

Rhodium Hydrogenation Catalysts Supported in Metal Organic Frameworks: Influence of the Framework on Catalytic Activity and Selectivity

Douglas T. Genna, Laura Y. Pfund, Danielle C. Samblanet, Antek G. Wong-Foy, Adam J. Matzger, and Melanie S. Sanford*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

Supporting Information

ABSTRACT: The cationic rhodium complexes (dppe)Rh-(COD)BF₄ and (MeCN)₂Rh(COD)BF₄ have been supported in metal–organic frameworks bearing anionic nodes (ZJU-28) and anionic linkers (MIL-101-SO₃) via ion exchange. These MOF-supported Rh species serve as recyclable catalysts for the hydrogenation of both the terminal alkene substrate 1-octene and the internal alkene substrate 2,3-dimethylbutene. The nature of the MOF support impacts various aspects of catalysis, including: (i) the rate of 1-octene hydrogenation, (ii)



the activity and recyclability of the catalyst in 2,3-dimethylbutene hydrogenation, and (iii) the size selectivity of hydrogenation with alkene substrates appended to calixarenes.

KEYWORDS: metal organic frameworks, hydrogenation, catalysis, rhodium, size exclusion

INTRODUCTION

The incorporation of transition-metal catalysts into metal organic frameworks (MOFs) has been the focus of extensive recent research efforts.^{1–12} Supporting a catalyst offers the potential for combining the benefits of homogeneous catalysis (e.g., mild conditions, well-defined catalyst structures and/or ligand environments) with those of heterogeneous catalysis (e.g., recyclability, high TON, site isolation).^{13–23} MOFs are particularly attractive supports due to their diverse functional groups, pore sizes, and pore geometries.^{24–26} Thus, they offer opportunities for tuning the secondary coordination environment around the transition-metal catalyst.

The vast majority of work in the area of MOF catalysis has focused on recyclability as the major benefit of MOF-supported catalysts.^{13–23} However, the modularity of MOFs also offers the potential for tuning catalyst performance. A grand challenge for the field is to develop recyclable MOF-supported catalysts in which variation of the framework structure (e.g., pore size, pore shape, pore functional groups) enables tuning of catalyst activity, selectivity, and/or stability. Recent reports have demonstrated promising examples of enhanced selectivity^{1–11,27–29} and/or catalyst stability^{30–32} using MOFsupported catalysts, but such efforts remain in their infancy.

We recently reported an ion exchange strategy for supporting cationic transition-metal complexes in anionic MOFs.³³ This approach avoids the requirement for covalent tethering of the catalyst to the framework.³⁴ As a result, it offers the potential to support the same catalyst in structurally different anionic MOFs.^{35–45} This would, in turn, enable an assessment of the impact of MOF structure on catalyst performance.

We report herein on the synthesis, characterization, and catalytic alkene hydrogenation reactivity and selectivity of cationic Rh complexes loaded into two different anionic MOFs: ZJU-28⁴⁶ and MIL-101-SO₃ (Figure 1).⁴⁷ We demonstrate that varying the MOF support impacts various aspects of catalyst



Figure 1. Catalyst loading via ion exchange using MOFs with anionic nodes or pendant anionic organic linkers.

Received: February 8, 2016 Revised: April 13, 2016 performance, including reaction rates, recyclability, turnover number, and size selectivity of alkene hydrogenation in these systems.

RESULTS AND DISCUSSION

Cation Exchange. We focused our efforts on ion exchange of the cationic Rh complexes (dppe)Rh(COD)BF₄ (1a) and $(MeCN)_2Rh(COD)BF_4$ (1b) into anionic MOFs (Figure 1), in order to study alkene hydrogenation catalysis.^{48–51} Two anionic MOFs with very different properties (ZJU-28 and MIL-101-SO₃) were selected for this study (Table 1). ZJU-28

Table 1. Comparison of the Properties of ZJU-28 and MIL-101-SO $_3$



was targeted due to our previous success at deploying ZJU-28-1a in catalytic hydrogenation reactions.³³ MIL-101-SO₃ was selected on the basis of two criteria: (1) the anionic charge of MIL-101-SO3 is centered on the organic linker, which is complementary to ZJU-28, which is anionic at the metal node; and (2) the high stability profile of the parent MIL-101 is well documented, and this property is expected to be advantageous for catalysis applications. ZJU-28 is prepared from InCl₃ and 4,4',4"-benzene-1,3,5-triyl-tribenzoate (BTB).46,52 It is an interpenetrated MOF containing two unique channels with pore window diameters of 9 and 7 Å, respectively. The inorganic nodes of ZJU-28 bear an overall charge of -1, as they are composed of In^{III} centers ligated to four carboxylate ligands. The monoanionic charge of the framework is balanced by the presence of NH2Me2+ guests derived from DMF solvent decomposition during synthesis. ZJU-28 exhibits modest thermal stability and is reported to decompose at \sim 120 °C.

MIL-101-SO₃ is synthesized from terephthalic acid sodium sulfonate and chromium(III) oxide.⁴⁷ MIL-101-SO₃ has a neutral inorganic node and a charged SO₃⁻ functional group appended to the organic linker. This monoanionic charge is balanced by either a proton or a Na cation. MIL-101-SO₃ has large pseudospherical pores (37 × 36 Å) with hexagonal pore windows (16 × 14 Å). This material has much higher thermal stability than ZJU-28, as it is reported to be stable to ~275 °C.

The cationic Rh complexes (dppe)Rh(COD)BF₄ (1a)⁵³ and (MeCN)₂Rh(COD)BF₄ (1b) were loaded into ZJU-28 and MIL-101-SO₃ by shaking suspensions of the corresponding MOF immersed in a 0.015 M DMF solution of 1a or 1b for 3 days. The resulting materials were then washed with DMF, dried at room temperature under vacuum, and analyzed using ICP-OES and powder X-ray diffraction (PXRD). As shown in Table 2, ICP-OES analysis showed comparable levels of Rh

Table 2. Incorporation of Rh Complexes 1a and 1b into ZJU-28 and MIL-101-SO₃

entry	MOF	wt % [M] ^a
1	ZJU-28	
2	ZJU-28-1a	3.5
3	ZJU-28-1b	2.2
4	MIL-101-SO ₃	
5	MIL-101-SO ₃ -1a	3.2
6	MIL-101-SO ₃ -1b	1.7

^{*a*}wt % Rh is calculated on the basis of the ratio of [Rh] to the wt % metal of the MOF. See Supporting Information for complete details.

uptake into ZJU-28 and MIL-101-SO₃ for each Rh complex.^{54–56} PXRD analyses of ZJU-28-1a/1b and MIL-101-SO₃-1a/1b were consistent with minimal structural changes during catalyst loading (see Supporting Information for full details).⁵⁷

Comparison of ZJU-28-1a and MIL-101-SO₃-1a: Hydrogenation of Terminal Olefins. ZJU-28-1a and MIL-101-SO₃-1a were first examined as catalysts for the hydrogenation of 1-octene to *n*-octane. These reactions were carried out in a batch pressure reactor at 75 °C (internal temperature) using 10 bar H₂ and 0.02 mol % [Rh] in neat 1-octene (6.4 mmol). The turnover numbers were determined via analysis of the crude reaction mixture by gas chromatography after 24 h. The two catalysts afforded comparable results, with ~4000 turnovers of 1-octene to *n*-octane in each case (Figure 2; theoretical maximum is 5000). Furthermore, both materials could be recycled at least 4 times, and the recycled materials afforded comparable TON (~4000) after 24 h.



Figure 2. Recycling of MOF-supported Rh catalysts in the hydrogenation of 1-octane.

Characterization of Materials after Recycling. PXRD and ICP-OES analyses were conducted on the spent catalysts after the four recycles. PXRD analysis showed that both materials remain crystalline after catalysis. ICP-OES of ZJU-28-1a showed no detectable loss of Rh, whereas analysis of MIL-101-SO₃-1a showed some leaching of Rh (3.2 wt % at the start versus 2.1 wt % after 4 recycles). To probe whether the observed hydrogenation reactivity is the result of soluble leached Rh, both ZJU-28-1a and MIL-101-SO₃-1a were subjected to a three-phase test with a Merrifield-resinsupported terminal alkene substrate. In this experiment, the MOF catalyst and supported substrate were suspended in acetone and subjected to 10 bar H_2 for 48 h at 75 °C. No hydrogenation of the supported alkene was detected with either catalyst (ZJU-28-1a or MIL-101-SO₃-1a). This result indicates that leached soluble Rh is not the active hydrogenation catalyst in these transformations. For comparison, the homogeneous complex 1a catalyzes complete hydrogenation of the supported alkene under otherwise identical conditions.³³

To more quantitatively compare the relative reactivity of these two catalysts, the reaction progress of 1-octene hydrogenation was monitored *in situ* via Raman spectroscopy. These experiments were conducted in a high pressure batch reactor retrofitted with a Raman probe.⁵⁸ The reactions were carried out at 75 °C (internal temperature) using 65 bar H₂ and 0.02 mol % of [Rh]. They were monitored based on disappearance of a Raman resonance at 1643 cm⁻¹ that is characteristic of 1-octene.

The reaction progress data for fresh ZJU-1a and MIL-101-SO₃-1a are overlaid in Figure 3. The hydrogenation reaction



Figure 3. Comparison of the reaction progress of the hydrogenation of 1-octene with fresh ZJU-28-1a and MIL-101-SO₃-1a (as-synthesized catalysts).

proceeded significantly slower with ZJU-28-1a, requiring ~14 h (~360 TON/h) for complete consumption of 1-octene. In contrast, complete consumption of 1-octene was observed within ~3 h (~1660 TON/h) with MIL-101-SO₃-1a. We next compared the performance of the two catalysts after seven recycles (eight total runs). As shown in Figure 4, the recycled MIL-101-SO₃-1a maintains higher hydrogenation activity than recycled ZJU-28-1a. However, the recycled MIL-101-1a is a slower catalyst than fresh MIL-101-SO₃-1a (complete consumption of starting material requires ~6 h (~800 TON/h) versus 4 h for the fresh material). This is likely due to Rh leaching, as the ICP results (above) show that the % Rh in MIL-101-SO₃-1a decreases as the material is recycled. In contrast, the recycled ZJU-28-1a shows slightly higher reactivity than fresh ZJU-28-1a, with complete conversion of starting material requiring ~11 h (~450 TON/h) versus 14 h, respectively.

Overall, these results show that ZJU-28-1a and MIL-101- SO_3 -1a are active and recyclable catalysts for the hydrogenation of 1-octene. Furthermore, hydrogenation catalysis is significantly faster with MIL-101- SO_3 -1a as compared to that with ZJU-28-1a, both before and after recycling. We hypothesize that this is due, at least in part, to the significantly larger pore sizes and pore windows of the MIL-101- SO_3 support compared



Figure 4. Comparison of the reaction progress of the hydrogenation of 1-octene with recycled ZJU-28-1a and MIL-101-SO₃-1a (materials recycled seven times for a total of eight runs).

to those of ZJU-28. Both of these features are expected to facilitate transport of reactants and products during catalysis.

2,3-Dimethylbutene Hydrogenation with MIL-101-SO₃-1a and ZJU-28-1a. Literature reports indicate that cationic rhodium complexes are generally poor catalysts for the hydrogenation of tetrasubstituted alkenes.^{59,60} Thus, we next selected 2,3-dimethylbutene as a more challenging substrate than 1-octene. As anticipated, the hydrogenation of 2,3-dimethylbutene required more forcing conditions than that of 1-octene. However, after some optimization, we identified reaction conditions that enabled a comparison of the supported Rh catalysts (0.003 mol % of [Rh] at 100 °C over 24 h under 75 bar of H₂).

As shown in Figure 5, ZJU-28-1a afforded low initial reactivity for the hydrogenation of 2,3-dimethylbutene under these standard conditions, providing a TON of 1500 (theoretical maximum TON = 30 000). Significant loss of activity was observed with each subsequent recycle of ZJU-28-1a, and after four recycles, this catalyst afforded just 289 turnovers. In contrast, MIL-101-SO₃-1a was a much more



Figure 5. Recycling of MOF-supported Rh catalysts ZJU-28-1a and MIL-101-SO₃-1a in the hydrogenation of 2,3-dimethylbutene to 2,3-dimethylbutane.

effective catalyst for the hydrogenation of 2,3-dimethylbutene, affording 8800 turnovers after 24 h. Furthermore, upon recycling, the activity of MIL-101-SO3-1a nearly doubled to 13 500 turnovers.⁶¹ This enhanced activity was largely maintained over three additional recycles.⁶²

PXRD and ICP-OES analyses were conducted on the spent catalysts after four recycles. In both cases, the PXRD diffractograms showed that the crystallinity of the material was maintained (Figures S4 and S6). In addition, the ICP-OES analysis showed minimal change in the Rh content of either material. For example, the recycled ZJU-28-1a contained 3.5 wt % [Rh, while the recycled MIL-101-SO₃-1a contained 3.2 wt % [Rh]. These latter results indicate that the observed differences in reactivity between the two materials in this transformation are not due to Rh leaching.

2,3-Dimethylbutene Hydrogenation with MIL-101-SO₃-1b and ZJU-28-1b. We next sought to probe whether the support-dependent activity and recyclability of these Rh hydrogenation catalysts is specific to Rh complex 1a [(dppe)- $Rh(COD)BF_4$]. As such, we examined the performance of MIL-101-SO₃-1b and ZJU-28-1b for the hydrogenation of 2,3dimethylbutene $[1b = (MeCN)_2Rh(COD)BF_4]$. As shown in Figure 6, both ZJU-28-1b and MIL-101-SO₃-1b afforded



Figure 6. Recycling of MOF-supported Rh catalysts ZJU-28-1b and MIL-101-SO₃-1b in the hydrogenation of 2,3-dimethylbutene to 2,3dimethylbutane.

significantly lower initial activity than ZJU-28-1a and MIL-101-SO₃-1a. For instance, the TON for the first run with MIL-101-SO₃-1a was 8800 while that with MIL-101-SO₃-1b was 5800. Furthermore, both catalysts exhibited poor recyclability, with precipitous drops in TON after five recycles. However, despite the lower initial reactivity and recyclability of 1b-based catalysts, these materials show similar trends in activity as a function of the MOF support. In other words, MIL-101-SO₃-1b affords much higher initial activity than the ZJU-28-supported Rh catalyst (initial TON = 5800 and 620, respectively). These data further demonstrate that the MOF support dramatically impacts catalyst activity.

Hydrogenation Selectivity for MIL-101-SO₃-1a and ZJU-28-1a. A final set of experiments was conducted to explore the impact of the MOF support on hydrogenation selectivity. The calixarene-tethered alkene substrates 2a and 2b

(Table 3) were employed for these investigations. These two substrates have different kinetic diameters (9.5 and 16 Å,

Table 3. Size Selective Hydrogenation of Calixarene Substrates 2a and 2b



2b, n = 8, kinetic diameter = 16 Å

catalyst	pore window	substrate	kinetic diameter	TON
1a	na	2a	9.5 Å	200
MIL-101-SO3-1a	16×14 Å	2a	9.5 Å	200
ZJU-28-1a	9 × 9 Å	2a	9.5 Å	0
1a	na	2b	16 Å	200
MIL-101-SO3-1a	16×14 Å	2b	16 Å	52
ZJU-28-1a	9 × 9 Å	2b	16 Å	0

respectively).⁶³ Because the pore windows of ZJU-28 and MIL-101-SO₃ are 9 \times 9 Å and 16 \times 14 Å, respectively, we anticipated that these materials should exhibit size-selective catalysis. Importantly, the observation of selectivity differences as a function of support would also provide evidence that catalysis occurs in the pores rather than on the surface of the MOF or on leached insoluble Rh particles.

The hydrogenation of 2a/b was conducted using 0.54 mol % of [Rh] in benzene at 35 $^{\circ}$ C for 24 h. C₆D₆ was utilized as the solvent in order to fully dissolve the calixarene substrates. The extent of hydrogenation of 2a/b was determined via ¹H NMR spectroscopic analysis of the crude reaction mixtures. The soluble catalyst 1a efficiently catalyzed the hydrogenation of 2a and **2b**, providing full conversion under the reaction conditions (TON = 185). With MIL-101-SO₃-1a, full conversion (TON = $\frac{1}{2}$ 185) was obtained with the smaller calixarene substrate 2a. However, the larger substrate 2b, which has a kinetic diameter close to the pore window of the MOF, afforded only partial hydrogenation (TON = 52) after 24 h. Finally, with ZJU-28-1a as the catalyst (which has a pore window that is smaller than the kinetic diameter of both of the calixarenes), no hydrogenation of either 2a or 2b was detected. Collectively, these results demonstrate that size-selective catalysis can be achieved by supporting the same catalyst in two structurally different metal organic frameworks.

CONCLUSIONS

This report describes the synthesis, characterization, and hydrogenation reactivity and selectivity of cationic Rh complexes supported in two different anionic MOFs: ZJU-28 and MIL-101-SO₃. This study reveals several important features of the MOF-supported catalysts. First, we demonstrate that ion exchange can be used to support transition-metal catalysts in two very different MOFs: ZJU-28 (which bears a negative charged at the node) and MIL-101-SO₃ (which bears a negative charge on the organic linker). Second, we show that these MOF-supported Rh species serve as recyclable catalysts for the hydrogenation of both terminal and internal alkenes. Third, we demonstrate that the nature of the MOF support impacts various aspects of catalysis, including: (a) the rate of 1-octene hydrogenation; (b) the activity (as measured by TON) and recyclability of the catalyst in 2,3-dimethylbutene hydrogenation; and (c) the size selectivity of the catalyst in the hydrogenation of alkenes appended to calixarenes. These studies pave the way for the use of MOF supports to modulate both reactivity and selectivity in a broader array of catalytic transformations.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00404.

Experimental details, PXRD diffractograms, Raman spectra, and NMR data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: mssanfor@umich.edu.

Notes

The authors declare no competing financial interest.

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(53) Complex 1a was formed *in situ* by the combination of 1 equiv of dppe and 1 equiv of $(COD)Rh(CH_3CN)_2BF_4$ in DMF.

(54) Notably, these values are below the theoretical maxima for Rh uptake, 18 wt % in MIL-101-SO₃ and 14 wt % in ZJU-28, respectively.

(55) No Rh incorporation was observed when the neutral MOF MIL-101 was subjected to DMF solutions of **1a** or **1b** under otherwise analogous conditions. In both cases, less than 0.01 wt % incorporation of Rh was detected by ICP-OES.

(56) As a control, we also subjected ZJU-28 and MIL-101-SO₃ to neutral metal complexes (e.g., $(COT)Fe(CO)_3$ and *trans*-Pd(PPh₃)₂Cl₂). In both cases, less than 0.01 wt % loading of the corresponding metal was observed.

(57) Our samples of MIL-101-SO₃ and MIL-101-SO₃-1a have BET surface areas of 1215 m²/g and 1100 m²/g, respectively. ZJU-28 and ZJU-28-1a both have measured surface areas of $< 50 \text{ m}^2/\text{g}$.

(58) These transformations were conducted on a 10-fold larger scale than the experiments in Figure 2, due to the nature of the reactor. See Supporting Information for full details about the reactor.

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(61) This unexpected increase in reactivity upon recycling may be due to some type of activation event of the catalyst that occurs during the first run. Ongoing work is focused on establishing the mechanistic origin of this effect.

(62) These results compare favorably to those obtained by Lin in the hydrogenation of 2,3-dimethylbutene catalyzed by mBPP-MOF-Co. A maximum TON of 170 was obtained in this previously reported system (although the conditions were considerably less forcing than ours, as the reaction was conducted in THF at 50 °C under 40 bar H_2). See ref 1 for complete details.

(63) Kinetic diameters were determined on the basis of the lowest energy conformation as calculated by the Spartan '04 program by Wave function.