Tailoring the breathing effect of a flexible MOF, COMOC-2 by a mixed metal approach

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Elucidate the fascinating breathing effect in Metal-Organic Frameworks (MOFs), a new series of mixed metal MOFs (MM-MOF) has been synthesized. The pure vanadium MOF VO(BPDC) ($BPDC^{2-}$= biphenyl-4,4'-dicarboxylate) also known as COMOC-2 (COMOC = Centre for Ordered Materials, Organometallics and Catalysis) and reported by our research group, is an isoreticular extension of the intensively studied and rigid framework MIL-47[1]. In contrast with MIL-47, the COMOC-2 is a flexible structure represented by a structural transition from a large pore (LP) to narrow pore (NP) system at CO_2 exposure. Replacing the V^{IV} by Al^{III} significantly 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 a one-pot synthesis method, a controlled amount of Al^{III}-dopant ions are introduced in the pristine framework. By this approach, precise tailoring of the breathing behavior in the bimetallic MOF is guaranteed. A variety of spectroscopic techniques combined with N_2 adsorption/desorption isotherms demonstrate the successful structure synthesis and also indicate the metal V/Al-ratio.

Furthermore, adsorption isotherms of methane and carbon dioxide are determined via a volumetric uptake technique. These measurements experimentally proof that the amount of doped Al^{III}-ions are in correlation with the flexibility of the structure. This excludes with increasing amount of Al-ions, the transformation steps **LP** -> **NP** -> **LP**, towards a completely open **LP** structure at every pressure range.

An in-depth study of the difference in sorption behavior between CH_4 and CO_2 at specific temperatures is performed with in-situ synchrotron X-ray powder diffraction measurements. Moreover, electron paramagnetic resonance (EPR) and electron–nuclear double resonance (ENDOR), together with synchrotron EXAFS and XANES V-K edge measurements are applied to reveal the nearest environment and oxidation state of the vanadium dopant ions and further elucidate the structure of the MM-MOFs.

A better fundamental understanding of this breathing effect, by using the combination of an experimental and theoretical approach, is essential for future MM-MOF applications in gas sorption, separation and sensing.

[1] Liu YY. , Couck S., Vandichel M., Grzywa M., Leus K., Biswas S., Volkmer D., Gascon J., Kapteijn F.,. Denayer J., Waroquier M., Van Speybroeck V., and Van Der Voort P., (2012). New V^{IV}-Based Metal–Organic Framework Having Framework Flexibility and High CO2 Adsorption Capacity. *Inorganic chemistry*,*52*(1), 113-120.
[2] Senkovska I., Hoffmann F., Fröba M., Getzschmann J., Böhlmann W., Kaskel S. (2009). New highly porous aluminium based metal-organic frameworks: Al (OH)(ndc)(ndc= 2, 6-naphthalene dicarboxylate) and Al (OH)(bpdc)(bpdc= 4, 4'-biphenyl dicarboxylate). *Microporous and Mesoporous Materials*, *122*(1), 93-98.