Gas-Phase Loading of \([\text{Zn}_4\text{O(btb)}_2]\) (MOF-177) with Organometallic CVD-Precursors: Inclusion Compounds of the Type \([\text{LnM}]_a\)@MOF-177 and the Formation of Cu and Pd Nanoparticles inside MOF-177.

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**Introduction**

The Metal-Organic Open Frameworks (MOFs) based on zinc carboxylate secondary building units \([\text{Zn}_2\text{O(RCOO)}_2]_\text{H}_2\text{O}\) \(^{23}\) which are linked together by di- or trifunctional carboxylates with arenne backbones introduced by O. M. Yaghi et al.,\(^1\) represent an interesting subclass of the rapidly growing family of coordination polymers exhibiting exceptionally high and permanent porosity.\(^2\) Applications of these materials centre around their gas-storage capacities and separation properties for hydrogen and hydrocarbons combined with comparably high chemical inertness and thermally robust behaviour, e.g. stability up to 350 °C in air.\(^3\)

In addition, MOFs have attracted interest as zeolite-type catalysts and/or as novel support materials for heterogeneous catalysts and as well as thin film materials for chemical sensing.\(^3\) For example, the loading of \([\text{Zn}_2\text{O(bdc)}]_\text{H}_2\text{O}\) (MOF-5; bdc = 1,4 benzene-dicarboxylate) with Pd by the \("\text{incipient wet impregnation method}\) using \([\text{Pd(acac)}]_2\) as precursor was recently demonstrated. Supported \(\text{Pd@MOF-5}\) catalysts (1 wt.\% Pd) were described exhibiting superior hydrogenation activity.\(^4\) Very recently, the synthesis of Pd nanoparticles inside chromium based MIL-101 was reported by Hwang et al.\(^5\) Desolvated MIL-101 was grafted with ethylenediamine.\(^6\)

The adsorption of \([\text{PdCl}_4]_2^-\) inside the cavities was achieved by solution impregnation only after protonation of the remaining amino group of the ethylenediamine in order to allow for ionic interactions. Finally the \([\text{PdCl}_4]_2^-\) was reduced with NaBH₄. The Pd loaded materials showed catalytic activity in the Heck reaction.

We rather focus on solvent-free gas-phase loading of MOFs via the adsorption of volatile organometallic all-hydrocarbon precursors known from Metal Organic Chemical Vapour Deposition (MOCVD) and reported on a series of inclusion compounds of the type \([\text{LnM}]_a\)@MOF-5 using \([\text{Zn}_2\text{O(bdc)}]_\text{H}_2\text{O}\) (MOF-5, bdc = benzene-1,4-dicarboxylate) as first test case.\(^6\) Small metal nano-particles (1.5 nm, e.g. Cu, Pd, Ru) can be formed inside the intact MOF-5 matrix by hydrogenolysis of the imbedded precursors leading to the nanocomposite systems \("\text{metals@MOFs}\). The method allows high metal loadings of 30-40 wt.% (e.g. Pd, Ru)\(^7\) as compared with the related work mentioned above. However, the MOF-5 host material is particularly labile when traces of water cannot be rigorously excluded\(^8\) and this property possibly limits its applicability as catalyst support. Recently, we discussed this aspect in the case of the composite material \(\text{Cu/ZnO@MOF-5}\) which was tested as catalyst for methanol synthesis from CO and H₂.\(^9\) In addition to that, the window opening of the cavities with 7.8 Å rules out a number of interesting MOCVD precursors with larger dimensions for inclusion and subsequent chemistry inside MOF-5. We were thus led to transfer our results from the MOF-5 to another closely related host material, MOF-177, i.e. \([\text{Zn}_2\text{O(btb)}]_2\) (btb = benzene-1,3,5-tribenzoate), exhibits the same octahedral SBU than MOF-5 but the trigonal linker btb leads to a hexagonal (6:3) net rather than the cubic (6:2) net of MOF-5. MOF-177 (Figure 1) is less sensitive to traces of water and exhibits a larger pore volume of 1.59 cm³g⁻¹ (MOF-5: 0.59 cm³g⁻¹) combined with a wider opening of the windows up to 14 nm, which allows the inclusion of large molecules, even C₆₀.\(^10\)

The highly porous and desolvated (activated) coordination polymer \([\text{Zn}_4\text{O(btb)}_2]\) \(\text{(btb = benzene-1,3,5-tribenzoate; MOF-177)}\) was loaded with the organometallic compounds \([\text{Cp}_2\text{Fe}]\), \([\text{Cp}^*_2\text{Zn}]\), \([\text{Cu(OCHMeCH}_2\text{NMe}_2\text{)}]_2\), \([\text{CpCuL}]\) (L = PMe₃, CN tBu) and \([\text{CpPd(η}^5\text{-C}_3\text{H}_5\text{)}]_{10}\) via solvent-free adsorption from the gas-phase. The inclusion compounds of the type \([\text{LnM}]_a\)@MOF-177, where \([\text{LnM}]\) indicates the respective compound and \(a\) denotes the number of molecules per formula unit of the MOF-177, were characterised by elemental analysis, FT-IR, solid state NMR spectroscopy and by powder X-ray diffraction (PXRD). Remarkably high effective loadings of up to 11 molecules \([\text{Cp}_2\text{Fe}]\) and 10 molecules \([\text{CpPd(η}^5\text{-C}_3\text{H}_5\text{)}]\) per cavity were determined. The analytical 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. Cu and Pd nanoparticles of about 2.6 nm in size were formed inside the cavities of MOF-177 by the thermally activated hydrogenolysis of the inclusion compounds \([\text{CpCuCNtBu}]_2\)@MOF-177 and by photolysis of \([\text{CpPd(η}^5\text{-C}_3\text{H}_5\text{)}]_{10}\)@MOF-177 in inert atmosphere (Ar). PXRD, FTIR and NMR studies revealed, that the MOF-177 matrix remained unchanged. \(\text{N}_2\) adsorption studies of the obtained materials Cu@MOF-177 (e.g.: 10.6 wt.% Cu, 2309 m²g⁻¹ and Pd@MOF-177 (e.g.: 32.5 wt.% Cu, 1063 m²g⁻¹) reveal high remaining specific surface areas (Langmuir model).