A107-06-280823

Influence of Hydrostatic Pressure on Metal-Organic Frameworks

A. Schneemann1

Department of Inorganic Chemistry, Technische Universität Dresden, 01069 Dresden, Germany

Andreas.Schneemann@tu-dresden.de

Metal-organic frameworks (MOFs) are porous materials build up from organic linker molecules and metal-cluster or ions.[1] One of their unique features that arises from their construction principle is their softness compared to traditional porous materials such as zeolites, activated charcoals or silica. This softness can lead to interesting new applications, since a subclass of MOFs called flexible MOFs can undergo structural changes between distinct defined states upon external stimuli, making them amenable as molecular switches, dampers, pressure absorbers or sensors.[2] However, this softness can also be a curse, since mechanical shaping methods and high pressure conditions in potential industrial applications can destruct their structural integrity and deteriorate their properties.

Within this contribution the influence of hydrostatic pressure on two systems will be discussed. First, the influence of high hydrostatic pressure on the archetypical MOF-5 (Zn4O(bdc)2 with bdc^{2-} = 1,4-benzenedicarboxylate) will be presented.[3] In Diamond Anvil Cell powder X-ray diffraction experiments we show that the intrusion of an alkylated organic guest molecule can fortify the structure of the material to unprecedented high pressures of over 9 GPa. Interestingly, the material retains its structural integrity after pressure release. In the second part the influence of the particle size on the mechanical response of the flexible metal-organic framework DUT-8(Cu) (Cu2(ndc)2(dabco) with ndc^{2-} = 2,6-naphthalenedicarboxylate and dabco = diazabicyclo[2.2.2]octane) is analysed using a hydraulic pressure jump cell for in-situ powder X-ray diffraction experiments.[4] Interestingly, for the material featuring macrosized crystals a phase transition from an open pore state to a much denser, closed pore state can be observed when the pressure is gradually increased, while for submicron sized crystals the material is significantly stiffer and the material remains in the open pore state over the entire applied pressure range. These two studies highlight two methods to fortify MOF structures against hydrostatic pressures, (a) by the inclusion of bulky guest molecules and (b) by engineering the particle size of the crystalline material.

[1] H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, Science, 2013, 341, 1230444.
[2] A. Schneemann, V. Bon, I. Senkovska, I. Schwedler, S. Kaskel, and R.A Fischer, Chemical Society Reviews, 2014, 43, 6062.
[3] S. J. Baxter, N. C. Burtch, J. D. Evans, A. D. Ready, A. P. Wilkinson and A. Schneemann, Chemistry of Materials, 2022, 34, 768.
[4] M. Maliuta, P. Kolodzeiski, V. Romaka, S. J. Baxter, L. Abylgazina, W. Xue, C. Sternemann, M. Paulus, S. Kaskel. I. Senkovska, S. Henke and A. Schneemann, Unpublished Results, 2023