Catalytic properties of MIL-101†

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A very high catalytic activity in the cyanosilylation reaction was observed for MIL-101, a chromium based metal–organic framework; moreover, MIL-101 is also a remarkably stable support for palladium in hydrogenation reactions, with significantly higher activity than *e.g.* palladium on activated carbon.

In the last decade, metal–organic frameworks (MOFs) have attracted considerable interest due to their remarkable properties such as high specific surface areas combined with a high crystallinity.[1,2] Due to these properties MOFs are promising materials for applications in gas storage,[3] separation processes,[4] and catalysis.[5] The use of MOFs as solid catalysts is particularly interesting, since the pore size and functionality of the framework can be adjusted over a wide range for a variety of catalytic reactions.[2] Even though a large number of different MOFs is known, until today only a few of them have been tested in catalytic reactions.

In pioneering work, Férey *et al.* published in 2005 the synthesis and characterisation of the metal–organic framework MIL-101 ($Cr_3X(H_2O)_2O(bdc)_3$; X = F, OH; bdc = benzene-1,4-dicarboxylate) showing a very high specific surface area as compared to other porous coordination polymers known until today ($S_{\mathrm{Langmuir}} = 5900\ \mathrm{m^2\ g^{-1}}$) and a high pore volume (approx. $2.0\ \mathrm{cm^3\ g^{-1}}$).[6] MIL-101 consists of μ_3-oxo bridged chromium(III)-trimers cross-linked by terephthalate groups. The chromium ions of the MIL-101 structure have a pseudo-octahedral coordination. The vertices of these pseudo-octahedra are occupied by the μ_3-O atom in the middle of the chromium trimers and four oxygen atoms derived from the carboxylate groups of the terephthalate linkers. The coordination sphere around each chromium is finally filled up by a water molecule, a fluorine atom or a hydroxyl group (Fig. 1).

MIL-101 is an ideal MOF for applications in heterogeneous catalysis due to the following reason. The pores and pore windows are big enough to give access for even large reactant molecules diffusing into the pores, but also large product molecules can move out of the network. For the catalytic activity of solid catalysts the accessibility of the catalytic sites is even more essential.[7] As mentioned above, the pseudo-octahedral coordination sphere around each chromium atom is completed with either water molecules, fluorine or a hydroxyl group. In contrast to the fluorine and the hydroxyl group, the coordinated water molecules can be easily removed in vacuum and at elevated temperature, and leave behind the chromium accessible for potential reactants.

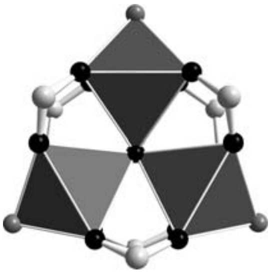

Fig. 1 Trimeric chromium(III)-cluster in MIL-101, the octahedra represent the chromium ions, carbon and oxygen atoms are in light grey and black, respectively; the medium grey atoms represent either an oxygen atom derived from a water molecule or a hydroxyl group or a fluorine atom.

MIL-101 samples were prepared according to a synthesis route reported by Férey *et al.*[8] The X-ray diffraction pattern of the green powder matches the calculated pattern and thus confirms the formation of MIL-101 (see ESI†, Fig. S1). The specific surface area of the obtained porous material amounts to $2367\ \mathrm{m^2\ g^{-1}}$ (S_{BET}, $p/p_0 = 0.1$) and was determined using nitrogen physisorption measurements (see ESI†, Fig. S5). In contrast to Férey *et al.* we could not observe any increase of the specific surface area *via* post-reaction hydrothermal treatment of MIL-101 in ethanol.

To evaluate the catalytic activity of MIL-101, we have used the cyanosilylation of aldehydes as a test reaction catalyzed by Lewis acids. Fujita *et al.* were the first to demonstrate the catalytic activity for a two-dimensional square network material [Cd(4,4′-bpy)$_2$](NO$_3$)$_2$.[9] The catalytic activity of $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylate) in the cyanosilylation of benzaldehyde was studied in detail, because this material also has well defined accessible Lewis acidic sites, exposed to the inner surface. However, only moderate yields of 57% (88.5% selectivity) were achieved after prolonged duration (72 h) with a high catalyst loading of 5 mol% referred to the amount of benzaldehyde.[10]

According to our results presented here, MIL-101 has a much higher activity towards the addition of trimethylsilylcyanide (TMSCN) to benzaldehyde (Scheme 1) as compared to other MOFs such as $Cu_3(BTC)_2$, even if a lower catalyst loading of only 0.5 mol% is used. In a typical reaction, 15 mg MIL-101 ($\sim$0.02 mmol) were used for the conversion of 4 mmol benzaldehyde in heptane at 313 K. An excess of 100% TMSCN was employed with respect to the amount of benzaldehyde. The composition of the reaction mixture was determined by GC-MS analysis (Fig. 2). All benzaldehyde is converted after 3 h leading to a product yield of 98.5%. In addition to this remarkable high catalytic activity, MIL-101 has the advantage that chromium(III) cannot be as easily reduced by the benzaldehyde, whereas

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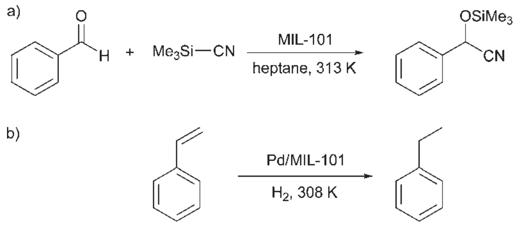

Scheme 1 (a) Addition of trimethylsilylcyanide to benzaldehyde, and (b) hydrogenation of styrene.

copper(II) in $Cu_3(BTC)_2$ is easily reduced leading to a decomposition of the framework at higher reaction temperatures. However, the framework of MIL-101 is intact after usage as a catalyst judging from the powder X-ray diffraction pattern of the catalyst after cyanosilylation (see ESI†, Fig. S2). Compared to the XRD pattern of the as made material a redistribution of the peak intensities but no change of the peak positions is observed. This finding is in accordance with the results of Férey *et al.* describing the same observation for a MIL-101 sample with incorporated Keggin polyanions.[6] The change in intensities can therefore be assigned to high-boiling residues of the catalytic reaction that are not completely removed *in vacuo*.

To prove the heterogeneous mechanism of the cyanosilylation catalysed by MIL-101, the catalyst was filtered off after 15 min reaction time and stirring of the filtrate continued at the same reaction temperature. The reaction was again monitored by GC-MS analysis and the concentrations of benzaldehyde and the product are shown in Fig. 2 (broken line). These results confirm the assumption of a heterogeneous mechanism since neither additional benzaldehyde is consumed nor is product formed after filtration.

For a more comprehensive study of the catalytic activity of MIL-101 in the cyanosilylation of benzaldehyde, a recycling test with three consecutive runs was performed (see ESI†, experimental section and Fig. S8). As mentioned before, a product yield of 98.5% is achieved in the first run after 3 h. In the second and the third run the product yields, determined after the same reaction time (3 h), decrease to 91.5% and 91.3%, respectively. In addition, a decrease of the reaction rate is observed from the first to the third run as can be seen from the declining slopes. Thus, MIL-101 can be reused several times as a catalyst in the cyanosilylation of benzaldehyde with a somewhat reduced activity.

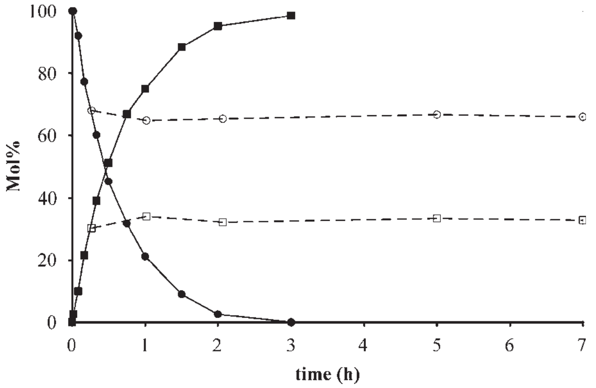

Fig. 2 Reactant and product concentration during the MIL-101 catalysed cyanosilylation of benzaldehyde, Solid line: ● concentration of benzaldehyde, ■ concentration of product. Broken line: filtration test, ○ concentration of benzaldehyde, □ concentration of product.

Besides the demonstrated catalytic activity of pure MIL-101, MIL-101 is also an attractive candidate for a catalyst support due to its high porosity and a relatively high thermal stability. Recently, we have shown that MOF-5 is a suitable catalyst support for palladium.[11] The supported catalyst, denoted as Pd/MOF-5, showed a higher activity towards the hydrogenation of styrene than palladium on activated carbon with similar palladium loadings. Unfortunately, one serious disadvantage of the Pd/MOF-5 catalyst is its instability in contact with water or humid air. Therefore, the aim of our continuous research was the preparation of other palladium supported MOFs combining both, high activity towards hydrogenation reactions and stability towards air and moisture. MIL-101 seemed to be the ideal palladium support for this aim, since it is long-term stable in air atmosphere and has a very high specific pore volume. Thus, a catalyst with palladium supported on MIL-101 (denoted Pd/MIL-101) was prepared and tested for catalytic activity and stability in liquid-phase and gas-phase hydrogenation, respectively, namely the hydrogenation of styrene, and the hydrogenation of acetylene in the presence of ethylene.

Supported palladium was prepared *via* incipient wetness impregnation of activated MIL-101 using $Pd(acac)_2$ (acac = acetylacetonate) as precursor diluted in chloroform.[11] The required volume of chloroform was determined by measuring the specific total pore volume (V_P = 1.46 cm^3 g^{-1}, p/p_0 = 0.9) of the synthesized MIL-101. The green powder was dried under reduced pressure at ambient temperature. For the conversion of the precursor into metallic palladium, $Pd(acac)_2$/MIL-101 was heated in a hydrogen flow at 473 K for 1 h. The specific surface area of palladium supported MIL-101 decreased to 2046 m^2 g^{-1} (S_{BET}, p/p_0 = 0.1) (see ESI†, Fig. S5). Thus, the loss of the specific surface area amounts to only 14% compared to 67% previously found for Pd/MOF-5. The powder X-ray diffraction patterns of MIL-101 and Pd/MIL-101 do not differ (see ESI†, Fig. S3) indicating the stability of the MIL-101 network under the employed reduction conditions.

The dispersion of palladium in the fresh Pd/MIL-101 material was analysed *via* hydrogen chemisorption. In the procedure, Pd/MIL-101 was flushed extensively in argon at 443 K to desorb all hydrogen and decompose palladium hydride species. Thereafter, the sample was cooled in argon, exposed to a flow of 5% H_2 in argon, and heated at 10 K min^{-1} to 443 K. The recorded total H_2 consumption amounted to 2.16 μmol H_2 for 63.5 mg of Pd/MIL-101. Assuming that only palladium interacts with hydrogen and that each surface palladium atom accommodates one hydrogen atom, this translates into a dispersion of about 72%, suggesting the diameter of the palladium particles is around 1.5 nm.[12]

In contrast to previously reported Pd/MOF-5, all Pd/MIL-101 materials could be synthesized and handled in an air atmosphere due to the superior stability of MIL-101. A nitrogen physisorption measurement repeated on a Pd/MIL-101 sample stored in air for two months confirmed the intended higher stability also for Pd/MIL-101, since storage-induced changes of the specific surface area were found to be negligible (see ESI†, Fig. S7).

The new air-stable catalyst was tested in the hydrogenation of styrene to evaluate the catalytic activity of Pd/MIL-101 and to compare the results with those obtained with other palladium

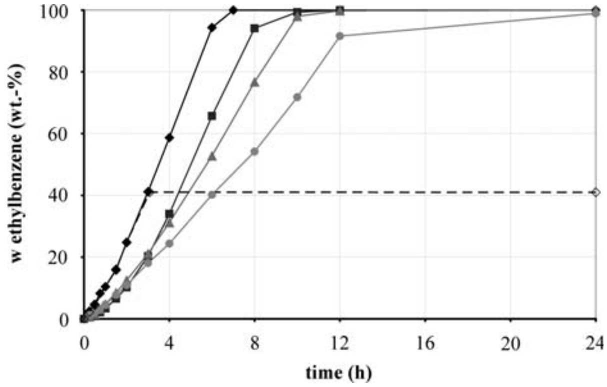

Fig. 3 Hydrogenation of styrene with different palladium supported catalysts (1 wt%): ◆ Pd/MIL-101, ■ Pd/MOF-5, ▲ Pd/Norit A, ● Pd/C; the broken line represents the filtration test.

supported catalysts. The reaction was carried out in a static hydrogen atmosphere (1 atm) at 308 K (Scheme 1) and was monitored by GC-MS analysis for 24 h. Fig. 3 depicts that the use of Pd/MIL-101 as a hydrogenation catalyst leads to a complete conversion of styrene to ethylbenzene after 7 h. Under the same reaction conditions, Pd/MOF-5 yields ∼80 wt% hydrogenation product after the same reaction time whereas Pd/Norit A affords ∼65 wt% and Pd/C less than 50 wt% ethylbenzene. To assure comparability, only supported catalysts with a palladium content of 1 wt% were used. The results prove the higher activity of Pd/MIL-101 towards the hydrogenation of styrene. Moreover, Pd/MIL-101 clearly shows the highest activity in the hydrogenation of *cis*-cyclooctene compared to all other palladium supported catalysts tested (see ESI†, Fig. S9). The higher activity as compared to Pd/MOF-5 may be caused by the larger pore size of Pd/MIL-101 and is an argument for the efficient integration of active sites inside the pore system and not outside.

As observed for MIL-101 used in cyanosilylation, the X-ray diffraction pattern of the used Pd/MIL-101 catalyst shows a similar redistribution of peak intensities compared to the one obtained for Pd/MIL-101 before hydrogenation (see ESI†, Fig. S4) caused by non-volatile residues of the hydrogenation reaction.

To eventually elucidate the long-term activity and stability of Pd/MIL-101 also at more severe reaction conditions, the catalyst was tested in the gas phase hydrogenation of an acetylene–ethylene mixture in a continuous fixed-bed reactor operated in repeated temperature cycles between 313 and 373 K. For the test, 20 mg of Pd/MIL-101 were diluted 1 : 10 with SiC. A gas mixture containing acetylene (1.7%), excess ethylene (42.9%), hydrogen (condition A: 3.4%, condition B: 2.1%) and nitrogen (balance) was continuously dosed to the reactor operated at 2 bar with a flow rate of 13.7 ml min^{-1} (STP). The temperature was increased from 313 to 373 K in 10 K steps, holding the temperature constant for about 3.3 h at each temperature, and repeating this program alternating with higher and lower hydrogen feed (*i.e.* conditions A, B).

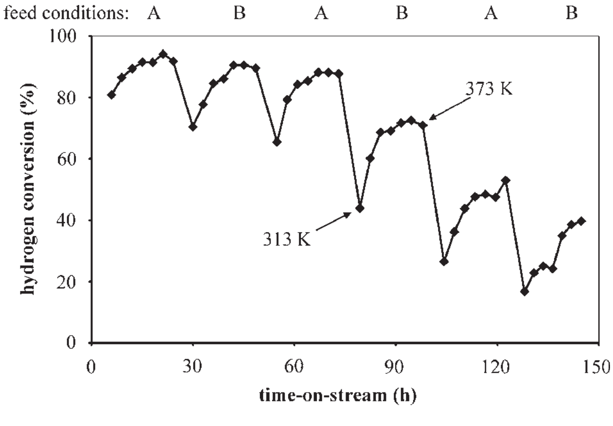

Fig. 4 Hydrogen conversion *vs.* time-on-stream in hydrogenation of a mixture of acetylene–ethylene using 1 wt% Pd/MIL-101 in a continuous fixed-bed reactor operated in repeated temperature cycles between 313 and 373 K feeding a gas mixture with a hydrogen content of 3.4% (condition A) or 2.1% (condition B).

Compared to the same total amount of palladium, Pd/MIL-101 showed an initial activity superior to that of all other tested catalysts such as 0.05 wt% Pd/ZnO or 0.05 wt% Pd/Al_2O_3, corresponding to the presumed high palladium dispersion (H_2 chemisorption) facilitated by the framework of MIL-101. For the feed condition “A” with higher hydrogen content, between 80 and 100% of acetylene was converted along with smaller amounts of ethylene (see ESI†, Fig. S10), ethane being the main product. Besides the high initial activity, Pd/MIL-101 showed also significant activity after about 145 h time-on-stream as shown in Fig. 4, indicating a remarkably slow deactivation of the catalyst also under harsh reaction conditions. The observed slow and continuous degradation in performance with time-on-stream could possibly be explained by blocking of the pores with residual hydrocarbon, but deserves further investigations.

Summarizing, pure MIL-101 has a significantly higher catalytic activity in the cyanosilylation of benzaldehyde than reported for $Cu_3(BTC)_2$ and other MOFs. Moreover, it is a suitable support for palladium which can be incorporated *via* incipient wetness impregnation. Compared to Pd/MOF-5 and commercial supported palladium catalysts, Pd/MIL-101 shows a better catalytic performance in the hydrogenation of styrene and cyclooctene, and a high and sustained activity in the gas phase hydrogenation of acetylene–ethylene mixtures, the essential advantage of Pd/MIL-101 over Pd/MOF-5 being its stability towards air, moisture and also (reducing) reaction conditions up to at least 373 K.

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