

## STRUCTURAL VARIABILITY, SHAPING AND CATALYSIS WITH d(0) METAL BASED MOFs

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### ABSTRACT

Metal-organic frameworks (MOFs) entered the porous materials scene about twenty years ago, and are currently among the most investigated compounds. The desire to develop robust, functional MOFs has increasingly driven research towards the highly stable MOFs made up of tetravalent cations (i.e. Zr<sup>4+</sup>, Ti<sup>4+</sup>, Ce<sup>4+</sup>). Here we present several examples of such new materials, their properties and catalytic potential. One of the most intriguing features that sets MOFs apart from other materials is the large-scale reversible structural variations that can be induced in response to e.g., adsorption of specific guests. This so-called breathing behavior is challenging to realize in tetravalent MOFs. However, by employing a conformationally flexible linker, *trans*-1,4-cyclohexanedicarboxylate (cdc), two breathing materials were obtained. The first, COK-69, consists of unprecedented [Ti<sub>3</sub>(μ<sub>3</sub>-O)(COO)<sub>6</sub>(O)<sub>2</sub>(H<sub>2</sub>O)] clusters interlinked by six cdc linkers in an **acs**-topology and is one of the few porous Ti<sup>4+</sup>-carboxylates.<sup>1</sup> Selective adsorption of guests of low polarity induces a switch between cdc's short axial and long equatorial conformations, allowing COK-69 to adopt a closed- (all linkers axial) or open-pore form (50% equatorial), respectively. A similar synthetic strategy (relying on titanocene dichloride as precursor), also enabled the formation of COK-70, a chain-based photoactive Ti-framework containing 4,4'-biphenyldicarboxylate linkers, which is an active catalyst for oxidative desulfurization (ODS) reactions. Breathing behavior was also achieved in ZrCDC, the cdc-analogue of the heavily studied Zr<sup>4+</sup>-MOF UiO-66.<sup>2</sup> Introducing flexibility in the latter is the most radical alteration of its properties to date. Upon guest-removal, 66% of the linkers shorten, which induces a contraction of the cubic material to tetragonal nanodomains (7-10 unit cells), and loss of long-range order within the crystallites. ZrCDC selectively adsorbs hydrogen-bond donating molecules to recover its crystalline state, a property that could be exploited in molecular separations and sensing. Mixing cdc<sup>2-</sup> and terephthalate (bdc) linkers in a single UiO-66 framework is possible, as shown by spin-diffusion NMR methods,<sup>3</sup> and leads to materials in which defects can selectively be created by thermal decomposition of the more labile cdc linkers. A wide range of cdc/bdc compositions can be accessed, which provides opportunities to increase the catalytic activity of the UiO-66 framework. Another strategy to achieve this is by introducing a hierarchical pore system. A novel synthesis route was explored to this end, to produce Zr-MOFs as gels consisting of 15 nm MOF nanoparticles.<sup>4</sup> These can be dried to form xero- or aerogels with ~20 nm mesopores, present as interparticle voids originating from the random packing of nanoparticles. The gel-state offers unique opportunities for shaping, as was demonstrated by the production of monolithic, mesoporous, pure-MOF spheres. Finally, a range of Ce<sup>4+</sup>-MOFs, analogues of the well-known Zr-MOFs based on the Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> cluster, have been synthesized and investigated for their redox-activity, associated with the Ce<sup>3+</sup>/Ce<sup>4+</sup> redox couple. UiO-66(Ce) and its isoreticular variants successfully catalyze the aerobic oxidations of

benzyl alcohol, employing TEMPO as redox mediator. XANES data further shows that reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> is possible without compromising framework stability.<sup>5</sup>

**REFERENCES:**

- [1] Bueken, *Angew. Chem. Int. Ed.* **2015**, 54, 13912.
- [2] Bueken, *Chem. Eur. J.* **2016**, 22, 3264.
- [3] Krajnc, *J. Magn. Res.* **2017**, 279, 22.
- [4] Bueken, *Chem. Sci.* **2017**, 8, 3939.
- [5] Lammert, *Chem. Comm.* **2015**, 51, 12578.