

Poster Presentation

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Crystallisation and conformation-controlled breathing of the Al-MOF CAU-13

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Within the last couple of years an enormous variety of metal-organic frameworks (MOFs) has been synthesized. Besides characteristics like large specific surface area or a defined interaction with gas molecules a “breathing” effect was described as well. During this breathing the atoms can undergo certain movements keeping the same structural topology and without losing crystallinity. Most known MOFs contain rigid aromatic linker molecules. A rare example of a MOF with flexible aliphatic linkers is [Al(OH)(trans CDC)] (CDC = cyclohexanedicarboxylate), known as CAU 13.[1] The structure was determined from PXRD-data using synchrotron radiation. In analogy to Al-MIL 53,[2] CAU 13 is build up from chains of corner-sharing AlO₆-octahedra interconnected by the linker molecules. Interestingly, the trans-CDC ion is incorporated in a,a- as well as e,e-conformation. Time-resolved in-situ EDXRD experiments at HASYLAB (DESY, Hamburg) show short induction times for the crystallization of CAU-13. Full crystallization occurs within two hours even at low reaction temperatures. CAU-13[3] shows porosity towards different adsorptives after thermal activation. In-situ temperature dependent PXRD experiments show a widening of the pores along the b-axis up to 350 °C. The flexibility of the linker molecules allows structural changes of the compound during adsorption. While the adsorption of hydrophilic molecules only cause a small breathing effect, the adsorption of xylene leads to drastic changes in the crystal structure. The a,a-CDC²⁻ ions change conformation to e,e-type to increase the cell volume per formula sum by 25 %. This combination of pore widening and conformational changes constitutes a new type of breathing in Metal-Organic Frameworks.

[1] F. Niekief, M. Ackermann, P. Guerrier, A. Rothkirch, N. Stock, *Inorg. Chem.* 2013, 52, 8699-8705., [2] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. – Eur. J.*, 2004, 10, 1373-1382., [3] F. Niekief, J. Lannoeye, H. Reinsch, A. S. Munn, A. Heerwig, I. Zizak, S. Kaskel, R. I. Walton, D. de Vos, P. Llewellyn, A. Lieb, G. Maurin, N. Stock, *Inorg. Chem.* 2014, submitted.

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