Nanometer-sized titania hosted inside MOF-5†

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Nanoscale titania particles were synthesized inside the porous coordination polymer [Zn₄O(bdc)₃] (bdc = 1,4-benzene-dicarboxylate, MOF-5) by adsorption of titanium isopropoxide from the gas-phase and subsequent dry oxidation and annealing. Nanoscale titania is a prominent quantum dot material for photovoltaics¹ and photocatalysis.² The wet-chemical synthesis of nano-TiO₂ particles with tailored morphology and size has reached a sophisticated state-of-the-art stage.¹⁻³ The imbedding of TiO₂ inside nanoporous (siliceous) matrices was suggested to increase the selectivity of photocatalytic reactions by caging effects.⁴ Thus, we were led to investigate the titania-loading of zeolite-like porous coordination polymers (PCPs, or so-called metal–organic frameworks, MOFs).⁵ The combination of tailored chemical function and spacial confinement of MOFs with the size, shape and surface-structure-dependent properties of TiO₂ is quite attractive. Herein we report the synthesis of nano-TiO₂ material inside the porous coordination polymer [Zn₄O(bdc)₃] (bdc = 1,4-benzene-dicarboxylate, MOF-5) by adsorption of titanium isopropoxide achieved by oxidative annealing of the precursor materials [Ti(OiPr)₄]@[MOF-5].†

The gas-phase loading of pure, fully desolvated MOF-⁵ with various molar equivalents a of [Ti(OiPr)₄] as a liquid and volatile precursor for TiO₂ was performed in a sealed glass tube under static vacuum (10⁻³ mbar) at room temperature for 24 h. The resulting [Ti(OiPr)₄]@[MOF-5] (I) was then converted to [TiO₂]@[MOF-5] (2; x < a) by thermal treatment in a dry oxygen stream (4.5 vol.% in Argon) at 220 °C for 8 h and further annealing under Ar in analogy to our previous work on [ZnO]@[MOF-5].⁵ The measured Ti-loads of 2 range from 4 to 12 wt.%, which correspond to 0.7 < x < 2.4 (±5%) for our series of loading experiments. A typical sample [TiO₂]@[TiO₂] of 6.3 (±0.3) wt.% Ti, i.e. x = 1.13 (±0.06), was selected for characterization. This sample is close to a 1:1 molar ratio of titania and host material and is denoted as 2 from here onwards.

Fig. 1 displays the IR spectra of [Ti(OiPr)₄] (A), the empty MOF-5 (B), [Ti(OiPr)₄]@[MOF-5] (C) and the title material [TiO₂]@[MOF-5] (D). The presence of physisorbed [Ti(OiPr)₄] for 1 is evidenced by the occurrence of the characteristic IR bands at 3364, 2969, 1621 cm⁻¹. The oxidative decomposition of the adsorbed [Ti(OiPr)₄] at 220 °C within 8 h results in a material, with an IR spectrum that still exhibits absorption bands of residual ligand fragments. The ¹³C-MAS-NMR spectra of this as-synthesized material [TiO₂]@[MOF-5] reveals signals attributed to hydrocarbon impurities of incompletely decomposed [Ti(OiPr)₄] (Fig. 2). These impurities were quantitatively removed upon annealing for two days at 250 °C under Ar as shown by IR and NMR (see Fig. 1C and D and Fig. 2B and C).

Upon the titania loading, the Langmuir surface dropped from 3400 m² g⁻¹ for the empty MOF-5 to 2284 m² g⁻¹ (standard N₂-adsorption studies at 77 K) for 2. The above described oxidation and annealing procedures for conversion of 1 into 2 had no effect on the powder X-ray diffraction peak positions (pattern) related to the MOF-5 matrix (Fig. 3). However, the data show a gradual inversion of the relative

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**Fig. 1** IR spectra of pure liquid [Ti(OiPr)₄] (A), pure activated MOF-5 (B), [Ti(OiPr)₄]@[MOF-5] (C) and the title material [TiO₂]@[MOF-5] (D, with a Ti loading of 6.3 wt.%, x = 1.13, after annealing at 250 °C for 2 days). Characteristic absorption bands of [Ti(OiPr)₄] are marked with an asterisk (*).

**Fig. 2** ¹³C-MAS-NMR spectra of [Ti(OiPr)₄]@[MOF-5] (A), as synthesized [TiO₂]@[MOF-5] (B) and annealed [TiO₂]@[MOF-5] (C). Peaks marked with an asterisk (*) belong to the MOF-5 matrix.