Heterogenization of Homogeneous Catalysts in Metal–Organic Frameworks via Cation Exchange

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S *Supporting Information*

ABSTRACT: This paper describes the heterogenization of single-site transition-metal catalysts in metal–organic frameworks (MOFs) via cation exchange. A variety of cationic complexes of Pd, Fe, Ir, Rh, and Ru have been incorporated into ZJU-28, and the new materials have been characterized by optical microscopy, inductively coupled plasma optical emission spectroscopy, and powder X-ray diffraction. MOF-supported $[Rh(dppe)(COD)]BF_4$ catalyzes the hydrogenation of 1-octene to *n*-octane. The activity of this supported catalyst compares favorably to its homogeneous counterpart, and it can be recycled at least four times. Overall, this work provides a new and general approach for supporting transition-metal catalysts in MOFs.

The heterogenization of single-site catalysts combines the classic benefits of heterogeneous catalysis (recyclability and easy removal from a reaction mixture) with the controlled ligand environment of homogeneous catalysts.[1−4] Over the past several years, metal–organic frameworks (MOFs) have been targeted as particularly attractive supports for such molecular catalysts because of their well-defined and highly tunable pore structures and high porosities.[5] Extensive work[6−11] has shown that ligands for single-site metal catalysts can be covalently linked to MOFs during the MOF synthesis process[8,12] or via postsynthetic modification.[13,14] These two approaches have yielded supported catalysts with modest to high activities for a variety of transformations (e.g., acetylations, Knoevenagel condensations, epoxidations, Mukaiyama aldol reactions, and C−H functionalizations). However, despite these successes, the covalent tethering approach has several key disadvantages. First, tethering (either pre- or post-MOF synthesis) is synthetically intensive, often requiring multiple steps to access a single catalyst structure. Second, covalent tethering necessitates perturbation of the ligand environment at the catalyst to accommodate the support.[7,8] This often deleteriously affects the reactivity and/or selectivity in comparison with the parent homogeneous catalyst.[7,9] Finally, in many instances the recyclability of the MOF-tethered catalyst is poor.[6a,7c,9]

We sought to address these challenges by developing a complementary approach for heterogenizing molecular transition-metal catalysts in MOFs. Our strategy was inspired by recent studies of anionic MOFs containing cationic guest molecules.[15−21] In these systems, the endogenous guests (most commonly $H_2NMe_2^+$) undergo facile exchange with exogenous cations, thereby enabling the incorporation of Li^+,[16] poly-aromatic pyridinium dyes,[15] the cationic form of the antiarrhythmic drug procainamide,[17] and tetralkylammonium cations.[19] Informed by similar approaches in the zeolite[22] and mesoporous aluminosilicate[23] literature, we hypothesized that an analogous ion-exchange process could be used to support cationic transition-metal catalysts in MOFs bearing anionic frameworks (Figure 1). Importantly, this approach would not
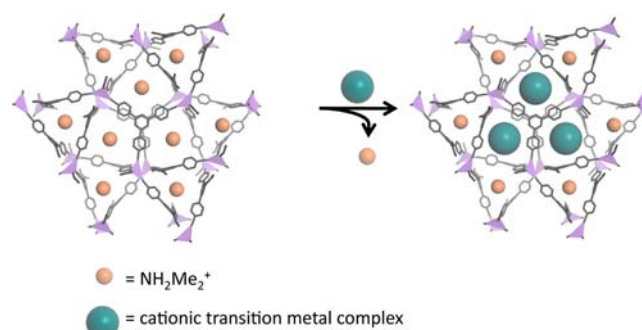
Figure 1. Proposed heterogenization of single-site transition-metal catalysts in ZJU-28 via cation exchange.

require synthetic modification of the existing ligands of the metal catalyst or the MOF. In principle, it should be effective for supporting diverse metal catalysts in a single MOF framework. Additionally, sequestering transition-metal complexes inside the pores of the MOF could potentially limit catalyst decomposition pathways. Herein we describe the use of this approach to construct a series of MOF-supported cationic transition-metal complexes. Furthermore, we demonstrate the application of one of these supported complexes as a recyclable alkene hydrogenation catalyst.

Our initial efforts focused on the exchange of endogenous $H_2NMe_2^+$ cations with cationic transition-metal complexes in anionic ZJU-28, a material selected on the basis of both its stability profile[24] and its well-known ability to participate in cation-exchange reactions.[15] Treatment of ZJU-28 with *N,N*-dimethylformamide (DMF) solutions of $[Pd(CH_3CN)_4][BF_4]_2$ (**1a**), $[FeCp(CO)_2(thf)]BF_4$ (**1b**), $[Ir(COD)(PCy_3)(py)]PF_6$ (**1c**), $[Rh(dppe)(COD)]BF_4$ (**1d**), and $[Ru(Cp^*)(CH_3CN)_3]$-OTf (**1e**) for 3 days resulted in partial exchange of $H_2NMe_2^+$ for the corresponding metal complex cations, forming ZJU-28-**1a**−**1e** (Table 1).[25] In each case, exchange was accompanied by a color change of the ZJU-28 crystals. Analysis of a cross

Table 1. Incorporation of Complexes 1a–f into ZJU-28 as Determined by ICP-OES

complex (product)	wt % 1a–f	% $H_2NMe_2^+$ displaced
1a (ZJU-28-**1a**)	5.1	34
1b (ZJU-28-**1b**)	2.2	28
1c (ZJU-28-**1c**)	8.1	30
1d (ZJU-28-**1d**)	3.5	24
1e (ZJU-28-**1e**)	4.9	35
1f (none)	0	0

section of ZJU-28-**1e** by optical microscopy showed that the orange Ru^{II} complex was dispersed throughout the crystal and not just on the outside surface (Figure S2 in the Supporting Information). This was further confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES), which showed that the transition-metal complexes **1a–e** were exchanged with 24–34% of the $H_2NMe_2^+$ guests, leading to materials containing 2–8 wt % **1**.

The supported catalysts ZJU-28-**1a–1e** were all characterized by powder X-ray diffraction (PXRD). As shown in Figure S7, the PXRD data for these materials were nearly identical to those for the parent ZJU-28, indicating that the cation-exchange process was not detrimental to the crystal structure of the material.

Several additional experiments were performed to assess whether neutral metal complexes would be taken up by ZJU-28 in a similar fashion and whether incorporation of cationic metal complexes that are too large to fit into the ZJU-28 pores would be observed. To probe the former, ZJU-28 was exposed to DMF solutions of the neutral complexes *trans*-Pd(PPh$_3$)$_2$Cl$_2$ and Fe(COT)(CO)$_3$ (COT = cyclooctatetraene) under our standard conditions. As anticipated, colorimetric and ICP-OES analyses showed that neither of these neutral complexes was taken up by the MOF. ZJU-28 was also treated with the cationic iron porphyrin complex Fe(TMPyP)(Cl) (**1f**) [TMPyP = 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin tetra(*p*-toluenesulfonate), which has a kinetic diameter of ∼19 Å. Since the size of the largest pore window of ZJU-28 is 8–9 Å, **1f** should be too large to diffuse into its pores. Consistent with this hypothesis, **1f** was not incorporated into the MOF, as confirmed by colorimetric and ICP-OES analyses.

To obtain a preliminary assessment of the catalytic competency of these materials, ZJU-28-**1d** was compared to its homogeneous counterpart [Rh(dppe)(COD)]BF$_4$ (**1d**) [dppe = 1,2-bis(diphenylphosphino)ethane; COD = 1,5-cyclooctadiene] in the catalytic hydrogenation of 1-octene. These reactions were performed using 0.2 mol % [Rh] at 35 °C under 10 atm H$_2$.[26] Initial studies were conducted in acetone, the optimal solvent for the homogeneous reaction.[27] As shown in Figure 2, the homogeneous and heterogeneous catalysts both afforded ∼450 turnovers (nearly complete conversion of 1-octene) after 4 h. The heterogeneous catalyst ZJU-28-**1d** exhibited lower initial reactivity (turnover frequency = 1800 h^{-1} for **1d** and 540 h^{-1} for ZJU-28-**1d** at 5 min) but overtook **1d** after 2 h. This is likely due to partial decomposition of **1d** over the course of the reaction. Consistent with this proposal, the homogeneous reaction solution changed color from orange to dark brown after 2 h; furthermore, when this solution was exposed to another 500 equiv of 1-octene under H$_2$, only 200 additional turnovers were observed after 4 h. In contrast, ZJU-28-**1d** could be recycled four times under these conditions with minimal loss of catalyst activity (Figure S4).[28]
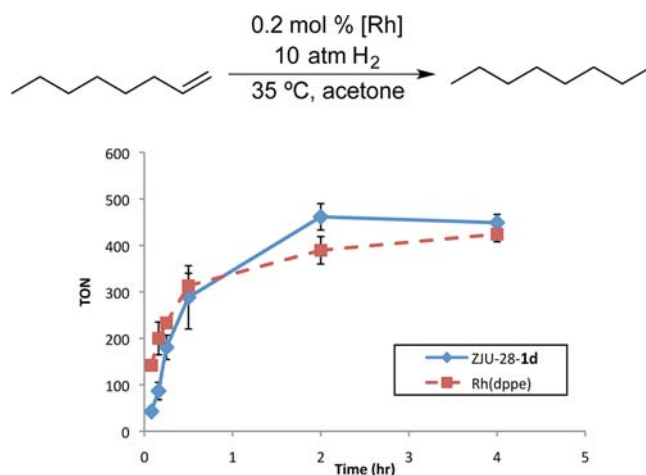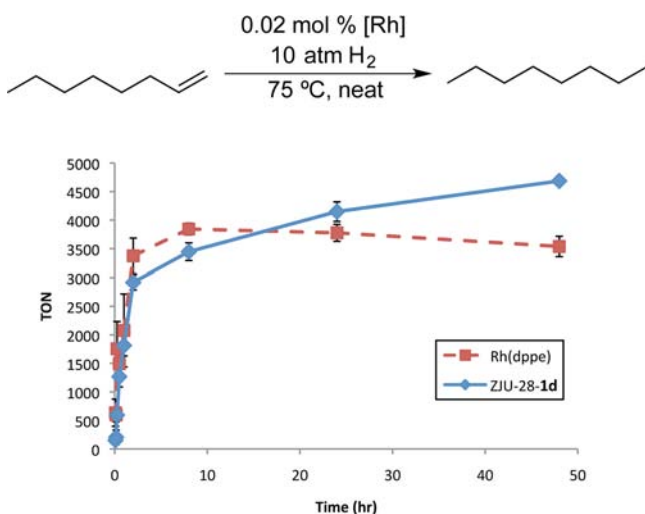

Figure 2. Hydrogenation of 1-octene to *n*-octane in acetone catalyzed by ZJU-28-**1d** (blue) and homogeneous **1d** (red). Conditions: 0.5 M 1-octene in acetone, 0.0013 mmol [Rh]. The maximum possible turnover number (TON) is 500.

To confirm that the active catalyst in ZJU-28-**1d** was heterogeneous (rather than a leached homogeneous Rh species), a three-phase test[29] was conducted using Merrifield resin-supported (*O*-linked) 1-hexenol as the alkene substrate. As shown in Figure S1, a solution of complex **1d** in acetone catalyzed the hydrogenation of the immobilized alkene, while no hydrogenation was observed with ZJU-28-**1d**.

As a further test of whether the catalytic activity required substrate diffusion into the pores of ZJU-28-**1d**, we used octa-*tert*-butyl-octa-*O*-allylcalix[8]arene[30] (**2**) as the alkene substrate. Substrate **2** has a kinetic diameter of >16 Å and therefore should be too large to diffuse into ZJU-28. As expected, hydrogenation of **2** was not detected with ZJU-28-**1d** (TON < 1), while the homogeneous catalyst **1d** effected 93 turnovers under otherwise identical conditions (eq 1).[31]
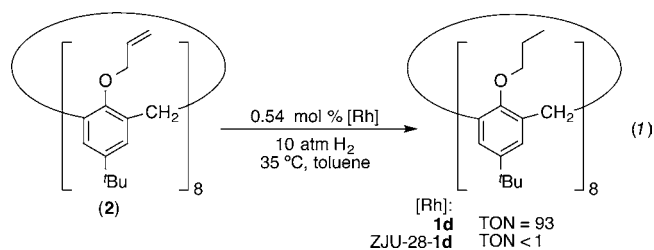

We next compared the hydrogenation of 1-octene with catalysts **1d** and ZJU-28-**1d** in the absence of solvent (neat in 1-octene). Under these conditions, the performance of ZJU-28-**1d** was superior to that of **1d** (Figure 3). Runs with **1d** showed poor reproducibility, with errors ranging from 150 to 750 turnovers;[32] furthermore, catalyst turnover ceased after 10 h, with concomitant formation of a black precipitate. In contrast, the performance of ZJU-28-**1d** was much more reproducible (with typical errors of 50−150 turnovers), and the reaction proceeded smoothly to convert 1-octene to *n*-octane completely over 48 h.[25] When the MOF catalyst was removed by filtration after 2 h and the mother liquor was repressurized with H$_2$, no additional turnovers were observed. This filter test experiment further supports the proposal that the MOF-supported catalyst, rather than leached homogeneous Rh, was responsible for the catalysis. In addition, ZJU-28-**1d** could be

$$\text{0.02 mol \% [Rh]} \atop \text{10 atm } H_2 \atop \text{75 °C, neat}$$

Figure 3. Hydrogenation of 1-octene to *n*-octane in neat 1-octene catalyzed by ZJU-28-**1d** (blue) and homogeneous **1d** (red). Conditions: 0.0013 mmol [Rh]. The maximum possible TON is 5000.

recycled four times with no erosion of the catalyst TON under our standard conditions (Figure 4).
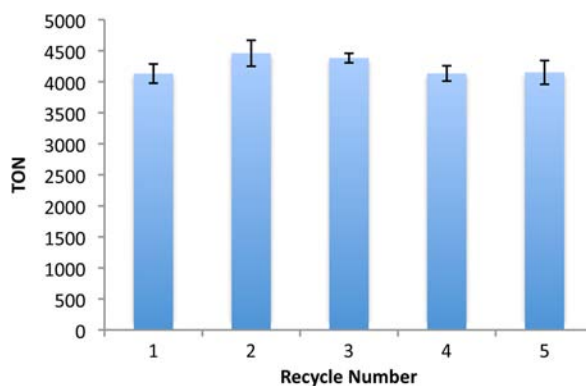
Figure 4. Recycling of ZJU-28-**1d** in the neat reduction of 1-octene to octane. Shown are TONs after 48 h using the standard catalytic conditions reported in Figure 3.

PXRD analysis of ZJU-28-**1d** following the final recycle showed that the crystalline material remained intact. Furthermore, the characteristic broad peaks typically associated with Rh nanoparticles at $2\theta = 41, 48, 70, 85,$ and $89°$ were not observed (Figure S3).[33] These data, in conjunction with the data from Figure 4, indicate that ZJU-28-**1d** is a robust, recyclable material under these catalytic hydrogenation conditions.

In conclusion, this communication has described a strategy for supporting molecular transition-metal catalysts in MOFs. The cation-exchange procedure enables the use of the native catalysts without modification of the ancillary ligands and/or MOF linkers. This method has been successfully applied to support a variety of different complexes. Furthermore, the Rh-containing MOF ZJU-28-**1d** was shown to be a recyclable catalyst for alkene hydrogenation that exhibited improved catalytic performance relative to its homogeneous counterpart **1d** under certain conditions. Ongoing work is focused on applying this strategy for the construction of new MOF-supported catalysts with tunable reactivity, stability, and selectivity.

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Notes

The authors declare no competing financial interest.

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(24) ZJU-28 is stable in the solid state upon heating to 120 °C. For thermogravimetric analysis, see Figure S5.

(25) For data on uptake with different concentrations of cationic metal complex **1d**, see Table S1.

(26) Hydrogenation was not observed with ZJU-28 as the catalyst.

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(28) We also conducted a filter test to assess whether traces of leached homogeneous Rh species could be responsible for catalysis with ZJU-28-**1d** in acetone. The reaction was run to 35% conversion, and then ZJU-28-**1d** was removed by filtration. When the mother liquor was repressurized with H_2, no additional turnovers were observed.

(29) For example, see: Weck, M.; Jones, C. W. *Inorg. Chem.* **2007**, *46*, 1865.

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(31) 1-Octene also undergoes hydrogenation under these conditions.

(32) This is likely due, at least in part, to the poor solubility of the cationic catalyst in this nonpolar medium.

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