resonance and X-ray Diffraction Monitoring of Temperature-Induced Breathing and Related Structural Transformations in Activated V-Doped MIL-53(Al)*. *The Journal of Physical Chemistry C*, 2016. **120**(31): p. 17400-17407.
- [4] Nevjestic, I., et al., *Sensing the framework state and guest molecules in MIL-53(Al) via the electron paramagnetic resonance spectrum of V(IV) dopant ions*. *Phys Chem Chem Phys*, 2017. **19**(36): p. 24545-24554.
- [5] Depauw, H., et al., *Discovery of a novel, large pore phase in a bimetallic Al/V metal–organic framework*. *Journal of Materials Chemistry A*, 2017. **5**(47): p. 24580-24584.