Pd@MOF-5: Limitations of Gas-Phase Infiltration and Solution Impregnation of $[Zn_4O(bdc)_3]$ (MOF-5) with Metal-Organic Palladium Precursors for Loading with Pd Nanoparticles.

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The limitations of the loading of the porous metal-organic framework $[Zn_4O(bdc)_3]$ (bdc = benzene-1,4-dicarboxylate; MOF-5 or IRMOF-1) with Pd nanoparticles was investigated. First, the volatile organometallic precursor $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ was employed to get the inclusion compound $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]_x$@MOF-5 via gas-phase infiltration at 10^{-3} mbar. A loading of four molecules $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ per formula unit of MOF-5 (x = 4) can be reached (35 wt.% Pd). Second, the metal-organic precursor $[Pd(acac)_2]$ (acac = 2,4-pentanedionate) was used and the inclusion materials $[Pd(acac)_2]_x$@MOF-5 of different Pd loadings were obtained by incipient wetness infiltration. However, the maximum loading was lower as compared with the former case with about two precursor molecules per formula unit of MOF-5. Both loading routes are suitable for the synthesis of Pd nanoparticles inside the porous host matrix. Homogenously distributed nanoparticles with diameter of 2.4(±0.2) nm can be achieved by photolysis of the inclusion compounds $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]_x$@MOF-5 ($x \leq 4$), while the hydrogenolysis of $[Pd(acac)_2]_x$@MOF-5 ($x \leq 2$) leads to a mixture of small particles inside the network (< 3 nm) and large Pd agglomerates (~ 40 nm) on the outer surface of the MOF-5 specimens. The pure Pd_x@MOF-5 materials proved to be stable under hydrogen pressure (2 bar) at 150 °C over many hours. Neither hydrogenation of the bdc linkers nor particle growth was observed. The new composite materials were characterized by $^1H/^{13}C$-MAS-NMR, powder XRD, ICP-AES, FT-IR, N_2 sorption measurements and high resolution TEM. Rising the Pd loading of a representative sample Pd_4@MOF-5 (35 wt.% Pd) by using $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ as precursor in a second cycle of gas phase infiltration and photolysis was accompanied by the collapse of the long-range crystalline order of the MOF.