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Investigations on stability and reusability of $[Pd(2\text{-pymo})_2]_n$ as hydrogenation catalyst

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ABSTRACT

The MOF $[Pd(2\text{-pymo})_2]_n$ (2-pymo = 2-pyrimidinolate) was used in the liquid-phase hydrogenation of 1-octene and cyclododecene. Up to a reaction time of 4 h, reactant shape selectivity could be observed, i.e. 1-octene was hydrogenated, but not the more bulky molecule cyclododecene. However, if the catalyst was exposed to hydrogen for more than 4 h, also the hydrogenation of cyclododecene took place. Visually a color change of the catalyst was observed and by XRD it was found that Pd^0 nanoparticles were formed and that the MOF $[Pd(2\text{-pymo})_2]_n$ was transformed into a new crystalline phase, where the Pd^0 seemed to be accessible. Additionally, Pd^0 was leached out and was available for hydrogenation. When reusing the MOF after reaction times less than 1 h, the reaction rate increased with every reuse. We assume that even in the first 4 h Pd^0 was formed, but could not be detected by XRD. In-situ XRD measurements exposing the MOF to hydrogen in the gas phase showed that the MOF was much more stable in gas phase hydrogenation, because the MOF structure remained intact even when Pd^0 was formed.

1. Introduction

Metal organic frameworks (MOFs) are hybrid materials which consist of metal-containing nodes linked by organic molecules through coordinating bonds. In this way, a three-dimensional crystalline porous framework is built up. MOFs possess unique properties such as uniform pores and high inner surface areas combined with a rich versatility due to the variation of metal nodes and organic linkers. Thus, MOFs have a high potential for applications in catalysis and in storage/separation processes. Recent reviews [1–3] summarized the diversity of catalysis with MOFs. In extracts, some examples are stated here. The nodes of the framework can act as metal active sites and can catalyze Lewis acid reactions like cyanosilylation, the oxidation of cycloalkanes, alkenes and alcohols and the hydrogenation of alkenes [1]. Homogeneous catalysts can also be incorporated in the framework by using metalloporphyrins, Schiff-base complexes and binaphthyl complexes as linker [2]. MOFs can also be used as host matrices for nanosized metallic particles, i.e. metal or metal oxide nanoparticles are supported on MOFs for hydrogenation and oxidation reactions [3].

In this work, we will focus on MOFs applied in heterogeneously catalyzed hydrogenation reactions. Therefore, sites with hydrogenation activity are needed. On the one hand, the MOF can be the support for these active sites, and on the other hand, the active sites can be part of the framework of the MOF itself. Several examples are known for MOFs as support for Pd nanoparticles. For instance, catalytic activity was observed for palladium loaded on MOF-5 by metal organic chemical vapor deposition in the hydrogenation of cyclooctene [4], palladium loaded on MOF-5 and on MIL-101 by incipient wetness impregnation in the hydrogenation of styrene [5,6] and palladium loaded on MOF-5 by coprecipitation in the hydrogenation of ethyl cinnamate [7]. The catalytic reactions took place at the accessible surface of the immobilized palladium nanoparticles.

MOFs can also be used as heterogeneous single-site hydrogenation catalysts. There are known mononuclear and binuclear coordination polymers with noble metals as nodes which can catalyze the hydrogenation of alkenes. Among these mononuclear Rh^+-, Pd^0-, Pd^{2+}-, Pt^0-, Pt^{2+}-coordination polymers [8–11] and mononuclear Ru^{2+}-coordination polymers [12,13] with diisocyanoarene linker are known which catalyzed the hydrogenation of 1-hexene. Moreover, a Pd^{2+}-MOF with pyrimidinolate linker catalyzed the hydrogenation of 1-octene [14]. Besides, binuclear Rh^{2+}- and Ru^{2+}-carboxylates are known which catalyzed the hydrogenation of ethylene [15,16].

For our investigations, we chose the well studied MOF $[Pd(2\text{-pymo})_2]_n$ (2-pymo = 2-pyrimidinolate) reported by Navarro et al. [14]. This MOF consists of Pd^{2+} ions bridged by *N*,*N*′-exobidentate 2-pymo linkers building up a three-dimensional open sodalite-like framework. The coordination of the Pd^{2+} centers is square-planar. The formed sodalite-like cage has an interior diameter of about 9 Å with apertures of 4.8 and 8.8 Å.

It was reported in [17] that $[Pd(2\text{-pymo})_2]_n$ showed hydrogenation activity in the conversion of 1-octene with molecular hydrogen to *n*-octane. A shape-selective effect was observed as

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1-octene was hydrogenated while cyclododecene was not converted after 5 h. Cyclododecene with a molecular diameter of about 9 Å (estimated by Chem3D) was too large to enter the pores of $[Pd(2\text{-pymo})_2]_n$. It can be supposed that the catalytic reaction occurred inside the MOF. Llabrés i Xamena et al. [17] proposed that the Pd^{2+} ions could expand their coordination sphere to take part in catalysis and that palladium hydrides played a role in the hydrogenation of 1-octene. However, no detailed mechanistic studies have been performed so far.

In the present work, mechanistic considerations are addressed by means of stability measurements and reuse experiments with the catalyst $[Pd(2\text{-pymo})_2]_n$. With the help of X-ray powder diffraction and ^1H solid-state NMR spectroscopy, it is shown how likely it is that a reaction mechanism known for homogeneous catalysis occurs at the Pd^{2+} centers of the MOF.

2. Mechanistic considerations

According to the shape-selective measurements reported in [17], the catalytic reaction took place inside the pores of the MOF, possibly at the Pd^{2+} centers. A catalytic cycle can be proposed based on the reaction mechanism known for homogeneous Pd^{2+} complexes because it can be seen as a type of homogeneous catalyst heterogenized in a coordination polymer framework. If homolytic and heterolytic H–H bond cleavages are considered, two different reaction pathways have to be taken into account. In the case of a homolytic H–H bond cleavage (Scheme 1 left), a cis-selective oxidative addition of hydrogen can occur which changes the palladium coordination geometry from square planar to octahedral and increases the palladium oxidation number from II to IV. As a third coordination site for the activation of the alkene is needed, one 2-pymo linker has to dissociate. After transfer of hydrogen to the alkene, the linker can reassociate. Via reductive elimination, the alkene can be split off and the original form of the catalyst can be reformed. If only few Pd^{2+} centers participated in the catalytic cycle, the dissociation of linkers would not lead to a complete collapse of the framework. But this cannot be assumed. It is more likely that most of the Pd^{2+} ions take part in the catalytic reaction and that the dissociation of linkers leads to the destruction of the framework.

In the case of a heterolytic H–H bond cleavage (Scheme 1 right), the basic 2-pyrimidinolate linker can be protonated, and a palladium hydride species can be formed. After the cis-selective addition of the alkene, the hydride can be transferred. Under reaction with a second hydrogen molecule, the alkane can be split off and the palladium hydride species can be reformed. The proposed heterolytic reaction mechanism could take place at the metal nodes of $[Pd(2\text{-pymo})_2]_n$, because the oxidation number of the Pd^{2+} centers does not change and the 4-fold linker coordination persists, since only two additional coordination sites at the Pd^{2+} centers are needed. Palladium could expand its coordination sphere from square planar to octahedral. However, for the hydride transfer, the alkene has to coordinate in cis-position so that there is no longer a planar coordination of the 2-pymo linker. It is questionable if the MOF tolerates such defects in the framework without disrupting the structure.

In addition, it should not be disregarded that Pd^{2+} centers can be reduced to Pd^0 under reductive reaction conditions during hydrogenation reactions. The reduction of $[Pd(2\text{-pymo})_2]_n$ can occur if Pd^{2+} ions are reduced by the electrons of the hydrogen molecules and the protons are added to the 2-pymo linkers (Scheme 1 right). It is more likely that the reduction of Pd^{2+} to Pd^0 occurs during the heterolytic catalytic cycle.

3. Experimental

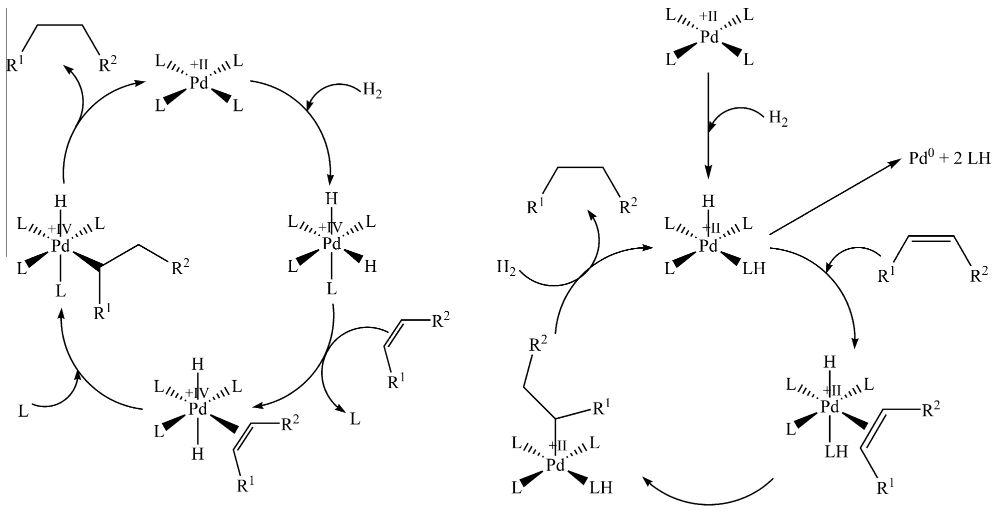
3.1. Synthesis of materials

The MOF $[Pd(2\text{-pymo})_2]_n$ was prepared according to a published procedure [18,19]. The chemicals potassium tetrachloropalladate(II) (99.99%, Alfa Aesar), 2-hydroxypyrimidine-hydrochloride (98%, ABCR) and sodium hydroxide (>98.8%, Th. Geyer) were used as received.

An aqueous solution of 4 mmol of potassium tetrachloropalladate(II) was mixed with an aqueous solution of 8 mmol of 2-hydroxypyrimidine-hydrochloride and stirred for 4 h at room temperature. The precipitate trans-$[PdCl_2(2\text{-Hpymo})_2]$ was filtered off. Afterwards, 4 mmol of sodium hydroxide were added to a water suspension of 4 mmol of trans-$[PdCl_2(2\text{-Hpymo})_2]$. The suspension was refluxed for 20 h and the MOF $[Pd(2\text{-pymo})_2]_n \cdot 3H_2O$ was obtained.

3.2. Characterization techniques

Ex situ X-ray powder patterns were collected at a Bruker D8 Advance diffractometer with Cu Kα radiation (1.5418 Å, 35 kV, 40 mA).



Scheme 1. Proposed homolytic (left) and heterolytic (right) hydrogenation mechanisms at the Pd^{2+} centers of the MOF $[Pd(2\text{-pymo})_2]_n$. (L = 2-pyrimidinolate).