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Hydroformylation of olefins over rhodium supported metal-organic framework catalysts of different structure

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ABSTRACT

The metal-organic framework IRMOF-3 has been synthesized and functionalized with supported rhodium species. The samples have been characterized by XRD, FTIR, SEM, TEM, XPS, AAS, and nitrogen sorption measurements. It is found that originally precipitated big particles consist of hierarchically structured agglomerated nanocrystals of *ca.* 10–15 nm size. The big particles contain a combined macro–meso–micro pore system allowing easy access to the catalytic sites. The Rh@IRMOF-3 supported catalyst has been catalytic tested in the hydroformylation of olefins to the corresponding aldehydes. Double bond shift isomerization has been observed as side reaction. *n*-Alkenes-1 of different chain lengths and bulky or less flexible olefins as cyclohexene, 2,2,4-trimethylpentene, and hexadiene-1,5 have been studied. The Rh@IRMOF-3 catalyst shows high activity and selectivity to *n*-aldehydes in the hydroformylation of linear alkene-1. The comparison of catalytic data obtained with the hydroformylation of *n*-hexene-1 over the different rhodium loaded MOFs as MOF-5, MIL-77, and MIL-101 show a significant influence of the MOF-structure on the catalytic properties.

1. Introduction

Porous metal-organic frameworks (MOFs) are well-known crystalline inorganic–organic hybrid materials, in which metal clusters and organic ligands are connected in space in order to form three-dimensional ordered frameworks. These materials possess a variety of properties such as high specific surface area and pore volume, tunable pore size, and an organic–inorganic hybrid character with a strictly alternating arrangement of organic linkers and metal oxide sites. The huge amount of possibilities to functionalize the MOF by exchange of organic linkers and metal compartments allow to vary the material properties to a large extent [1–8]. The outstanding properties of MOFs make them interesting for the application in gas storage, separation, catalysis, and others [9–14]. Therefore, MOFs attracted attention for use as catalyst or catalytic support. IRMOF-3 is an amino-functionalized MOF, which is isostructural with MOF-5. It is an interesting material for the application as catalytic support for rhodium in the hydroformylation of olefins.

Discovered by Otto Roelen in 1938 [15], the hydroformylation is the reaction of olefinic double bonds with synthesis gas yielding linear and branched aldehydes as primary products. Linear aldehydes, which are more valuable than branched aldehydes, can be used for the production of alcohols. Approximately, 9 million metric tons of aldehydes and alcohols are annually produced using this reaction [16]. These products are important feed stocks for the synthesis of plasticizers, detergents, adhesives, solvents, pharmaceuticals, and agrochemicals as well [17,18].

Even though the traditional use of cobalt or rhodium complexes as homogeneous catalysts in industrial hydroformylation is effective, the homogeneous process suffers from problems of catalyst recovery. Therefore, many efforts have been undertaken to immobilize these catalysts on supports as silica, alumina, micro and mesoporous materials like zeolites and MCM-41, activated carbons, and organic polymers [19–32]. However, it is still a challenge due to the loss of activity [16]. Porous metal-organic frameworks give new opportunities for the heterogenization of homogeneous catalysts. The hybrid nature with defined separated and strictly alternatively arranged inorganic units (metal oxides) and organic linkers should allow a high dispersion of active metal species of

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unique structure in a single site manner throughout the MOF framework. High porosity and large pore openings may enhance the mass transfer properties. Both are expected to improve the catalytic performance.

This study deals with the preparation, characterization, and testing of the rhodium supported metal-organic framework IRMOF-3 catalyst without addition of further ligands. The catalyst activity is compared with MOFs of other pore sizes. The aim is to check the catalytic performance of the rhodium supported MOF catalyst in the hydroformylation reaction.

2. Experiment

2.1. Materials

IRMOF-3 was solvothermally synthesized by an optimized procedure based on literature [33,34]. The starting materials included $H_2NC_6H_3$-1,4-$(COOH)_2$ (2-aminoterephthalic acid) and $Zn(NO_3)_2$ (zinc nitrate). DEF (diethylformamide) was used as solvent. Prior to use, the DEF was distilled and dried over calcium hydride.

In detail, 2.537 g (~14 mmol) of $H_2NC_6H_3$-1,4-$(COOH)_2$ (Sigma–Aldrich) and 11.003 g (~42 mmol) of $Zn(NO_3)_2 \cdot 4H_2O$ (Merck) were dissolved in 350 mL of DEF (Sigma–Aldrich) in a glass reactor which was equipped with a dry tube on the top filled with calcium hydride. The reaction mixture was heated to 105 °C under stirring. Then it was allowed to crystallize at 105 °C for 24 h under static condition. The following work up was carried out under argon atmosphere and use of dried solvents to obtain pure IRMOF-3.

The crystallized product was filtered off and washed three times with 10 mL of CH_2Cl_2 (dichloromethane). The resulting solid was suspended in 50 mL of DEF and heated under refluxing at 130 °C for 1 h. The solid was filtered off and washed again with 3 × 10 mL of CH_2Cl_2. Next, it was given into 50 mL of CH_2Cl_2, slightly shaken, and allowed to stay overnight at room temperature. The solid was again filtered off and the above mentioned procedure was repeated twice in order to remove non-reacted aminoterephthalic acid and the low volatile DEF solvent from the synthesis product. Finally, the product was dried at 105 °C under vacuum to obtain the as-synthesized IRMOF-3. The small and large porous metal-organic frameworks, MIL-77 and MIL-101, were synthesized according to procedures given in Refs. [35,36].

For rhodium loading onto the support under argon atmosphere, 10 mg of Rh(acac)(cod) [(acetylacetonato)(cycloocta-1,5-diene)rhodium(I)] were poured into a beaker glass containing 28 mL of acetonitrile (Baker) and 20 mL of toluene (Merck) under stirring. A clear pale yellow solution was formed. Then 4 g of the as-synthesized IRMOF-3 were added under slight stirring. The suspension was slowly heated to *ca.* 70 °C to evaporate the solvents. The obtained product was washed three times with 5 mL of toluene and dried at 70 °C under vacuum. The resulting Rh@IRMOF-3 catalyst was used for catalytic testing.

2.2. Characterization

The IRMOF-3 and Rh@IRMOF-3 were characterized in detail by XRD, FTIR, SEM, TEM, XPS, AAS, and nitrogen sorption measurements. The XRD measurements were carried out on the STADI-P (STOE) X-ray diffractometer using monochromatic CuK_α radiation ($\lambda = 1.5418$ Å). SEM images were recorded on the DSM 960A electron microscope operating at 10.0 kV (Carl Zeiss, Oberkochen) with a resolution of 4 nm. The samples were placed on sample plates and coated with a very thin layer of gold by using a plasma distribution method. The base vacuum of the chamber was *ca.* 2×10^{-5} -kPa. TEM measurements were carried out with a LIBRA 120 electron microscope (Carl Zeiss, Oberkochen) at 120 kV with a resolution of 0.35 nm. Images were recorded with a digital camera with 2000 × 2000 pixels. IR spectroscopic measurements were performed on a Nicolet 380 FTIR spectrometer coupled with smart orbit ATR device with a resolution of 4 cm^{-1}. XPS measurements were done at an ESCALAB220iXL spectrometer (Thermo Fisher) with monochromatic AlK_α radiation ($E = 1486.6$ eV). The samples were fixed on a stainless steel sample holder with double adhesive carbon tape. The binding energies were referred to C_{1s} at 284.8 eV. For determination of the binding energy and peak area the peak were fitted with Gaussian–Lorentzian curves. The base pressure of the UHV chamber was below 1×10^{-7} Pa. Nitrogen adsorption measurements were performed on an ASAP 2010 sorption system. Before measurements, the samples were dried by heating at 150 °C under reduced pressure. Nitrogen adsorption measurements were carried out at −196 °C. The rhodium content was determined by atomic absorption spectrometry with an AAS-Analyst 300 device (Perkin Elmer). A nitrous oxide/acetylene or air/acetylene mixture was used for the burner system.

2.3. Catalysis

Linear alkene-1 substrates with 6–12 carbon atoms such as *n*-hexene-1 (⩾97%, Aldrich), *n*-octene-1 (⩾98%, Aldrich), *n*-decene-1 (⩾95%, Acros), and *n*-dodecene-1 (93–95%, Acros) were used to investigate the catalytic performance of Rh@IRMOF-3 in the hydroformylation of olefins in more detail. Additionally, some bulky or less reactive olefins as cyclohexene (⩾99%, Sigma–Aldrich), 2,4,4-trimethylpentene (⩾99%, Sigma–Aldrich), and hexadiene-1,5 were involved in the study. For comparison, rhodium loaded MIL-77 and MIL-101 were tested in the hydroformylation of *n*-hexene-1.

All hydroformylation experiments were carried out in a 100 mL PARR reactor at 100 °C and 50 bar ($CO/H_2 = 1$) under stirring at *ca.* 1000 rpm. Toluene was used as solvent. Typically, for *n*-hexene-1 hydroformylation, 95 mg of Rh@IRMOF-3, 12.5 mL of *n*-hexene-1, and 30 mL of toluene were loaded into the reactor. The *n*-hexene-1 to catalyst molar ratio based on rhodium was *ca.* 100,000/1. After loading, the reactor was evacuated and purged with argon. The procedure was repeated in order to remove air and residual moisture. Thereafter, the reactor was immediately loaded with synthesis gas up to a pressure of 50 bar at room temperature. Finally, the reaction mixture was heated under stirring at *ca.* 1000 rpm and maintained at a temperature of 100 °C during the course of reaction. The reactor was equipped with a gas introduction stirrer. The reactions of the other olefins were carried out in the same way. The molar olefin/Rh ratio was kept constant.

3. Results and discussion

3.1. Characterization

The X-ray diffraction patterns of the as-synthesized IRMOF-3 and the used Rh@IRMOF-3 catalyst are shown in Fig. 1. The reflections are well resolved and the observed patterns correspond to the structure of IRMOF-3 [34]. The similarity of XRD patterns obtained for the as-synthesized and the used rhodium loaded material indicates that the structure of the MOF framework is maintained after Rh loading and even catalytic testing. The FTIR spectra of the as-synthesized form and the supported catalyst are shown in Fig. 2. They are very well resolved and show the typical vibration bands observed with benzene carboxylate present as a linker. The absorbances observed between 1600–1330 cm^{-1} and 830–750 cm^{-1} are related to the vibrations of the carboxyl and the amino substituted phenyl groups. The very strong vibration band located at *ca.* 1255 cm^{-1} in both samples are assigned to the C–N stretch vibrations of amino groups attached to the