Effects of gas exposure on the EPR spectrum of V(IV) doped into the Metal-Organic Framework MIL-53(Al).

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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 MIL-53(Al), which consists of Al(OH) chains linked together by BDC (1,4-benzenedicarboxylate) creating a lattice with large one-dimensional pores. After activation (emptying the pores) the structure exhibits the breathing phenomenon: the framework can reversibly change from an open (large pore) to a closed (narrow pore) structure depending on conditions like temperature and pressure. EPR spectroscopy using V(IV) as a paramagnetic probe is able to distinguish between the large pore and the narrow pore state of V-doped MIL-53(Al). Recently the g and ^{51}V A tensors for these dopant ions were determined in both states and the transition between both was investigated using EPR and XRD measurements.[1-3]

In the present study we investigate the changes to the structure when introducing different gases at various temperatures. First, the effect of air on the large pore structure was studied. Increasing air pressure leads to a clear broadening of the spectrum. Measuring the temperature dependence of this broadening showed increase of the linewidth with decreasing temperature, following an Arrhenius behaviour with an activation energy of 12 kJ/mole. Secondly, we found that exposure of the large pore structure to CO_2 causes most of the sample to convert to the narrow pore state, with a non-negligible part still in the large pore state. Exposing the narrow pore state to CO_2 and O_2 has no effect on the EPR spectrum, which suggests that these gases cannot access the pores for this state.

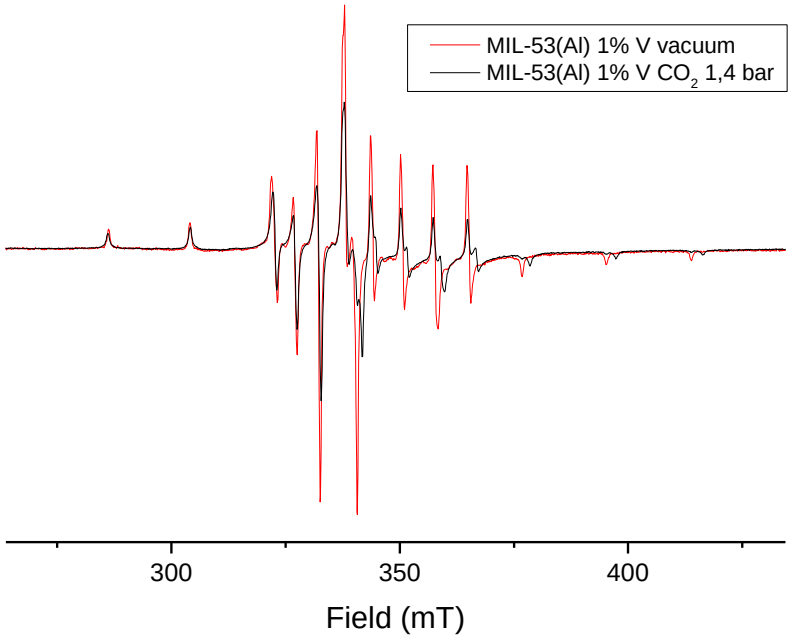

Figure 1: X-band EPR spectrum of V-doped MIL-53(Al) before and after exposure to CO_2. The structure started in the large pore state and changed to mostly the narrow pore state.

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