Regulating the breathing effect of a flexible biphenyl MOF, by a mixed metal approach

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Metal Organic Frameworks (MOFs) are a class of crystalline materials with an almost unlimited choice of building blocks, allowing a very precise control over morphology, pore size and functionalities in the walls. MOFs are built up by metal nodes (secondary building units or SBUs) connected to organic linkers. These materials are of proper industrial interest for their potential applications in heterogeneous catalysis, separation and adsorption. The goal of this study is to obtain an improved insight into the structure and the breathing phenomena of COMOC-2 (VO(BPDC), COMOC=Centre for Ordered Materials, Organometallics and Catalysis)[1] after replacing the Vanadium by an Aluminum center which results in a mixed-metal MOF COMOC-2-V-Al.

COMOC-2 is an isoreticular framework of MIL-47, instead of terephthalic acid, here 4,4’-bicarboxylate is used as a bridging ligand. The COMOC-2 framework shows a pronounced flexibility in contrast with the rigid MIL-47. Replacing the V\textsuperscript{IV} by Al\textsuperscript{III} increases the flexibility barrier of the framework. Gradually, with increasing amount of Aluminum a transformation into the complete rigid variant DUT-5 occurs.[2]

Via both a one pot synthesis and post synthetic modification the structure is doped with Al\textsuperscript{III}. A variety of spectroscopic techniques combined with N\textsubscript{2}-adsorption/desorption isotherms demonstrate the successful structure synthesis and indicate the metal (V/Al) relation. Adsorption isotherms of methane and carbon dioxide are determined via a gravimetric uptake technique. A more in-depth study of a difference in sorption behavior between CH\textsubscript{4} and CO\textsubscript{2} at specific temperatures is done with in-situ synchrotron X-ray powder diffraction measurements. Electron paramagnetic resonance (EPR) and electron–nuclear double resonance (ENDOR) are applied to reveal the nearest environment of the paramagnetic V\textsuperscript{IV} dopant ions.[3]


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