

Temperature-induced breathing effect of V-doped MIL-53(Al) monitored *in situ* by Electron Paramagnetic Resonance and X-Ray Diffraction

Irena Nevjestic,^{a*} Hannes Depauw,^b Karen Leus,^b Pascal Van Der Voort,^b Freddy Callens,^a Henk Vrielinck^a

a) Ghent University, Dept. Solid State Sciences, Krijgslaan 281-S1, B-9000 Gent (Belgium)

b) Ghent University, Dept. of Inorganic and Physical Chemistry, Krijgslaan 281-S3, B-9000 Gent (Belgium)

* irena.nevjestic@ugent.be

In an attempt to explore the mechanism and effects of breathing in the Al-Metal Organic Framework (MOF) MIL-53(Al)¹ further, we doped this MOF with low concentrations (1-5%) of paramagnetic V^{IV} ions (3d¹, S=1/2) and studied the resulting structures with Electron Paramagnetic Resonance (EPR) spectroscopy and X-Ray Diffraction (XRD). A detailed analysis of hyperfine interactions allowed us to establish the success of the doping procedure: in as-synthesized MIL-53(Al) frameworks V^{IV} ions are incorporated as V^{IV}=O molecular ions, substituting for Al^{III}-OH².

After activation, the doped MOFs exhibit temperature-induced breathing. This was monitored by *in situ* XRD in vacuum and in air at ambient pressure. The EPR spectra of V^{IV}=O in the narrow pore (NP) and the large pore (LP) state of MIL-53(Al) are clearly distinguishable. The temperature-induced changes between NP and LP states were also followed with *in situ* EPR spectroscopy using the V^{IV} centers as local probes.

Both EPR and XRD techniques show that in the temperature range 350-400 K the fraction of sample in the LP state gradually increases. When lowering the temperature from 450 K to RT, the LP state is retained in vacuum, whereas in air, close to RT, part of the sample returns to the NP state by uptake of water.

The XRD data additionally show that between 320 K and 350 K, MIL-53(Al) in the NP state undergoes a continuous change of the lattice parameters and reaches a metastable intermediate state before transforming into the LP state. These changes are not resolved in the EPR spectra, which however reveal another interesting phenomenon. When cooling the sample down in air below 375 K the V^{IV}=O EPR spectrum in LP MIL-53(Al) exhibits a progressive line broadening. This is due to an exchange interaction between the V^{IV}=O centers and O₂ molecules. This effect is absent for V^{IV}=O in the NP state. The consequences of these findings for the applications of this MOF in heterogeneous catalysis, gas separation and sensing will be discussed.

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2. I. Nevjestic, H. Depauw, K. Leus, V. Kalendra, I. Caretti, G. Jeschke, S. Van Doorslaer, F. Callens, P. Van Der Voort and H. Vrielinck, *ChemPhysChem*, 2015, 16, 2968-2973.