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A Salicylaldimine-based Metal-Organic Framework Enables Highly Active Olefin Hydrogenation with Iron and Cobalt Catalysts

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Supporting Information Placeholder

ABSTRACT: A robust and porous Zr metal-organic framework, sal-MOF, of UiO topology was synthesized using a salicylaldimine (sal)-derived dicarboxylate bridging ligand. Post-synthetic metalation of sal-MOF with iron(II) or cobalt(II) chloride followed by treatment with $NaBEt_3H$ in THF resulted in Fe- and Co-functionalized MOFs (sal-M-MOF, M=Fe or Co) which are highly active solid catalysts for hydrogenation of alkenes. Impressively, sal-Fe-MOF displayed very high turnover numbers of up to 145,000 for alkene hydrogenation, and was recycled and reused more than 15 times. This work highlights the unique opportunity of developing MOF-based earth-abundant catalysts for sustainable chemical synthesis.

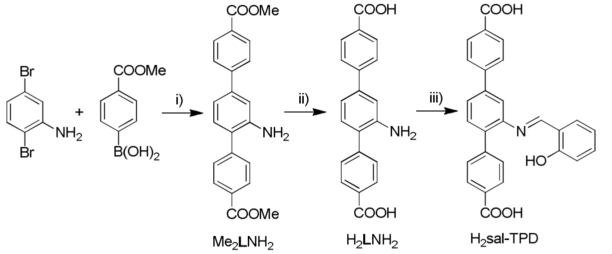
Although precious metal complexes dominate the homogeneous catalysis literature, few of them have found industrial applications owing to their high price and inherent toxicity.[1] The replacement of precious metals with earth-abundant and less toxic elements, i.e., base metals, is thus at the forefront of contemporary molecular catalysis, with significant progress being made in the past few years.[2-9] Nevertheless, homogeneous catalysts containing base metals are prone to deactivation via intermolecular pathways. Steric protection around the metal centers by elaborately designed, sterically hindered ligands is a common strategy for designing stable catalysts, often at the expense of catalytic activities. Immobilization of homogeneous catalysts in structurally regular porous solid supports can provide catalytic site isolation without relying on bulky ligands, thus offering an alternative route to obtaining highly active base metal catalysts. Such solid catalysts can be also readily recovered and reused, mitigating undesired metal leaching into the organic products. Herein we report the first use of a metal-organic framework (MOF) for immobilizing highly active Fe(II)- and Co(II)-salicylaldimine catalysts for hydrogenation of alkenes.

Hydrogenation of olefins is one of the most important reactions in organic synthesis, though many industrially important hydrogenation reactions still rely on precious metal catalysts.[10] Significant efforts have in recent years been devoted to discovering earth-abundant metal catalysts, particularly based on iron and cobalt complexes,[5,11-19] but many of these catalyst systems have limited lifetimes and modest activities. Parallel efforts have been devoted to the development of zeolite- and silica-supported iron- and cobalt-based heterogeneous hydrogenation catalysts,[20,21] bare or protected metallic nanoparticles,[22-28] or iron oxide nanoparticle-based catalysts.[29] However, the activities and lifetimes of these heterogeneous hydrogenation catalysts are still far from satisfactory.

As a new class of porous molecular materials, MOFs have attracted increasing interest in recent years owing to their potential applications in many areas, including gas storage, separation, chemical sensing, drug delivery, and catalysis.[30-39] In particular, MOFs have provided an interesting platform for engineering single-site solid catalysts for various organic transformations.[40-49] The pores and channels in MOFs serve as confined space for the attachment or encapsulation of molecular catalysts, providing catalytic site isolation and thus preventing bimolecular catalyst deactivation.[50,51] Incorporation of orthogonal secondary functional groups to MOF backbones allows convenient generation of different metal complexes, enabling screening and discovery of novel molecular catalysts. In this work, a MOF containing an orthogonal salicyladimine (sal) moiety (sal-MOF) was synthesized and post-synthetically metalated with iron and cobalt salts to afford robust and highly active single-site solid catalysts for olefin hydrogenation.

sal-MOF was constructed from the dicarboxylate bridging ligand, sal-TPD (Scheme 1) and the Zr-based secondary building unit (SBU) to afford a UiO framework of $Zr_6O_4(OH)_4$(sal-TPD)$_6$.[52-54] UiO-type MOFs have been used for many catalytic reactions owing to their excellent stability.[51,55,56] H_2sal-TPD was synthesized from 2,5-dibromoaniline as shown in Scheme 1 with an overall yield of 14%.

Scheme 1. Synthesis of H_2sal-TPD.[a]



[a]Reagents: (i) $Pd(OAc)_2$, CsF, PPh_3, THF, reflux, 12 h, 25% yield; (ii) KOH, MeOH, THF, 12 h, rt, and then TFA, THF, 2 h, rt, 90% yield; (iii) salicylaldehyde, DMSO, MeOH, 12 h, 60% yield.

sal-MOF was synthesized by heating $ZrCl_4$ and H_2sal-TPD in a DMF solution in the presence of trifluoroacetic acid. Single crystal X-ray diffraction studies reveal a UiO-type structure for sal-MOF, which crystallizes in the $Fm\overline{3}m$ space group and contains both octahedral and tetrahedral cages with edges measuring 15 Å. The asymmetric unit consists of 1/48 of the $Zr_6O_4(OH)_4(O_2CR)_{12}$ SBUs and 1/8 of the bridging ligands. As the sal groups could not be accurately located on the electron density map due to partial decomposition of H_2sal-TPD during MOF synthesis and crystallographic disorder of the side chains, the presence of the sal moiety in the MOF was instead established and quantified by ^{1}H NMR spectra of digested MOF samples. NMR studies consistently revealed ~80% of the sal moiety remains intact in the sal-MOF under the synthesis conditions (Figure S4, supporting information [SI]). The powder X-ray diffraction (PXRD) pattern of sal-MOF is identical to the pattern simulated from the single crystal structure (Figure 1d). Nitrogen sorption measurements indicate sal-MOF is highly porous with a BET surface area of 3311 m^2/g and pore sizes of 8.2 Å and 11.1 Å (Figure 1b; Figure S10, SI)

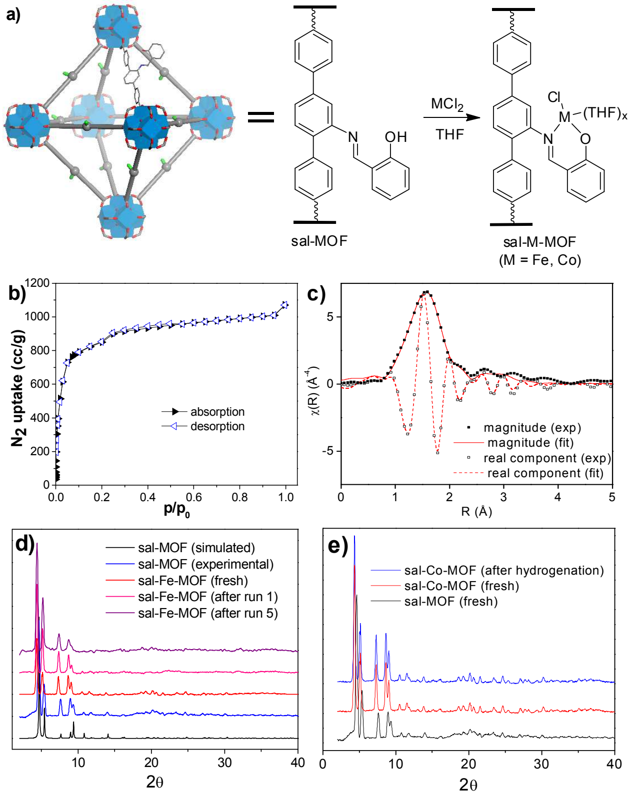


Figure 1. a) Post-synthetic metalation of sal-MOF to form sal-M-MOFs. b) Nitrogen sorption isotherm of sal-MOF. c) Experimental EXAFS spectra at the Fe K-edge of sal-Fe-MOF and fits in R-space showing the magnitude (solid squares, solid line) and real component (hollow squares, dash line) of the Fourier Transform. d) PXRD pattern simulated from the CIF file (black), and PXRD patterns of pristine sal-MOF (blue), freshly prepared sal-Fe-MOF (red), sal-Fe-MOF recovered from the 1st (pink) and 5th run (purple) of 1-octene hydrogenation. e) PXRD patterns of pristine sal-MOF (black), freshly prepared sal-Co-MOF (red), and sal-Co-MOF recovered from hydrogenation of 1-octene (blue).

Post-synthetic metalation was performed by treating sal-MOF with 5.0 equiv of $FeCl_2{\bullet}4H_2O$ in THF to afford sal-Fe-MOF as a brown solid, or with 7.0 equiv of $CoCl_2$ in THF to afford sal-Co-MOF as a greenish blue solid. Crystallinity of sal-MOF was maintained upon metalation as evidenced by similar PXRD patterns of sal-MOF and sal-M-MOFs (Figures 1d & 1e). Inductively coupled plasma-mass spectrometry (ICP-MS) analyses of the digested metalated MOFs provided Fe and Co loadings of 66% and 6% for sal-Fe-MOF and sal-Co-MOF, respectively. The Co loading increased to 80% when the MOF was first treated *t*-BuOK. ^1H NMR spectra of digested sal-Fe and sal-Co MOFs showed that the sal moiety remained intact within the MOFs upon metalation. sal-Fe-MOF and sal-Co-MOF give BET surface areas of 3101 and 3366 m^2/g, respectively, with pore size distributions remaining essentially unchanged from pristine sal-MOF (Figures S8-S10, SI). The surface area and pore aperture dimensions confirm the presence of open channels in the MOF, which suggests the Fe and Co sites are accessible to alkenes during catalytic reactions.

Due to disorder and incomplete functionalization and metalation of the sal-MOF, the Fe coordination environment in sal-Fe-MOF cannot be studied by X-ray crystallography. Instead, we performed X-ray absorption spectroscopy (XAS) at the Fe K-edge to investigate the Fe coordination environment. A model of the pre-catalyst was generated based on the single crystal structures of $Fe_4(sal)_4Cl_4(THF)_2$ (Figure 2a; see below) and Fe(*t*-Busal)$_2$.[57] Fitting the extended X-ray absorption fine structure (EXAFS) region of the XAS spectrum with the structure model reveals a Fe(II) complex containing the sal moiety, one chloride, and two to three THF solvent molecules as ligands (Figure 1c). DFT calculations suggest minimal energy differences (~2.5 kcal/mol) between five- and six-coordinate Fe(II) structures (Figure 2b). As EXAFS fits the average coordination environment for all Fe atoms in the sample, it is reasonable that the sample contains a mixture of five- and six-coordinate species, presumably due to the ease of losing coordinated THF molecules during sample handling.

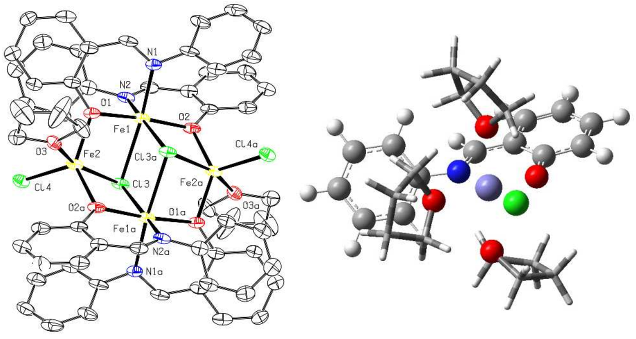
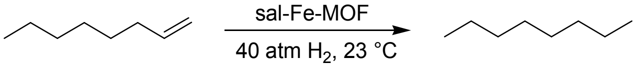


Figure 2. Crystal structure of $Fe_4(sal)_4Cl_4(THF)_2$ (left) and DFT calculated structure of Fe(sal)Cl(THF)$_3$ (right).

Table 1: Optimization of reaction conditions for sal-Fe-MOF catalyzed hydrogenation of 1-octene.[a]



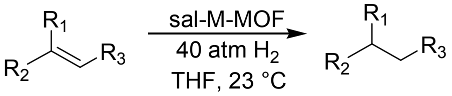
Entry	Catalyst Treatment	Solvent	Time	Yield (%)
1	$NaBEt_3H$	THF	16 h	100
2	*n*-BuLi	THF	18 h	0
3	EtMgCl	THF	18 h	0
4	Et_2Zn	THF	18 h	0
5	$NaBEt_3H$	THF	16 h	100[b]
6	$NaBEt_3H$/Hg[c]	THF	16 h	100[b]
7	$NaBEt_3H$	toluene	16 h	92[b]

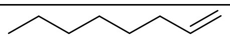
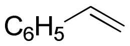
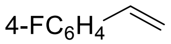
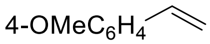
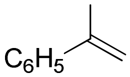
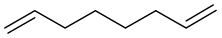
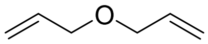
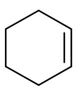
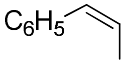
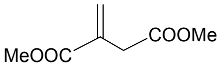
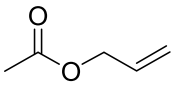
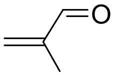
[a]Reaction conditions: 3.0 mg sal-Fe-MOF (0.1 mol% Fe), 0.8 mol% cat. treatment, 1.56 mmol 1-octene, 0.5 mL solvent. [b]0.01 mol% Fe. [c]One drop of Hg was added before adding 1-octene.

Conditions for hydrogenation were optimized by treating sal-Fe-MOF with several organometallic reagents. Upon treatment with $NaEt_3BH$ in THF, sal-Fe-MOF is a highly active catalyst for hydrogenation of olefins. Treatment of 0.01 mol% sal-MOF-Fe with $NaBEt_3H$ (8 equiv w.r.t. Fe) in THF for 1 h followed by washing with THF led to a highly active hydrogenation catalyst that completely converted 1-octene to *n*-octane under 40 atm H_2 at room temperature in 18 h. The rate of hydrogenation was unchanged in the presence of mercury (Table 1, entry 6), which suggests that *in situ*-generated Fe nanoparticles were not responsible for the observed catalysis and that Fe-hydride is the active species. Additionally, sal-Fe-MOF displayed higher catalytic activity in THF compared to methylene chloride and hydrocarbon solvents. Impressively, under the optimized reaction conditions, sal-Fe-MOF gave a turnover number (TON) of $1.45{\times}10^5$ for the hydrogenation of 1-octene (Table 2, entry 2).

sal-Fe-MOF displayed excellent activity in the hydrogenation of a wide range of aliphatic and aromatic terminal alkenes (Table 2). At 0.05-0.01 mol% catalyst loading, styrene and other alkoxy- and halogen-functionalized substrates were hydrogenated with complete conversion, affording the corresponding products in 93-100% yield (Table 2, entries 4, 7, and 8). Importantly, a TON of 44000 was obtained for hydrogenation of styrene. sal-Fe-MOF also displayed high TONs and excellent yields for the hydrogenation of *gem*-disubstituted alkenes, such as α-methyl styrene, and dialkenes such as 1,7-octadiene and allyl ether (Table 2, entries 10, 12, and 14). Although the internal olefin, cyclohexene, was readily hydrogenated, *cis*-*β*-methyl styrene required longer reaction times. sal-Fe-MOF is tolerant of aldehyde, ketone, and ester functional groups. Functionalized alkenes such as dimethyl itaconate, allyl acetate and methylacrylaldehyde were selectively reduced to dimethyl 2-methylsuccinate, propyl acetate, and isobutyraldehyde, respectively (Table 2, entries 18, 19, and 21).

Table 2: Sal-M-MOF catalyzed hydrogenation of olefins.^{a}



Entry	Substrate	M	Time	% Yield	TON
1		Fe	18 h	100	10000
2			8 d	94	145000^{b}
3		Co	18 h	75	25000
4		Fe	18 h	100	10000
5			24 h	44	44000^{c}
6		Co	18 h	55	18300
7		Fe	48 h	100	>20000^{d}
8		Fe	24 h	100	>10000
9		Co	18 h	100	>2000^{e}
10		Fe	18 h	100	>10000
11		Co	18 h	100	>2000^{e}
12		Fe	24 h	100	>2000^{e}
13		Co	18 h	100	>2000^{e}
14		Fe	24 h	100	>1000^{f}
15		Fe	18 h	100	>1000^{f}
16		Co	18 h	100	>2000^{e}
17		Fe	70 h	36	360^{f}
18		Fe	24 h	62	620^{f}
19		Fe	70 h	64	640^{f}
20		Co	72 h	0	0^{e}
21		Fe	3 d	76	760^{f}

^{a}Reaction conditions: 0.01 mol% sal-Fe-MOF or 0.003 mol% sal-Co-MOF, 10 equiv $NaBEt_3H$ (1.0 M in THF), alkene, THF, 40 atm H_2, 23 °C. ^{b}6.5 × 10^{-4} mol% catalyst. ^{c}0.001 mol% catalyst. ^{d}0.005 mol% catalyst. ^{e}0.05 mol% catalyst. ^{f}0.1 mol% catalyst.

Remarkably, at a 0.5 mol% catalyst loading, sal-Fe-MOF could be recovered and reused for 1-octene hydrogenation at least 8 times without loss of catalytic activity (Figure 3) or MOF crystallinity (Figure 1d). Excellent yields (89-99%) of *n*-octane were obtained consistently in the reuse experiments with no observation of alkene isomerization or other byproducts. The catalytic activity of sal-Fe-MOF dropped significantly after run 9 and poor conversion of 1-octene was observed at run 11 even after a longer reaction time (Figure 3). Interestingly, the catalyst could be regenerated by simply treating with 10 equiv. of $NaBEt_3H$ followed by washing with THF. The regenerated MOF catalyst could be recovered and reused another 6 times before further deactivation. The decrease in activity could be attributed to multiple factors including cumulative iron site deactivation by trace amounts of air or water and diminished MOF crystallinity following repeated recycling and reuse experiments. The heterogeneity of sal-Fe-MOF was confirmed by several experiments. The PXRD patterns of sal-Fe-MOF recovered from the 1st and 5th run remained unchanged from that of pristine sal-Fe-MOF (Figure 1d), indicating the stability of the MOF framework under the catalytic conditions. Additionally, ICP-MS analyses showed that the amounts of Fe and Zr leaching into the supernatant after the 1st run were 0.074% and 0.004%, respectively, and after the 4th run were 0.069% and 0.003%, respectively. Moreover, no further hydrogenation was observed after removal of sal-Fe-MOF from the reaction mixture (Scheme S2, SI). An additional control experiment was performed with only $FeCl_2$ and $NaBEt_3H$ at a loading equivalent to the amount of iron leached from the MOF. No conversion was observed by NMR spectroscopy, showing that the leached iron species is not responsible for the catalytic activity.

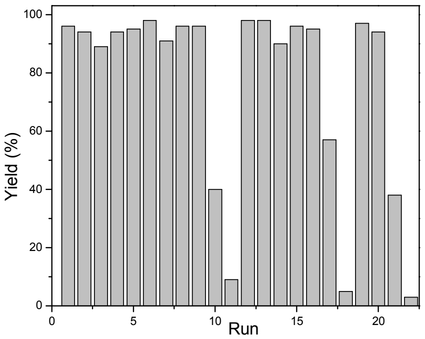


Figure 3. Plot of yield (%) of *n*-octane at various runs in the recycle and reuse of sal-Fe-MOF (0.5 mol% Fe) for hydrogenation of 1-octene. Sal-Fe-MOF was regenerated after run 11 and run 18 by treating with $NaBEt_3H$ in THF.

sal-Co-MOF is also active in olefin hydrogenation upon treatment with 8 equiv. of $NaBEt_3H$ in THF. At 0.05 mol% Co-loading, several aliphatic and aromatic alkenes, including dienes and internal olefins, were hydrogenated with full conversion (Table 2, entries 3, 6, 9, 11, 13, and 17). A maximum TON of 25000 was observed for sal-MOF-Co with 1-octene as the substrate. The sal-Co-MOF recovered from the dehydrogenation showed the same PXRD pattern as the pristine sal-MOF (Figure 1e), indicating that the sal-Co-MOF framework is also stable under the catalytic conditions.

We also prepared molecular $(sal)Fe(THF)_xCl$ species in order to investigate the role of the framework in stabilizing the sal-M catalysts. Repeated synthetic attempts under a variety of conditions afforded a tetrameric species with the formula of $Fe_4(sal)_4Cl_4(THF)_2$ as revealed by single crystal X-ray diffraction (Figure 2a). Formation of such a tetranuclear complex is expected as low-coordination-number Fe species are not stable in solution and can oligomerize through the Cl- or O-bridging ligands. In contrast, oligomerization is prohibited in sal-M-MOFs due to isolation of the metal sites. Importantly, $Fe_4(sal)_4Cl_4(THF)_2$ was inactive towards olefin hydrogenation following the same treatment with 8 equiv. of $NaBEt_3H$, revealing the critical role of site isolation for stabilizing the low-coordinate sal-M catalysts.

In summary, we have developed a novel post-synthetic metalation strategy to discover MOF-supported base metal catalysts which do not possess homogeneous counterparts. The UiO MOF bearing the M-salicylaldimine moiety (M = Fe and Co) are highly active single-site solid catalysts for alkene hydrogenation, and can be readily recycled and reused. This work thus shows that MOFs provide a new platform for discovering base metal catalysts with potential application in practical synthesis of fine chemicals.

ASSOCIATED CONTENT

Supporting Information

General experimental section; synthesis and characterization of the ligand and MOFs; MOF-catalyzed hydrogenation reactions; MOF catalyst recycle and reuse procedures; EXAFS details and fits; DFT calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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