Loading of porous metal–organic open frameworks with organometallic CVD precursors: inclusion compounds of the type [LₙM]ₐ@MOF-5

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The highly porous coordination polymer [Zn₄O(bdc)]₃ (bdc = benzene-1,4-dicarboxylate; MOF-5 or IRMOF-1) was loaded with typical MOCVD precursor molecules 1–10 for metals such as Fe, Pt, Pd, Au, Cu, Zn, Sn. Exposure of [Zn₄O(bdc)]₃ to the vapour of the volatile organometallic compounds, e.g. ferrocene (3), resulted in the formation of inclusion compounds of the type [LₙM]ₐ@MOF-5, where [LₙM] indicates the MOCVD precursor and a denotes the effective number of molecules per cavity of the MOF-5 lattice. The obtained inclusion compounds were characterised by C/H combustion analysis, determination of the metal content by atomic absorption spectroscopy, FT-IR and solid state NMR spectroscopy and by powder X-ray diffraction. The data prove that the host lattice and the guest molecules interact only by weak van der Waals forces without any change of the framework or the chemical nature of the included molecules. Rapid desorption is observed for small and comparably volatile compounds such as pentacarbonyliron or diethylzinc. Less labile inclusion compounds were obtained for cyclopentadienyl complexes as guest molecules, e.g. a rather high loading of six molecules of ferrocene per cavity was observed. Careful hydrolysis/calcination of [Zn(C₅H₇)₂]@MOF-5 resulted in the composite (ZnO)ₐ@MOF-5 pointing to the possibility to develop a subsequent chemistry of the embedded precursor molecules to yield novel nanocomposite materials based on MOFs as host matrices and MOCVD precursors in general.

Introduction

The materials chemistry of metal–organic coordination polymers exhibiting 2-D or 3-D extended structures of interconnected cavities or channels is rapidly emerging as a particularly flourishing and fascinating field of chemical complexity. From the materials design point of view these classes of hybrid compounds merge concepts from classic inorganic solid-state structural chemistry with the full potential of Werner-type coordination compounds providing molecular control of structural details and chemical functionality. A selection of current review articles is given, which highlight essential principles and applications of metal–organic coordination polymers.1

The so-called Metal–Organic Open Frameworks (MOFs) typically based on zinc and copper carboxylate structural motifs, being introduced more recently namely by Yaghi et al., represent an interesting subclass of highly porous coordination polymers because of promising gas-storage capacities for hydrogen and hydrocarbons combined with comparably high chemical inertness and thermally robust behavior, e.g. stability up to 350 °C in air.2 For example, so-called MOF-177, i.e. [Zn₄O(btbt)₃] (btb = benzene-1,3,5-tribenzoate), exhibits the highest N₂-absorption capacity at 77 K ever measured for a porous material. This property corresponds to an equivalent Langmuir surface area (hypothetical monolayer of adsorbed N₂) of 4500 m² g⁻¹ with a value of 0.69 cm³ g⁻¹ for the total volume of the micropores.2d Thus, porous coordination polymers including MOFs have attracted interest as novel zeolite-type catalysts and/or as novel support materials for heterogeneous catalysts.3 The related supramolecular host guest chemistry of zinc carboxylate based MOFs, especially related to catalysis, is however rather poorly developed and appears to be just at its beginning. Even more generally, the inclusion chemistry of porous coordination polymers seems largely limited to more or less trivial small molecules, such as solvent, template or ligand molecules accompanying their synthesis. Nevertheless, the recent work by Raymond et al. on certain reactive organometallic intermediates captured inside the cavity of a special supramolecular coordination polyhedra points in a new direction.4 The same holds for the work by Moon et al. on a redox-active porous metal–organic framework producing silver nanoparticles from Ag(I) ions at room temperature.5

The demonstration of the inclusion of C₆₀ and other large polycyclic dye molecules (e.g. Astrazon Orange R) into the cavities of MOF-177 single crystals has attracted our attention to that field recently.2 Looking back on our experience with the precursor chemistry for Metal–Organic Chemical Vapor Deposition (MOCVD) of thin films,6 it occurred to us that many typical MOCVD precursors should behave quite similarly to these large organic guest molecules. They should also be efficiently and selectively absorbed by MOFs, as long as these precursors have matching size and shape to fit into the cavity and are volatile enough. We communicated some preliminary results on the gas-phase loading of micro-crystalline

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