

Shape Selective Hydrogenation of Alkenes with Supported Pd@MOF-5 Catalyst in Supercritical Carbon Dioxide

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Received: September 23, 2010 / Accepted: October 14, 2010 / Published: February 28, 2011.

Abstract: The metal-organic framework MOF-5 has been synthesized by solvothermal method. Obtained material consists of nano-sized particle of ca. 100 nm size. The material has been physico-chemical characterized regarding structural and textural properties by XRD, FTIR, nitrogen adsorption/desorption, thermal analysis and ESA experiments. Palladium supported MOF-5 catalyst has been prepared by adsorption inclusion method. The catalyst was activated by treatment with supercritical carbon dioxide (scCO₂) followed by mild reduction with hydrogen solved in scCO₂. The obtained catalyst is shown to be stable and active and shape selective in hydrogenation reactions of alkenes using supercritical carbon dioxide as reaction medium. The catalytic active Pd species are located inside the pores. Positive surface charging seems to prevent deposition of active species at the crystal surface of the MOF. The catalyst is long time stable and re-useably. These findings show the potential of porous MOFs for applications under supercritical conditions and resisted repeated pressuring to 120 bar at elevated temperature.

Key words: Metal-organic framework, MOF-5, supercritical CO₂, catalysis, hydrogenation, catalyst preparation.

1. Introduction

Porous metal-organic frameworks (MOF) are an emerging class of new crystalline materials [1-2]. Characteristic properties of three-dimensional porous MOFs with respect to applications are: (i) extra large pore volumes and specific surface areas; (ii) defined aperture sizes extend from small micropores into the region of mesopores; (iii) high metal content and uniformity of sites due to highly crystalline nature of materials; (iv) the open structure of 3D nanoporous MOFs should diminish transport restrictions and hybrid character allow high mobility of incorporated

guests; (v) accessibility of sites, strict alternative periodic arrangement leads to defined separation; (vi) high dispersion of loaded metals [3-7].

A few potential catalytic applications of MOFs have been addressed [1], albeit expected to be limited due to some disadvantages such as a decreased thermal, mechanical and chemical stability of MOFs especially under catalytic reaction conditions. Therefore, although known for more than 10 years, reports on catalytic investigations or applications of metal-organic frameworks are just starting. Different types of MOFs have been tested in hydrogenation [8, 9], oxydation [10-15], acid base reaction [16-21], catalysis for fine chemicals and others [22-27]. The catalytic use of MOFs under supercritical conditions has not been

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reported so far.

Conversion, selectivity and space time yield of conventional heterogeneous hydrogenations are often limited because of mass transport limitations. One approach to improve the reactor performance is the application of supercritical fluids as alternative solvent. In contrast to a classical three phase reaction, no phase boundary gas-liquid occurs. Due to high diffusion coefficients, the mass transfer in the supercritical phase is superior. The hydrogen atom efficiency is markedly improved by stoichiometric composition of starting materials. The product separation can be achieved by simple depressurisation of the reaction mixture. Often, carbon dioxide is used as supercritical solvent because it is disposable, sustainable and non-toxic [28-30].

In this study, we present the preparation and testing of Pd supported metal-organic framework MOF-5 (Fig. 1) as novel catalyst for the hydrogenation of cyclohexene and cyclooctene with hydrogen in supercritical carbon dioxide. The sufficient thermal, mechanical and catalytic stability of the nanoparticulate MOF-5 type material is shown.

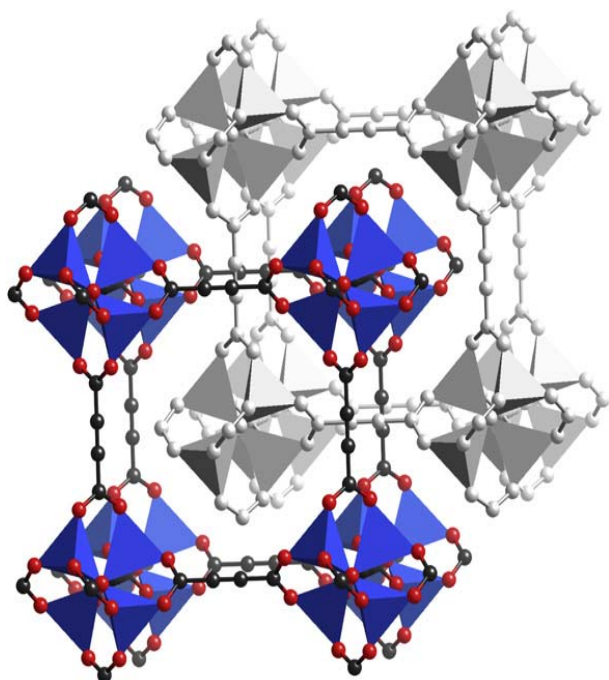


Fig. 1 Structure of metal-organic framework MOF-5 showing pore entrances and large cavity [2b].

2. Experimental

MOF-5 was solvothermally synthesized. E.g., 2.07g of $Zn(NO_3)_2 \times 4H_2O$ and 0.862 g p-benzenedicarboxylic acid were dissolved in diethylformamide and refluxed under stirring at 130 °C. The crystalline product was filtered off, washed and solvent exchanged with dichloromethane. An advanced method for catalyst preparation was utilized including the adsorption of metal precursor from organic solution followed by in situ removal of solvent and remaining organic impurities by repeated pressuring and depressuring with supercritical CO_2 . For supporting of Pd species by adsorption, 3 g of MOF-5 was given into ca 80 mL toluene containing the appropriate amount of $Pd(acac)_2$ at 80 °C. The yellow pale solution was stirred until nearly decoloured. The product was filtered off and allowed to remove excess of solvent under flowing air at room temperature by standing in a fume cupboard. Thereafter, the catalyst precursor was reduced with hydrogen in supercritical carbon dioxide at elevated temperature.

The material has been physico-chemical characterized regarding structural and textural properties by XRD, FTIR, Nitrogen adsorption, thermal analysis and ESA (electroacoustic sonic amplitude) experiments.

XRD powder diffraction pattern were recorded on a STOE STADIP diffractometer using $Cu_{K\alpha}$ radiation. The IR spectra of powdered samples were measured using a Nicolet 380 FTIR spectrometer in the ATR mode. Thermoanalytical measurements were carried out with a TGA 90 thermal balance (Setaram) under nitrogen flow using alumina sample holders. The heating rate was 10 K/min. The nitrogen adsorption/desorption measurements were carried out on an ASAP 2010 sorptomat (Micromeritics). Samples were activated at 180 and 300 °C in vacuum to remove residual solvents. Particle sizes of the highly dispers materials were determined by acoustic attenuation spectroscopy using an APS-100 particle sizer (PA-

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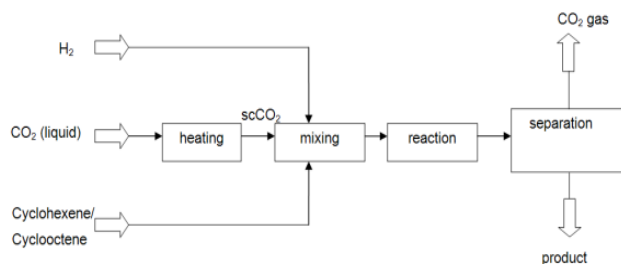


Fig. 2 Catalytic set up for hydrogenation of alkenes in supercritical carbon dioxide.

Partikelanalytik Messgeräte). For this the samples were suspended in alcoholic solvent. An ESA set up was used for Zeta potential measurement and recharging experiments.

For activation and catalytic testing the Pd@MOF-5 loaded with 1 ma.-% Pd was placed together with glass beads into a stainless steel flow reactor (internal diameter 10 mm). The catalyst was repeatedly pressurized with carbon dioxide up to a pressure of 120 bar and 60 °C in order to remove organics. Then the catalyst was reduced with hydrogen in flowing supercritical carbon dioxide at pressure ca. 80 bar and a temperature of 60 °C.

For catalytic testing, the catalyst was contacted with a mixture of 5.7 mL/min. liquid carbon dioxide and 0.3 mL of cyclohexene or 0.4 mL cyclooctene containing hydrogen in nearly stoichiometric amounts at 75 bar and 40 to 60 °C. The catalytic fluid flowed through the fixed bed tubular reactor from top to bottom. After passing the catalyst, the reaction mixture was depressurized to 20 bar and cooled to -18 °C to remove the reaction product for weight balancing and GC analysis. The reaction product were analysed by gas chromatography. A scheme of the supercritical catalytic set up is shown in Fig. 2.

3. Results and Discussion

The crystallinity of the starting MOF-5 was checked by XRD (Fig. 3). The XRD pattern is well resolved showing the typical pattern of the meta-organic framework type MOF-5 [2]. Thermal stability and decomposition behaviour was investigated by combined TG/DTA measurements (Fig. 4), displaying

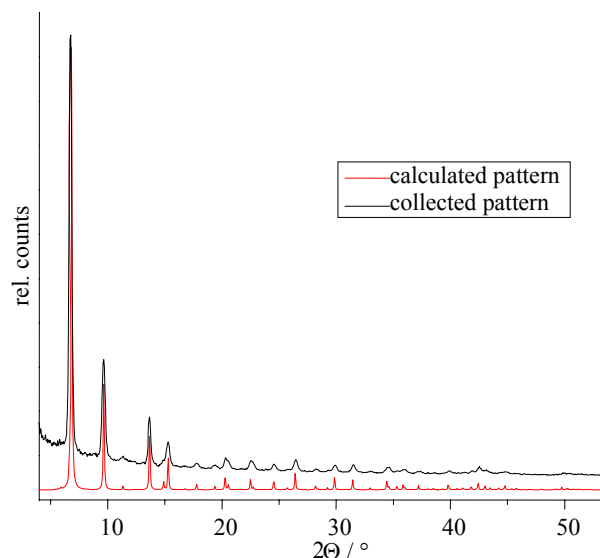


Fig. 3 XRD pattern of metal-organic framework MOF-5.

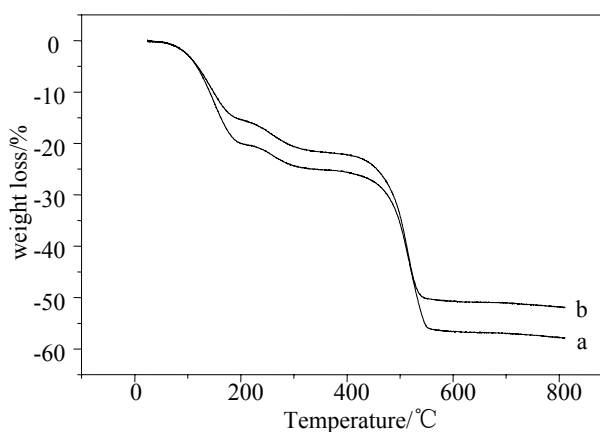


Fig. 4 TG plot of MOF-5 synthesized at a) 130 °C and b) 145 °C.

three distinct main weight losses near 150, 230 and 450 °C due to desorption of weak and coordinative bound synthesis solvent and material decomposition by destruction of organic linker, respectively. The weight loss due to oxidative removal of the organic component is in line with the theoretical composition of MOF-5. The synthesis temperature influences the weight losses of samples possibly indicating textural differences.

Textural properties of MOF-5 were investigated by nitrogen sorption measurements at liquid nitrogen temperature. For this, samples were activated by heating and pumping under vacuum at 180 °C and 300 °C, respectively. The adsorption and desorption isotherms are shown in Fig. 5. The specific surface area

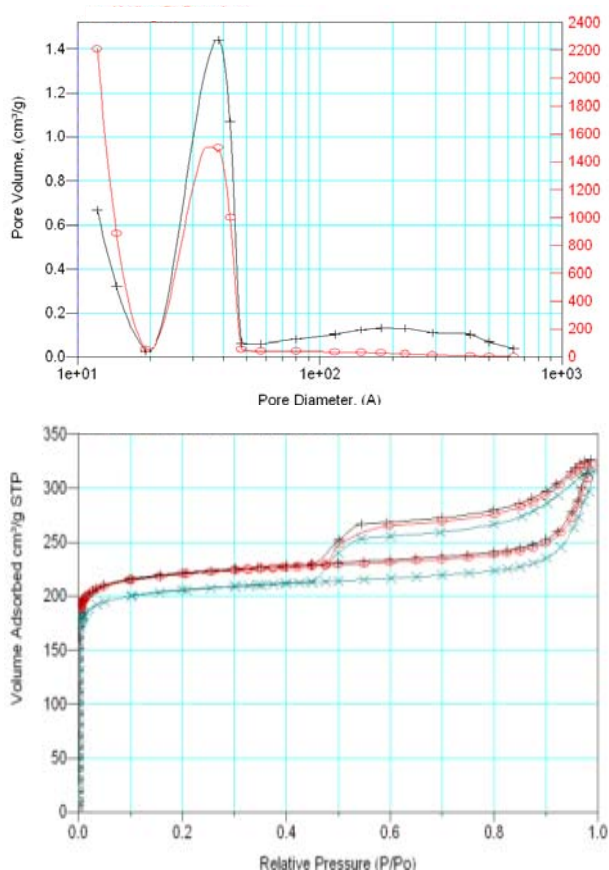


Fig. 5 Nitrogen adsorption/desorption isotherms of MOF-5 pellets shaped at a pressure of 30 kP/cm² and activated at 180 °C and 300 °C in vacuum. Sorption step at $p/p_0 = 0.5$ is due to nitrogen uptake by mesopores (top), and pore size distribution of a MOF-5 sample containing intraparticle mesopores of 3-4 nm size (bottom).

of MOF-5 was ca. 800 m²/g. According to BET measurements the optimum synthesis temperature was 130 °C. With raising activation temperature from 180 °C to 300 °C an increase of the specific sorption capacity was observed. It was attributed to removal of inclusions. The material contains also some mesoporosity indicated by the additional adsorption step at a relative pressure of ca. 0.5. The size of mesopores was estimated to be ca. 3-4 nm.

For application and testing mechanical stability the shaping ability of the catalyst is of importance. Our shaping experiments revealed that MOF-5 can be pressed into pellets with minor loss in nitrogen adsorption capacity at 30 kP/cm² showing a specific surface area of 800 m²/g. The structure collapses

partially at a pressure of 100 kP/cm². The nitrogen uptake of the latter sample was also distinctly lower. The mesopores were only slightly sensitive to pressure during shaping experiments. This proves to intracrystalline porosity. Their presence further improves the mass transfer properties. Electric surface charges (Zeta-potential) and particle sizes of materials have great impact on the supporting behaviour of matter and were not reported so far for porous MOFs.

Because so far electroacoustic studies with MOFs were not reported, measurements were carried out with two structural different MOF-samples, MOF-2 and MOF-5, to ensure the validity of data. The measurements revealed that under certain synthesis conditions MOF-2 (Zn tricoboxylate) and MOF-5 (zinc dicoboxylate) form nanoparticles of 36 nm and 105 nm size, respectively (Fig. 6).

The outer surface MOF-5 particles is strongly positively charged with a zeta potential of $\zeta = +15$ mV. For comparison the ζ -potential of an available MOF-2 was measured. The particles were also positively charged with $\zeta = +4.9$ mV. The positive surface charging was confirmed by recharging experiments with charged surfactants (Fig. 7). This is also an outstanding property. The positive surface charge may suppress adsorption of Pd²⁺ ions on the crystal surface and direct adsorption of palladium to inner particle sites.

For catalytic testing, first the hydrogenation of cyclohexene in supercritical carbon dioxide was studied (Scheme 1). The hydrogenation was complete at a reaction temperature of 60 °C and a residence time of lower 30 sec. The selectivity to cyclohexane was ca. 99% (Fig. 8). Only some benzene (0.5%) has been detected as side product [30]. The unusual occurrence of dehydrogenation in the presence of hydrogen might be due to the near stoichiometric cyclohexene to hydrogen ratio in the feed. For the estimation of the apparent turn-over-frequency, TOF (mol_{alkene}/mol_{palladium} × h⁻¹), the concentration of starting materials was increased until loss of conversion was observed. This way a TOF

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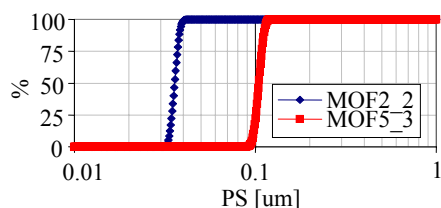


Fig. 6 Mean particle size distribution PS/ μm of MOF-2 and MOF-5 determined by attenuation spectroscopy.

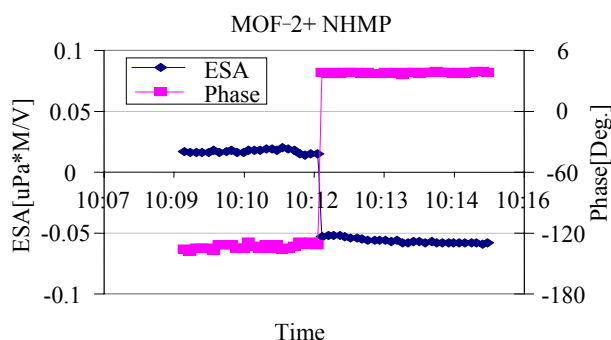
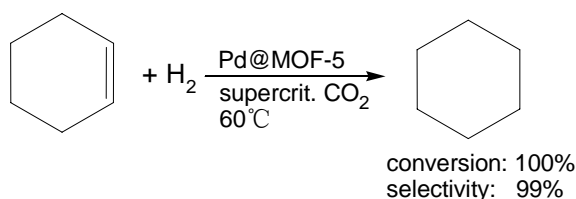


Fig. 7 Reverse charging of positively charged MOF-2 by addition of anionic surfactant (sodium hexametaphosphate (NHMP)). The stepwise change of the electrokinetic sonic amplitude (ESA) and of the phase indicates the invert point of the surface charge of the particles during the course of surfactant addition.



Scheme 1 Hydrogenation of cyclohexene in supercritical carbon dioxide.

of ca. 640 h^{-1} has been calculated. The catalyst was long time stable and active over longer periods of time (Fig. 8) and could be re-used in different runs. Indeed, the catalyst was used ca. 4 weeks with daily new start of reaction. Also fast pressure changes did not affect the catalytic activity. Nearly no pressure drop was observed. Hence, the high porosity makes MOFs superior to other porous materials of similar pore size in terms of diffusivity and dispersion of supported active metal particles as shown below. Also the mesopores might improve the accessibility of active sites by starting materials and diminish mass transfer restrictions for reaction products. In contrast to

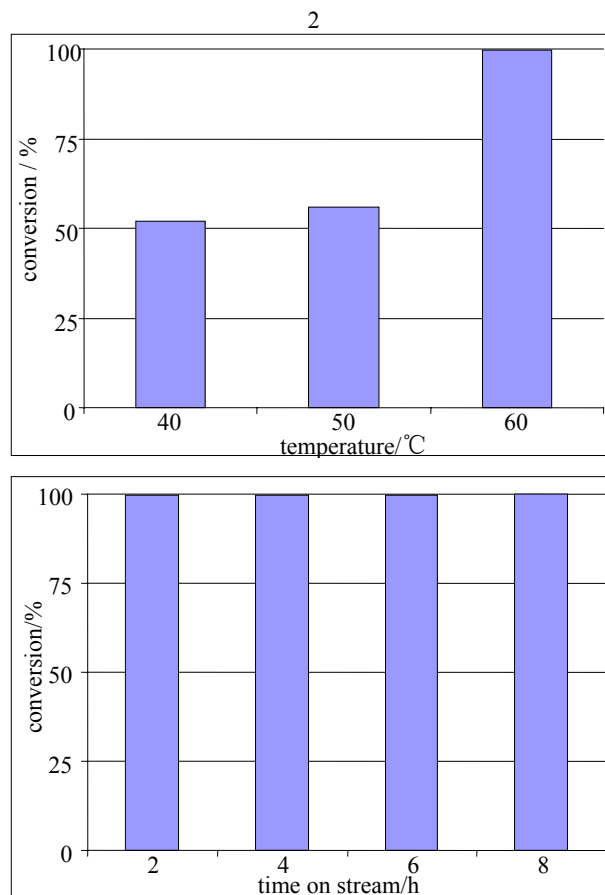


Fig. 8 Influence of the temperature on the conversion (top) and the long-time stability of the Pd-MOF-5 catalytic in the hydrogenation of cyclohexene under supercritical conditions expressed as conversion vs. time on stream (bottom).

cyclohexene, the catalyst was nearly not active in the hydrogenation of the larger cyclooctene. Obviously, MOFs are shape (size) selective catalysts. The effective aperture size of MOF-5 pores is between the size of cyclohexene and cyclooctene and amounts to 6-7 Å. The active Pd sites are located in the pores. Otherwise, cyclooctene should be hydrogenated too [31]. It is well known from non-supercritical catalytic experiments, that cyclooctene is hydrogenated over Pd catalysts even at low temperature [32]. These findings confirm recent findings of shape selective properties of MOFs².

4. Conclusion

In conclusion, in this contribution, we demonstrate, that MOF-5 is a superior material for the application as catalyst or catalyst support in green catalysis using

supercritical carbon dioxide. It behaves shape selective and is highly accessible provided molecule dimension fits the aperture size. It can be concluded that the same should hold for application in selective separation or adsorption of valueables from supercritical non-aqueous solvents. It is long time stable. This might be connected with solvent properties of supercritical CO₂ dissolving any type of side products formed during reaction. The solvothermal synthesis route under normal pressure allows the synthesis of nanoparticulate MOF-5 materials. Another important new feature is, that contrast to common porous material like silicates, the particle surface of this MOF is positively charged. This might explain that the catalytic active metal species are preferentially located in the pores.

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