Catalytic properties of MIL-101

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Experimental

Materials

Heptane, octane and hexadecane were dried with sodium/benzophenone and were stored under argon. Chloroform, analytical grade, was purchased from Fisher Scientific and was used without further purification.

Reagents were purchased from the following distributors:

- Chromium(III) nitrate nonahydrate, ≥ 98%: Riedel-de-Haën
- Terephthalic acid, ≥ 99%: Acros
- Hydrofluoric acid, 38-40 % in water: Merck
- Palladium(II) acetylacetonate, 99 %: Acros
- Styrene, 99 %, stabilised: Acros
- Cyclooctene, 95 %, stabilised, Acros
- Benzaldehyde, ≥98 %: Acros, freshly distilled prior to use
- Trimethylsilylcyanide, 98 %: ABCR

Synthesis of MIL-101

A solution containing 6.00 g (15 mmol) $Cr(NO_3)_3 \cdot 9 H_2O$, 3.76 g (23 mmol), 1,4-benzene dicarboxylic acid (H_2BDC), 0.75 ml of hydrofluoric acid (38-40 % in water) and 75 ml H_2O was introduced in a 250-ml Teflon-liner. The mixture was placed in an autoclave and was heated to 493 K for 9 h. After cooling, the reaction mixture was filtered trough a large pore fritted glass filter (G 1) to eliminate excess of recrystallised terephthalic acid. The product was separated from water by using a small pore fritted glas filter (G 4). Finally, the solid was dried at 423 K, first in air for 4 h and at reduced pressure over night to obtain activated, fine powdered MIL-101.

Synthesis of $Pd(acac)_2$/MIL-101

12 mg (0.04 mmol) $Pd(acac)_2$ (acac = acetylacetonate) were dissolved in 0.6 ml of chloroform. The solution was added slowly drop-wise to 400 mg of activated MIL-101 during continuous stirring. The formed precursor catalyst was dried over night at room temperature and under reduced pressure.

Cyanosilylation of benzaldehyde, filtration test, recycling test

Prior to the reaction, 15 mg (~ 0.02 mmol) MIL-101 were activated in vacuum at 393 K over night. After cooling to 313 K, the flask was flushed with argon and 17 ml heptane containing octane and hexadecane as internal standards were introduced. After addition of 425 mg (4 mmol) freshly distilled benzaldehyde, 794 mg (8 mmol) trimethylsilylcyanide (TMSCN) were added. The reaction mixture was stirred at 313 K and the reaction was monitored using a SHIMADZU GCMS QP5000 equipped with a non-polar BPX5 column (5 % Phenyl polysilphenylene-siloxane) from SGE.

For the filtration test, the reaction mixture was filtered off after 15 minutes reaction time using a 0.45 µm PTFE filter and was transferred into an argon flushed flask held at 313 K with a syringe. Stirring was continued and the composition of the reaction mixture was determined using GC-MS analysis.

For the recycling test, the reaction mixture was filtered off after completion of the reaction leaving behind the catalyst. The catalyst was activated again in vacuum at 393 K over night and was used a second time for the cyanosilylation of benzaldehyde. The same procedure was repeated for a third run. The composition of the reaction mixture was again determined using GC-MS analysis.

Hydrogenation of styrene, filtration test

Hydrogenation of styrene was carried out in solution in a static hydrogen atmosphere (1 atm) at 308 K. In a typical reaction, 50 mg of dried, fine powdered Pd(acac)$_2$/MIL-101 were placed in a glass flask and heated in a H_2 flow at 473 K for 1 h to obtain Pd/MIL-101. After cooling to 308 K, 5.00 g styrene (48 mmol, precursor catalyst to substrate weight ratio 1:100) were added and the reaction was controlled using GC-MS analysis (SHIMADZU GCMS QP5000 equipped with a non-polar BPX5 column (5 % Phenyl polysilphenylene-siloxane) from SGE).

For the filtration test, the reaction mixture was filtered off after 3 h using a 0.45 µm PTFE filter. The catalyst was separated and the solution was allowed to react further in a second vial under the same reaction conditions.

Hydrogenation of cyclooctene

The hydrogenation of cyclooctene was performed in an analogous manner as for styrene. Instead of styrene, 5.00 g (45 mmol) of cyclooctene were added to the catalyst.

Characterisation

X-ray powder diffraction

X-ray diffraction (XRD) patterns were obtained in transmission geometry using a Stoe StadiP X-ray diffractometer equipped with an imaging plate position sensitive detector and CuKα_1 (λ = 0.15405 nm) radiation (40 kV, 30 mA).

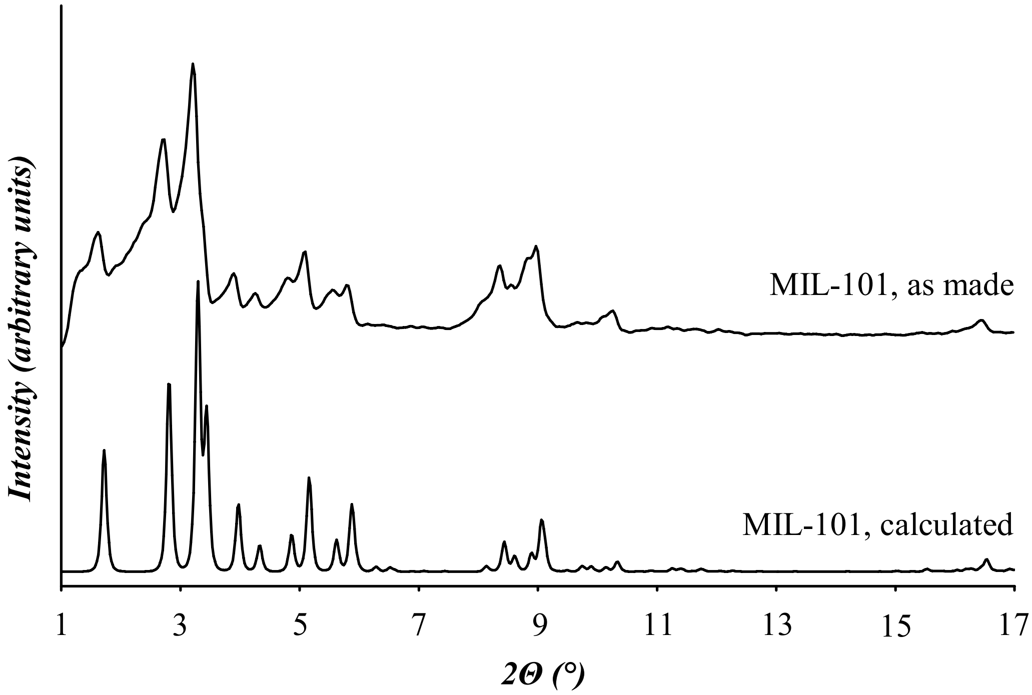

Fig. S1 Comparison of the XRD patterns of the synthesised MIL-101 and the calculated one.

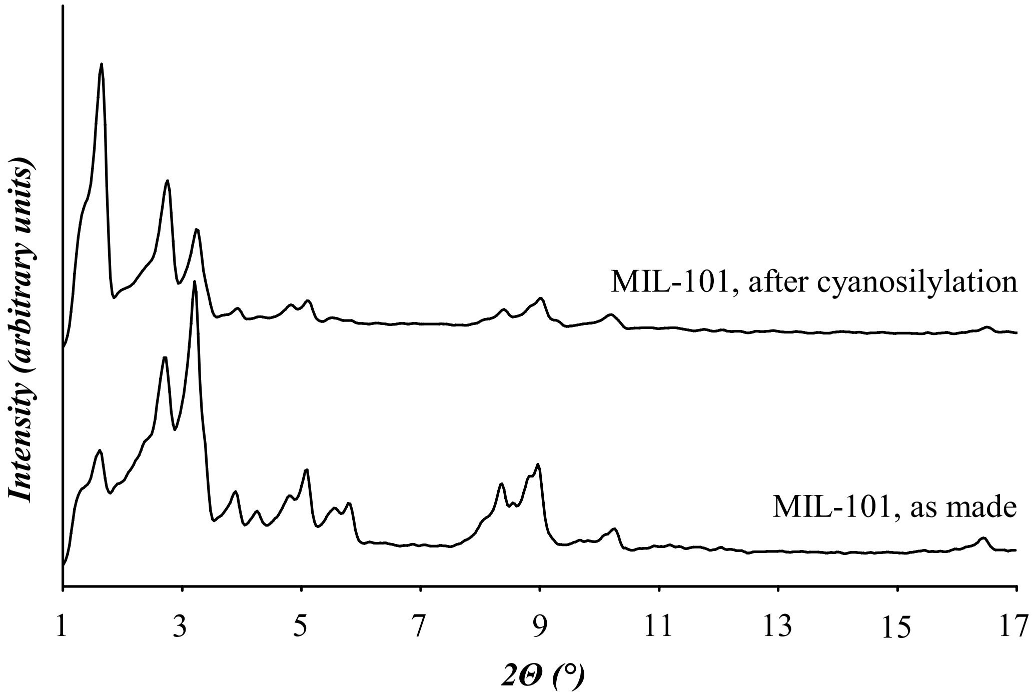

Fig. S2 X-ray diffraction patterns of MIL-101 before and after cyanosilylation.

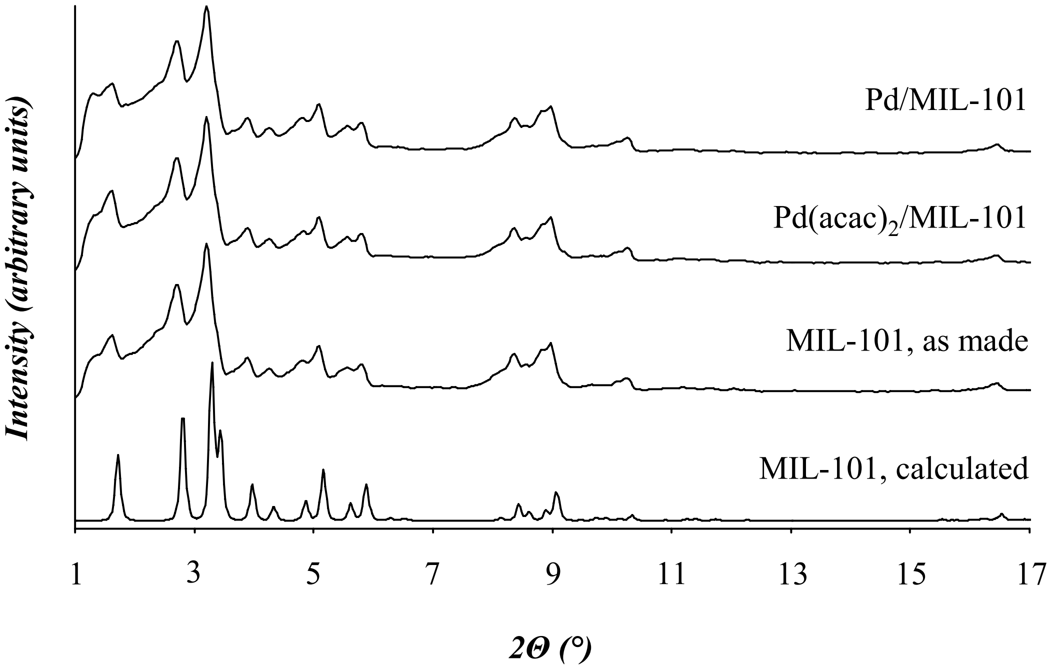

Fig. S3 Comparison of the XRD patterns of as made MIL-101, $Pd(acac)_2$/MIL-101 and Pd/MIL-101, in addition the calculated XRD pattern of MIL-101 is shown.

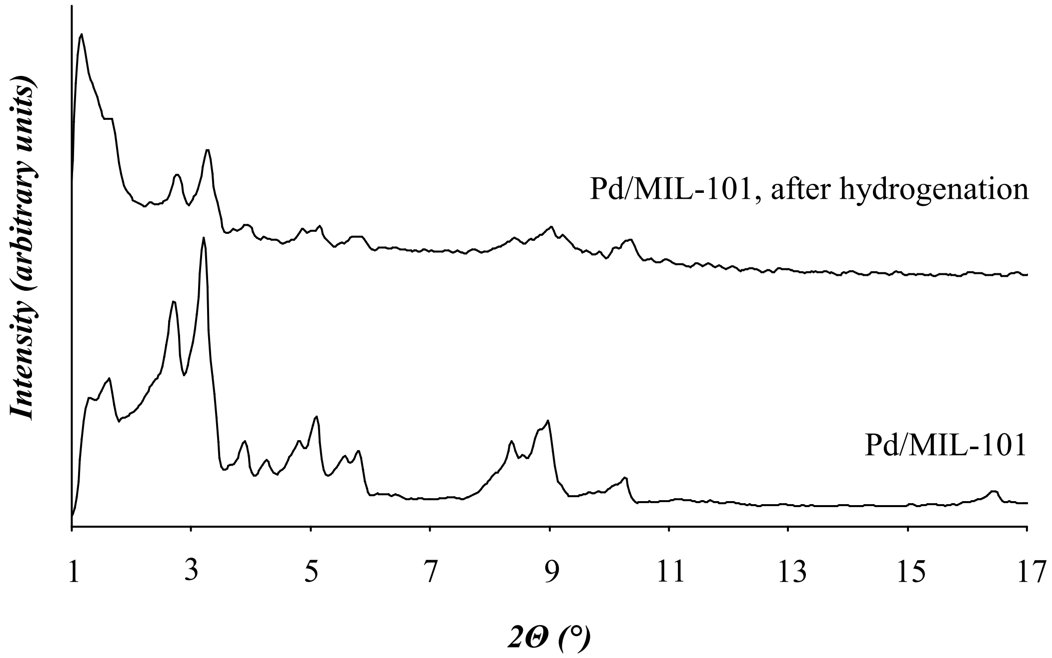

Fig. S4 XRD patterns of Pd/MIL-101 before and after hydrogenation of styrene.

N_2-Physisorption

Nitrogen physisorption isotherms were measured at 77 K using a Quantachrome AUTOSORB 1 C apparatus. Specific surface areas were calculated using the single point BET plot at $p/p_0 = 0.1$ and the specific total pore volume was measured at $p/p_0 = 0.9$.

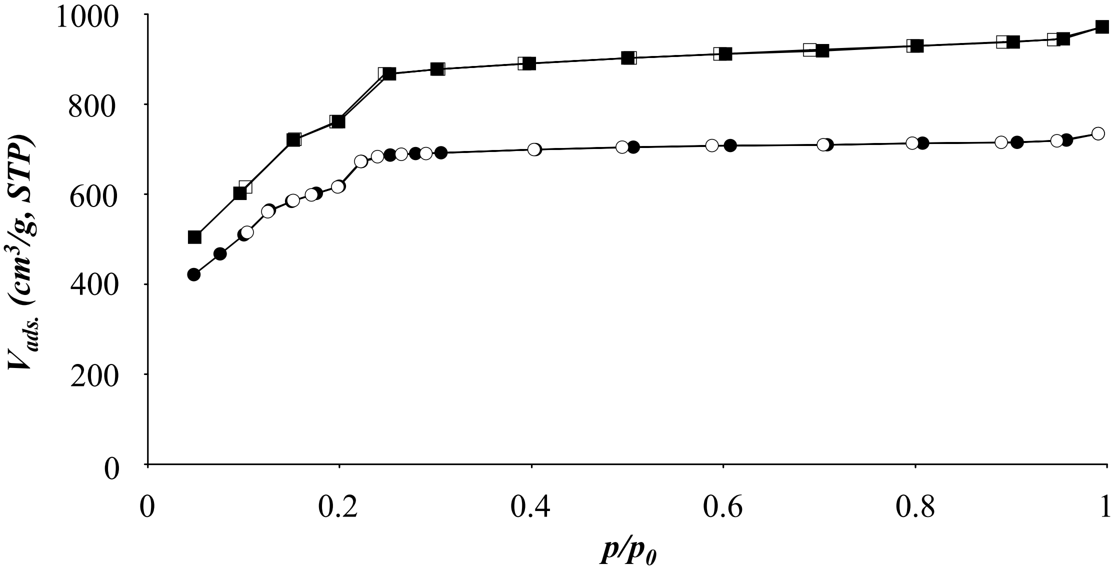

Fig. S5 Nitrogen adsorption isotherms of pure MIL-101 (■), and Pd/MIL-101 (●, 1 wt-% Pd,), □ and ○ represent the respective desorption isotherms.

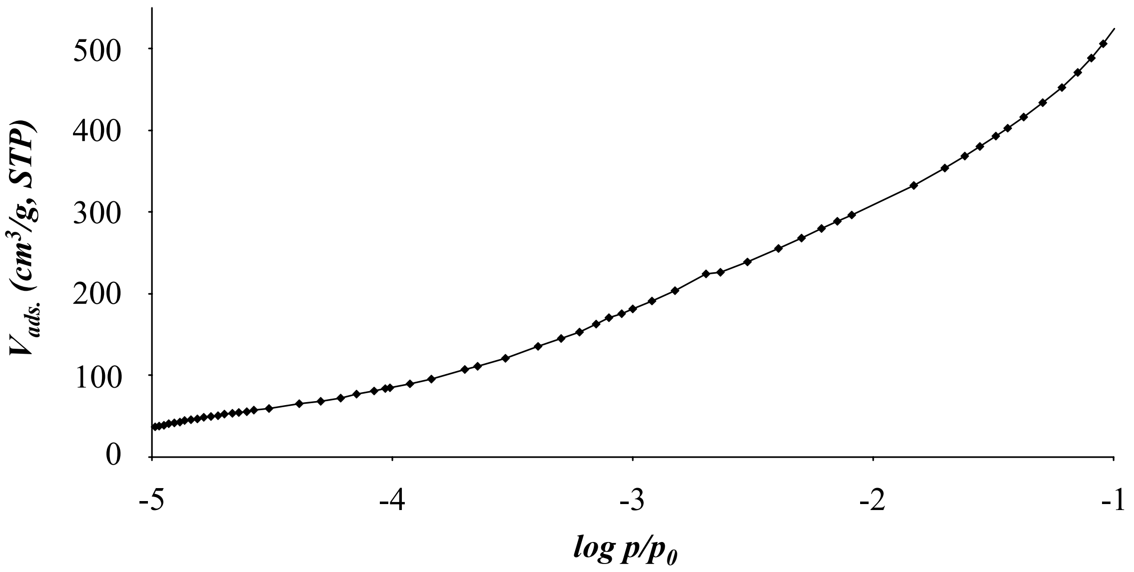

Fig. S6 Nitrogen low pressure adsorption isotherm of pure MIL-101.

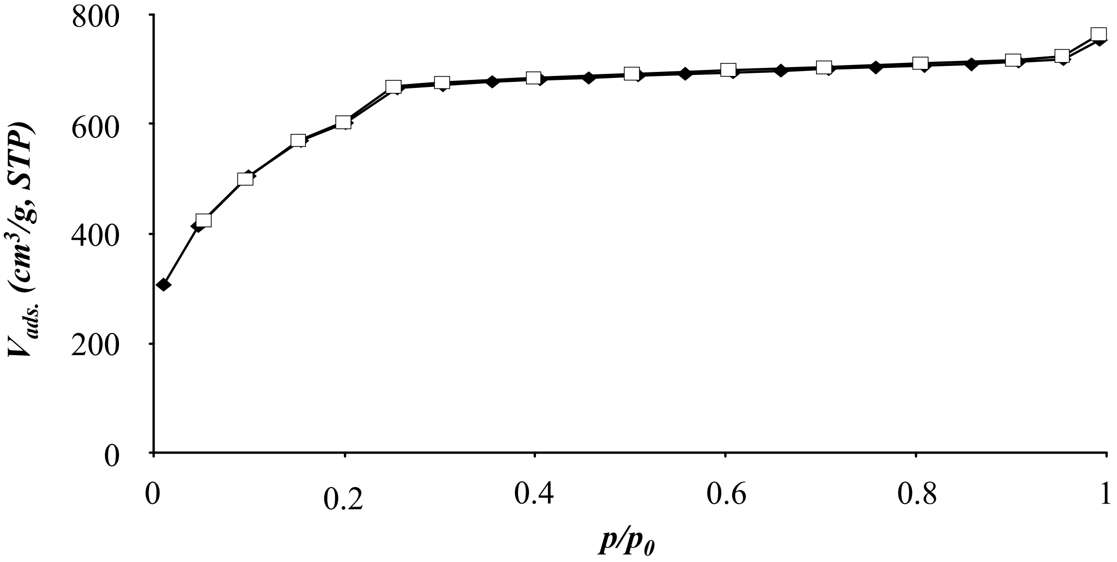

Fig. S7 Nitrogen adsorption isotherms of Pd/MIL-101 (◆, 1 wt-% Pd,), □ shows the same sample exposed to air atmosphere for two months.

Additional catalytic data

Cyanosilylation, recycling test

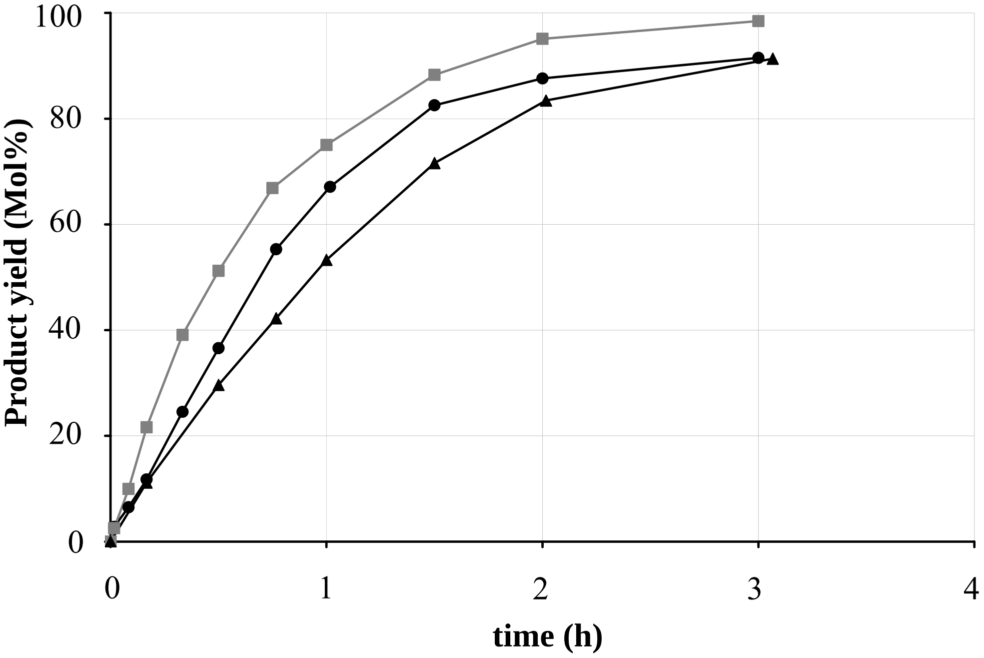

Fig. S8 Product concentration during the MIL-101 catalysed cyanosilylation of benzaldehyde; ■ 1st run, ● 2nd run; ▲ 3rd run.

Hydrogenation of cyclooctene

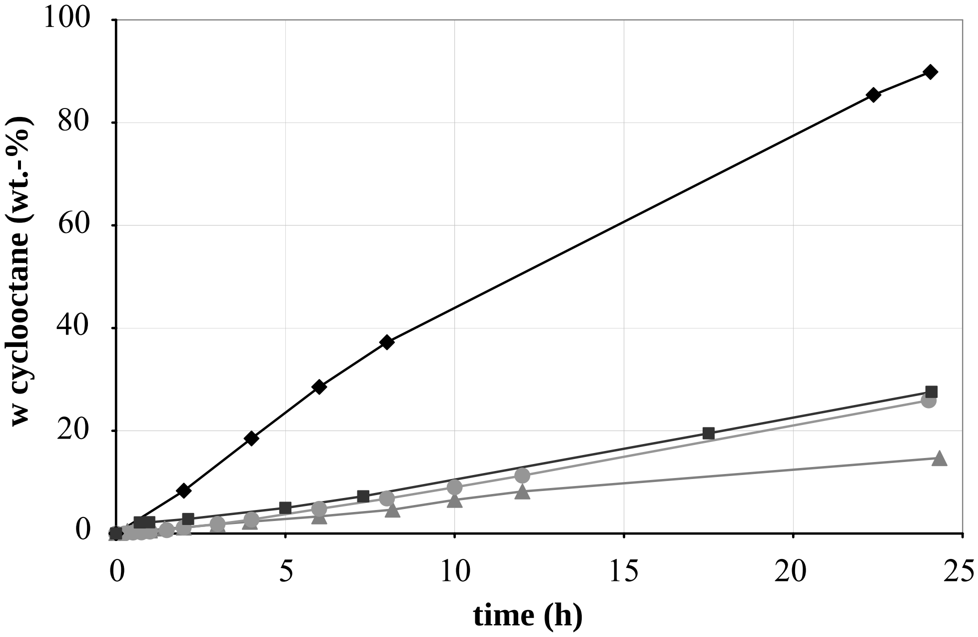

Fig. S9 Hydrogenation of *cis*-cyclooctene with different palladium supported catalysts (1 wt.-%): ◆ Pd/MIL-101, ■ Pd/MOF-5, ▲ Pd/Norit A, ● Pd/C.

Hydrogenation of acetylene / ethylene

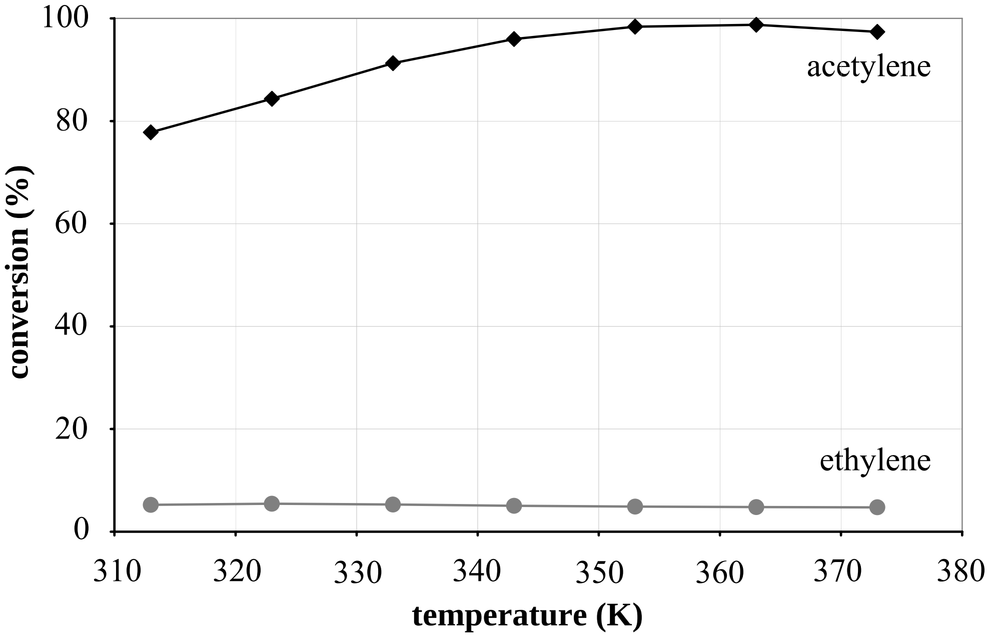

Fig. S10 Initial conversion of acetylene and ethylene vs. temperature in hydrogenation of a mixture of acetylene / ethylene using 1 wt.-% Pd/MIL-101 in a continuous fixed-bed reactor operated in repeated temperature cycles.