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Mendeleev Commun., 2022, **32**, 320–322

Mendeleev Communications

Metal–organic framework ZIF-8 loaded with rhodium nanoparticles as a catalyst for hydroformylation

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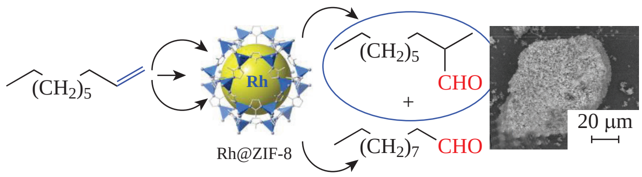
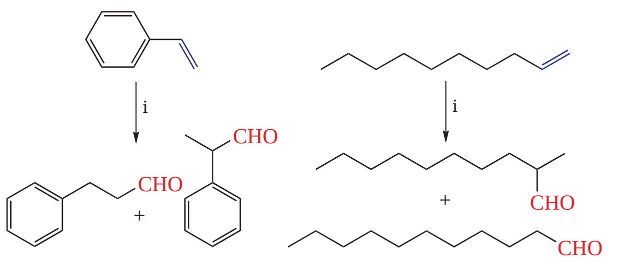
DOI: 10.1016/j.mencom.2022.05.009

Porous metal–organic framework ZIF-8 materials containing incorporated rhodium (Rh@ZIF-8) and rhodium chloride ($RhCl_3$@ZIF-8) nanoparticles were obtained and tested as a catalytic reaction vessel in the reactions of hydroformylation of 1-decene and styrene. Catalytic tests with Rh@ZIF-8 showed that the selectivity and conversion of the hydroformylation reaction depended on the size of the substrate molecule. The incorporation of catalytic nanoparticles into the pores of a metal–organic framework opens up new possibilities for regioselective hydroformylation.



Keywords: hydroformylation, metal–organic frameworks, reaction vessel, catalyst, rhodium nanoparticles, regioselectivity.

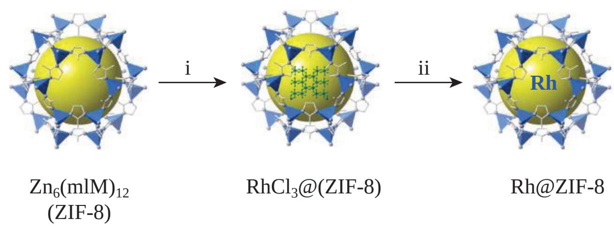
Metal-organic frameworks (MOFs) are porous crystalline materials[1–8] that have a periodic three-dimensional structure due to coordination bonds between metal ions or their clusters and organic ligands and are characterized by a large inner surface area, low density and thermal stability.[9,10] These unique properties of MOFs, which can be tailored by selecting suitable metal ions and organic ligands,[11] make them desirable in a variety of applications including gas storage and separation,[12,13] drug delivery,[1,4] water harvesting[14] and energy conversion.[4] MOFs are also popular catalysts for various chemical processes[15,16] such as hydrogen production from inorganic hydrides,[17] hydrogenation of unsaturated hydrocarbons,[18] reduction of some organic[19,20] and inorganic[21,22] compounds, hydrogenation of aldehydes,[23] oxidation of alcohols,[24] reduction of carbon dioxide,[25] *etc*. In contrast to these reactions, the hydroformylation of alkenes with carbon monoxide and hydrogen to obtain aldehydes[26] (Scheme 1) was traditionally catalyzed by homogeneous rhodium[27] and cobalt[28] catalysts, which were rather difficult to separate from the reaction mixture, while heterogeneous catalysts had much lower efficiency and regioselectivity.[16] To solve this problem, porous MOFs were proposed as ‘reaction vessels’[29] for rhodium nanoparticles to produce catalysts with a large surface area and, as a result, high catalytic activity in the hydroformylation reaction.[30]



Scheme 1 *Reagents and conditions*: i, CO/H_2 (5 MPa), Rh@ZIF-8, toluene, 100 °C, 12 h.

In this work, the popular ZIF-8 MOFs loaded with rhodium (Rh@ZIF-8) and rhodium chloride ($RhCl_3$@ZIF-8) nanoparticles are tested in the catalytic hydroformylation of styrene and 1-decene (see Scheme 1).

$Zn_6(mIM)_{12}$ (ZIF-8) was obtained as a precipitate by the reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole (HmIM) in methanol[31] at room temperature and then activated by drying under high vacuum at 50 °C for 8 h. Catalytically active rhodium nanoparticles were introduced into its pores according to the previously described[32] two-step procedure (Scheme 2). At the first step, the activated MOF is kept in a solution of rhodium chloride in DMF at room temperature for 7 days in air to produce a fine, pale-straw crystalline powder of $RhCl_3$@ZIF-8. Its subsequent reduction with $NaBH_4$ at the second step leads to the formation of the target product Rh@ZIF-8 as a fine crystalline powder of the same color.



Scheme 2 *Reagents and conditions*: i, $RhCl_3$, DMF, room temperature; ii, $NaBH_4$, H_2O, room temperature.

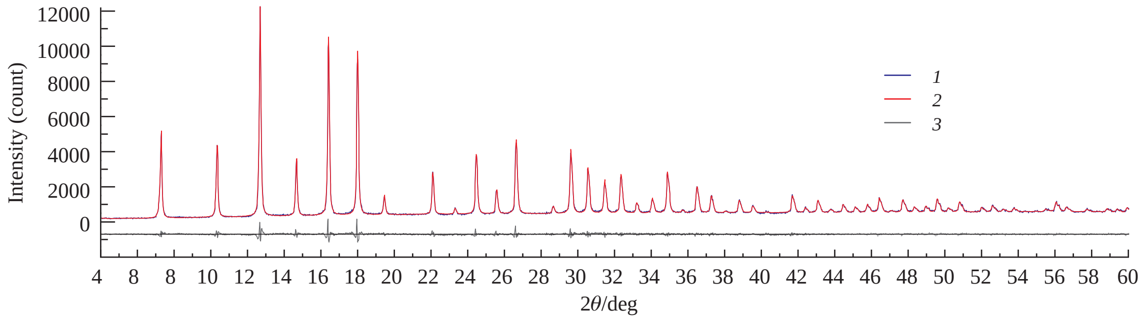


Figure 1 X-ray diffraction patterns (*1*) obtained for the powdered Rh@ZIF-8 sample, (*2*) calculated for ZIF-8 and (*3*) their difference. For ZIF-8 and $RhCl_3$@ZIF-8, see Figures S1 and S2 in Online Supplementary Materials.

After these manipulations, MOF retained its crystal structure. X-ray diffraction analysis of powdered samples of $RhCl_3$@ZIF-8 and Rh@ZIF-8 (Figure 1, curve *1*) showed that they are almost exclusively the crystalline phase of ZIF-8 (Figure 1, curve *3*) with the contribution of rhodium nanoparticles incorporated into it so small that they do not affect the diffractograms. Indeed, their elemental composition, determined by scanning electron microscopy in combination with energy-dispersive X-ray spectroscopy, corresponded to Rh@ZIF-8 [Figure 2(*a*)] and $RhCl_3$@ZIF-8 [Figure 2(*b*)] with 0.27 wt% rhodium evenly distributed in the samples.

The catalytic activity of the obtained crystalline products $RhCl_3$@ZIF-8 and Rh@ZIF-8 was tested in the hydroformylation reaction (see Scheme 1), usually catalyzed by rhodium complexes. An important feature of this reaction is the formation of two possible regioisomers, a linear aldehyde and a branched aldehyde. However, the use of a MOF loaded with catalytically active rhodium nanoparticles as a 'reaction vessel' can increase the regioselectivity of hydroformylation towards one of the regioisomers.[33]

In the hydroformylation of styrene, both $RhCl_3$@ZIF-8 and Rh@ZIF-8 exhibited catalytic activity; however, the achieved conversion of the starting alkene was different (2 and 12%, respectively). In the ^{1}H NMR spectra of the reaction mixture obtained in the presence of Rh@ZIF-8, weak signals of the CHO group (doublet at 10.92 ppm) of the branched isomer were observed. However, the main product was 2-phenylpropanal (retention time 4.5 min), as confirmed by the fragmentation pattern characteristic of linear aldehydes in gas chromatography-mass spectrometry (GC-MS) analysis data (Figure S3, see Online Supplementary Materials). It was present in a mixture with 3-phenylpropanal (retention time 4.3 min) at a ratio of branched to linear isomer of 5.25 : 1. In the presence of $RhCl_3$@ZIF-8, only 3-phenylpropanal (retention time 4.53 min) was found in small amounts (Figure S4). The catalytic activity of $RhCl_3$@ZIF-8 and Rh@ZIF-8 in styrene hydroformylation reactions and its absence for the starting MOF additionally confirms the incorporation of catalytically active rhodium species into these crystalline materials.

One of the reasons for the poor catalytic activity of $RhCl_3$@ZIF-8 and Rh@ZIF-8 in this reaction may be the mismatch between the pore sizes in ZIF-8 and the size of the styrene molecule. As a result, hydroformylation mainly occurs outside the ZIF-8 pore due to leakage of catalytically active species.

The replacement of styrene with 1-decene in the hydroformylation reaction led to a noticeable increase in the catalytic activity of Rh@ZIF-8; substrate conversion reached 89%. GC-MS (Figure S5) and NMR spectroscopy confirmed the presence of both branched and linear isomers in the reaction mixture at the respective ratio of 1.325 : 1, as evidenced by the signals of the CHO (aldehyde) group in the ^{1}H NMR spectra (triplet at 9.61 ppm and doublet at 9.76 and 9.75 ppm, respectively). Thus, the use of Rh@ZIF-8 as a catalyst for hydroformylation of 1-decene provides little selectivity towards the branched isomer.

We performed a leaching test to investigate the stability of the catalyst during the catalytic reaction. In the leaching test, the reaction was stopped after 1 h, and the catalyst was removed by filtration. The reaction was further continued with the filtrate. However, after 24 h, we did not observe any increment in the formation of the product, which clearly indicates that the active species were not leached during the catalytic reaction.

Both obtained MOF-based materials showed catalytic activity in the hydroformylation reactions of styrene and 1-decene. In the case of the former substrate, they provided only a low conversion from 2 to 12%, probably due to the non-optimal size of the styrene molecule. However, the use of the latter substrate resulted in a higher conversion with little regioselectivity towards one of the isomers. Thus, this finding offers new possibilities for the heterogenous catalysis of regioselective hydroformylation.

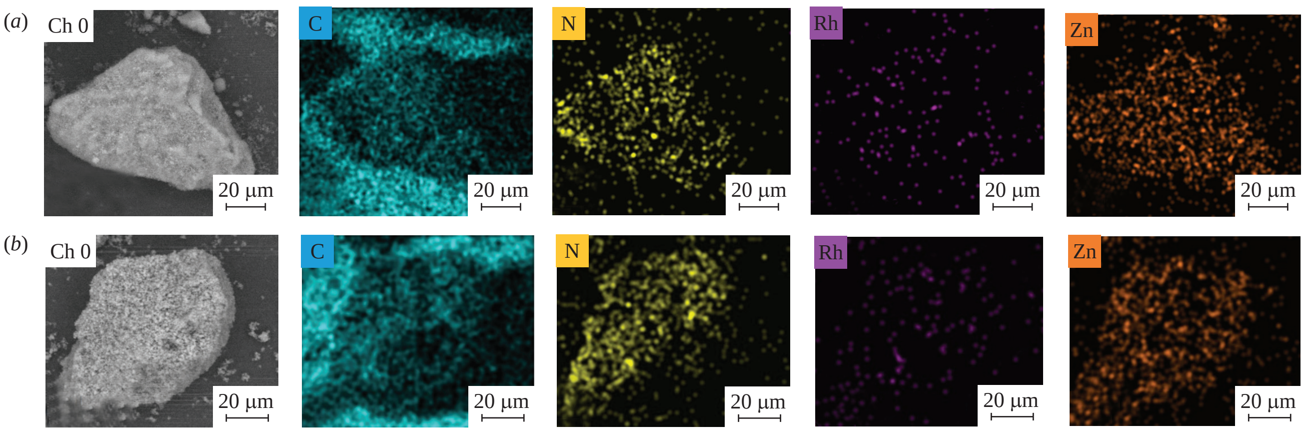


Figure 2 Distribution of chemical elements in powdered samples of (*a*) Rh@ZIF-8 and (*b*) $RhCl_3$@ZIF-8 according to energy-dispersive X-ray spectroscopy data.

This work was supported by the Russian Foundation for Basic Research (project nos. 18-29-04020 and 19-29-08032). Powder X-ray diffraction data were collected using the equipment of Center for molecular composition studies of INEOS RAS with the financial support from the Ministry of Science and Higher Education of the Russian Federation.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.009.

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Received: 15th October 2021; Com. 21/6726