Breathing of V-doped MIL-53(AI) monitored in situ by Electron Paramagnetic Resonance and X-ray diffraction

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Metal-Organic Frameworks (MOFs) are three-dimensional crystalline porous materials constructed of metal ions connected via organic bridges. Their large surface area and the possibility of tailoring their structure (e.g. pore size, shape, components) towards desired properties makes this class of materials promising for a wide range of applications, such as catalysis, gas storage, gas separation, sensing and fuel cell technology. Two characteristic types of MOFs with one-dimensional pores, originally synthesized by Férey's group, are MIL-47 [VO(BDC); BDC = terephthalate or 1,4-benzenedicarboxylate, MIL = Materials of the Institute Lavoisier] ¹ and MIL-53(AI) [AI(OH)(BDC)].² It is reported that MIL-47(V) showed good catalytic performance but the framework exhibited a limited stability in the presence of water³. This problem may be solved by doping the highly stable MIL-53(AI) framework with catalytically active V^{IV}-ions.

In collaboration between the Center for Ordered Materials, Organometallics and Catalysis (promoter P. Van Der Voort) and the research group Electron Magnetic Resonance (promoters F. Callens and H. Vrielinck), different loadings of V-ions were introduced in the MIL-53(AI) structure (see Fig.1). From the resulting frameworks the gas sorption capacity (at T<300K) was studied. For samples with low V-loading, temperature-induced breathing (T>300K) was monitored by *in situ* X-ray Powder Diffraction and Electron Paramagnetic Resonance (EPR) in air and in vacuum. In EPR, the V^{IV} ions (3d¹ configuration, S=1/2) were used as local probes to detect changes in the MIL-53(AI) framework.



Figure 1 Schematic structure of the bimetallic V/Al-MIL-53 framework. Aluminium: blue, vanadium: green, oxygen: red, carbon: grey

References

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