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Turning MIL-53(Al) Redox-Active by Functionalization of the Bridging OH-Group with 1,1′-Ferrocenediyl-Dimethylsilane

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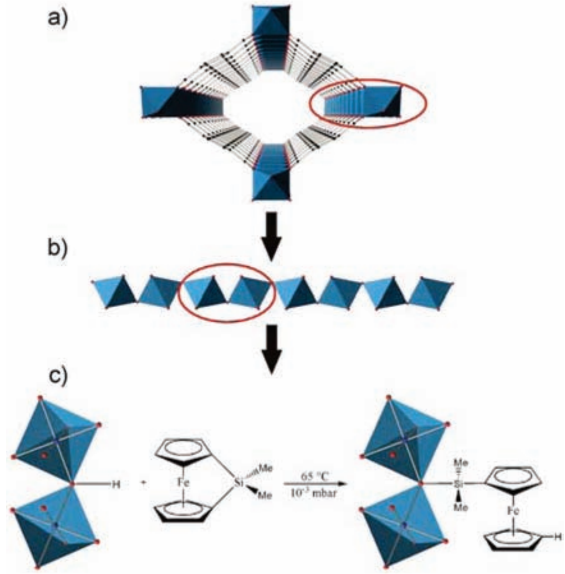
One challenge in porous coordination polymer (PCP) chemistry is the functionalization of the framework.[1] The general ideas and visions around this perspective of PCPs were introduced already in 1990 by Hoskins and Robson.[2] PCPs may thus be fine-tuned for catalytic, sensing, or gas adsorption and separation applications.[3] For example, the doping of PCPs with metal nanoparticles has been demonstrated in the context of using PCPs as support matrices for heterogeneous catalysts.[4] Likewise, the covalent bonding of optical or redox active species to the network may be important for the use of PCPs as functional materials for integrated devices.[5]

PCP framework functionalization can be accomplished by the use of linkers bearing the desired functional substituents. However then, orthogonality of these functional groups with the growth chemistry of the framework is required. Thus, very precise control of the reaction conditions for a PCP synthesis especially under solvothermal conditions is needed, and the parameter field is screened by combinatorical methods.[6] Protective groups may be used, but the deprotect conditions can destroy the network or the demerged groups are bulky and stay trapped inside the pores of the PCP. Such a protection/deprotection concept is a special case of the alternative idea of postsynthesis modification of PCPs,[7] known from other porous solid state materials (zeolites,[8] carbon nanotubes,[9] and oragnosilicates[9]). Cohen et al. were among the first to report on the postsynthetic linker modification of metal−organic frameworks (MOFs).[10]

In the present work we show the first example of a third concept of postsynthetic PCP functionalization, which targets surface exposed OH-groups which bridge the metal centers of the secondary building units (SBUs) in a number of PCPs. We chose $[Al(OH)(bdc)]_n$ (MIL-53(Al), bdc = 1,4-benzendicarboxylic acid) as the test framework[11] and 1,1′-ferrocenediyl-dimethylsilane (**1**) as the reagent for the functionalization. The high reactivity of **1** toward surface hydroxyl groups is known.[12,13]

The incorporation of **1** into MIL-53(Al) was done following the previously published protocol of solvent-free gas-phase loading of the same PCP with the parent ferrocene as the guest.[14] The same loading was also tried with the topologically similar network of MIL-47(V). The only structural difference of these two PCPs is the different bridging group. In the case of MIL-47(V) an oxid ion rather than a hydroxy group is in the bridging position between two vanadium atoms.[11] Interestingly the expected incorporation of **1** under the same reaction conditions does not occur for MIL-47(V) (ferrocene however can be incorporated). We explain this phenomenon with the lack of flexibility and ridigity of the MIL-47(V) network in contrast to MIL-53(Al).[15] The powder diffraction pattern of the material derived according to Scheme 1 can be fully indexed in space group *Imma* with the following cell parameters: a = 6.638(2), b = 16.700(3), c = 12.923(3) Å, V = 1461.0 Å^3. The change of the parameters b and c is smaller as observed for with ferrocene$_{0.5}$@MIL-53(Al) (a = 6.619(2), b = 16.883(3), c = 12.579(2) Å, V = 1405.6 Å^3; c.f. MIL-53(Al)_*ht*: a = 6.608(1), b = 16.675(3), c =12.813(2) Å, V = 1419.6 Å^3). But the change of the cell volume is quite pronounced due to the high steric effect of **1** resulting in the enlarged parameter a. The PXRD data also show the expected change of the intensity of the first two reflexes as a consequence of pore filling. However, a satisfying structure refinement could not be derived by Rietveld methods which in fact is assigned to the disordering of **1** inside the channels in contrast to the well ordered ferrocene reference case.[14]

Scheme 1 [a]



[a] (a) View along the *a*-xis of MIL-53(Al)_*ht*. (b) Single chain of AlO_6 octahedra. (c) Ring-opening reaction of **1** with the bridging HO-group between two AlO_6 octahedra of MIL-53(Al) (oxygen atoms are labeled red and aluminum atoms blue).

Different from the ferrocene adsorption in MIL-53(Al), the TG analysis now shows no weight loss at all up to the decomposition temperature of the network itself (475 °C; e.g. 500 °C for MIL-53(Al)_*ht*). This indicates a very strong binding of **1** to the framework. From elemental analysis, the empirical formula $\mathbf{1}_{0.25}$@MIL-53(Al) is derived revealing a loading of 0.25(±0.01) mol equiv of **1** per formula unit of MIL-53(Al). The reason for the lower loading as compared with ferrocene is surely the larger steric demand of **1**. The ^{13}C solid state MAS NMR shows five signals which can be attributed to the ring-opened structure of **1** covalently coordinated to the MIL-53(Al) network (Scheme 1, Figure 1). The signal at 67 ppm is assigned to an η^5-C_5H_5 ring and is not shifted compared with ferrocene$_{0.5}$@MIL-53(Al). A δ(Si) of 4.09 ppm is in agreement with the known shifts for Si in ring-opened derivatives of **1**.[12]

The selective H-transfer from the surface Al_2OH moiety (Scheme 1) pointing inward the channels to the Cp-ring of the adsorbate

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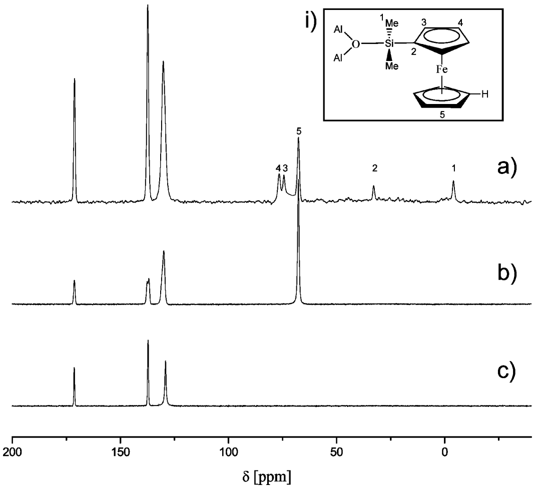

Figure 1. (a) ^{13}C solid state magic angle spinning NMR of $\mathbf{1}_{0.25}$MIL-53(Al). (b) ^{13}C MAS NMR of ferrocene@MIL-53(Al). (c) ^{13}C MAS NMR of MIL-53(Al)_*ht* (*ht* = high temperature). Insert (i) shows the model of the covalent bonding of **1** to the network (see also Figures S3−S5).

molecule was proven by a ^{2}H-labeling study. First, postsynthetic labeling by refluxing the activated MIL-53(Al)_*ht* in pure D_2O (99.9%) at 120 °C was tried. Interestingly, the ^{2}H solid state NMR of the activated compound showed no OD signals. Together with the ^{27}Al solid state NMR this fact rules out the presence of amorphous aluminum hydroxide as contamination of our MIL-53(Al)_*ht* (see Figure S6). Second, in situ labeling of MIL-53(Al) during the hydrothermal synthesis was done using D_2O instead of H_2O as the solvent. After activation at 350 °C/10^{-3} mbar, one signal at −1.0 ppm appeared in the ^{2}H MAS NMR spectrum, which is assigned to the OD-group. However, the H/D exchange was still not quantitative. In the ^{1}H MAS NMR the characteristic resonance at 1.7 ppm for the OH-group was seen. The selectively labeled $[\mathrm{Al(OD)(bdc)}]_n$ (MIL-53(Al)-d_1) was loaded with **1** as described before (Scheme 1) without any change of conditions. The ^{2}H MAS NMR spectrum of the labeled derivative $\mathbf{1}_{0.25}$@MIL-53(Al)-d_1 showed two signals at −1.0 and −4.0 ppm in a roughly 3:1 intensity ratio (Figure S3). From the elemental analysis data we know that only every forth hydroxy group is functionalized by **1**. The new signal at −4.0 ppm can thus be assigned to the transferred ^{2}H of the hydroxyl group to the Cp-ring of **1**. Cyclovoltammetry (Figures S7, S8) of $\mathbf{1}_{0.25}$@MIL-53(Al) revealed the expected reversible electrochemical activity with some small shift of 60 mV toward a more positive potential due to the immobilization and trapping of the ferrocene species inside the channels of MIL-53(Al). Despite the loading of the channels with ferrocenyl substituents, the material still reversibly adsorbs small molecules such as benzene (up to about 13 wt%, see Figure S8). We tested $\mathbf{1}_{0.25}$@MIL-53(Al) as a redox catalyst for liquid-phase benzene oxidation with aqueous hydrogen peroxide (30%) and selectively obtained phenol (Figure 2; for details, see Supporting Information). The conditions were not optimized; the conversion of ∼15% was low, and some decomposition of the catalyst cannot be ruled out (Figures S9−S11). Nevertheless, the proof of concept for turning MIL53(Al) into a redox-active functional material is demonstrated. Reducing the ferrocenyl loading is straightforward and is likely to increase the mobility of species inside the channels and will thus affect the catalyst efficiency. Related studies for gas-phase oxidation reactions are underway.

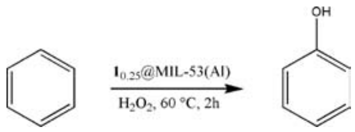

Figure 2. Liquid-phase benzene oxidation with $\mathbf{1}_{0.25}$@MIL-53(Al) as redox catalyst.

In summary, we presented a new, nontrivial, selective, and efficient functionalization of the "inorganic" part rather than the "organic" part of a quite representative porous coordination polymer. The method may be extendable to other PCPs with larger pores and/or interconnected channels with terminal and/or metal ion bridging hydroxyl groups being accessible at the inner surface. The ring-opening reaction may be useful to graft other metallocene species or related complexes to PCPs with propeties other than redox, for example, reactivity as single site catalysts.

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Supporting Information Available: Powder XRD, TG data, ^{29}Si MAS NMR, CV, catalysis test of $\mathbf{1}_{0.25}$@MIL-53(Al). This material is available free of charge via the Internet at http://pubs.acs.org.

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