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Promoting Frustrated Lewis Pair for Heterogeneous Chemoselective Hydrogenation via Tailored Pore Environment within Metal-Organic Framework

Zheng Niu, Weijie Zhang, Pui Ching Lan, Briana Aguila, and Shengqian Ma*

Abstract: Frustrated Lewis pairs (FLPs) have recently been advanced as efficient metal-free catalysts for catalytic hydrogenation, but their performance in chemoselective hydrogenation, particularly in heterogeneous systems, has not yet been achieved. In this work, we demonstrate that, via delicately tailoring the pore environment within metal-organic framework (MOF), FLP not only can be stabilized but also can be rendered with interesting performance in chemoselective hydrogenation of α, β-unsaturated organic compounds, which otherwise cannot be achieved for FLP in a homogeneous system. Specifically, directly using hydrogen gas under moderate pressure, the FLP anchored within the MOF that features open metal sites and hydroxyl groups on the pore walls can serve as a highly efficient heterogeneous catalyst to selectively reduce the imine bond in α, β-unsaturated imine substrates to afford unsaturated amine compounds. The density functional theory (DFT) calculation studies indicate that the –OH group and open metal site in the MOF can preferentially interact with the C=N group (rather than the C=C group) of α, β-unsaturated imines to activate it, thus promoting the selectivity for the formation of unsaturated amines. Our work not only lays a foundation to develop MOF-FLP as a new platform for heterogeneous chemoselective catalysis, but also paves a new avenue for the design of precious metal-free chemoselective catalysts.

Catalytic hydrogenation of organic compounds containing unsaturated bonds has drawn comprehensive attention since the early 20th century, given the atom economy and cleanliness of the transformation as well as its ubiquitousness in industrial processes. Heterogeneous hydrogenation catalysis has been dominated by precious metals (Pd/Pt/Ru/Rh/Ir). These catalysts have shown high efficiency and selectivity compared to stoichiometric reductants. However, the scarcity and high cost of precious metal catalysts cast a shadow on their broader applications in industry. Moreover, chemoselective hydrogenation, e.g., selective reduction of α, β-unsaturated organic compounds, has been a challenging topic since the early stage of hydrogenation development, which would need the delicate design and manipulation of the catalyst system.

The emergence of frustrated Lewis pairs (FLPs), as pioneered by Stephan in 2006, suggests different pathways for the activation of H₂ and other small molecules. Tremendous progress has been witnessed for the development of FLPs as metal-free catalysts for the hydrogenation of many types of unsaturated compounds, including olefins, alkynes, imines, esters, ketones, and aziridines. Chemoselective hydrogenation of α, β-unsaturated organic compounds has been reported for some FLP catalysts in homogeneous systems but with the tendency to preferentially reduce the carbon–carbon double bond, which is thermodynamically favored. It remains a significant challenge for FLP catalysts to selectively hydrogenate α, β-unsaturated organic compounds to afford the relevant olefin product let alone in heterogeneous systems.

Recently, we demonstrated the successful introduction of Lewis pair (LP) into metal-organic framework (MOF), which exhibited enhanced stability and excellent recyclability, as well as interesting catalysis performance for imine reduction reactions and hydrogenation of olefins. Indeed, the diverse yet tunable features of MOFs make them an efficient platform to engineer heterogeneous catalysts for various organic transformations that traditional porous materials simply cannot provide. On the basis of our recent success, to promote FLP for heterogeneous chemoselective hydrogenation of α, β-unsaturated organic compounds, we postulate that the MOF pore environment can be delicately tailored with “ports” to anchor FLP, meanwhile “activation” groups preferably interact with the targeted double bond in the substrate, thereby producing selective reduction during the hydrogenation process (Scheme 1).

We selected the MOF, MIL-101 (Cr) as the platform considering that it can be prepared with the secondary building unit (SBU) in the form of Cr₄(μ₃-O)(COO)₆(OH)(H₂O); we envision that upon dehydration, the SBU can expose two Cr(III) sites with one as the “port” to anchor FLP and the other, together with the hydroxyl group residing at the third Cr(III) site, to preferably interact with the targeted double bond in the substrate...
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to facilitate its “activation” (Scheme 2). Bearing this in mind, in this work we successfully anchored the FLP of B(C$_6$F$_5$)$_2$(Mes)/DABCO into MIL-101 (Cr), and directly using H$_2$ gas at room temperature the resultant MIL-101 (Cr)-FLP can selectively hydrogenate the imine bond in α, β-unsaturated imine compounds to afford unsaturated amine compounds, which cannot be achieved for FLP in a homogeneous system. Our work presents the first example of an FLP-based catalyst capable of selectively hydrogenating α, β-unsaturated organic compounds, thereby paving a new avenue for the design of precious metal-free chemoselective heterogeneous catalysts.

Scheme 2. Illustration of “activation” process based on Cr$_{6}$(µ$_2$-O)(COO)$_{2}$(OH)(H$_2$O)$_2$ cluster in MIL-101(Cr)-FLP-H$_2$.

MIL-101(Cr) possessing the SBU of Cr$_{6}$(µ$_2$-O)(COO)$_{2}$(OH)(H$_2$O)$_2$ was prepared according to the procedure reported in the literature$^{14}$ and was dehydrated before the introduction of FLP. The Lewis base of 1, 4-diazabicyclo[2.2.2]octane (DABCO) that features two binding nitrogens, with one to anchor at the open Cr(III) and the other to interact with the Lewis acid, was first grafted into MOF to form MIL-101 (Cr)-LB (Scheme S1). In order to stabilize the anchored FLP, Lewis acid B(C$_6$F$_5$)$_2$(Mes) was added into MIL-101 (Cr)-LB, and then reacted with H$_2$ to afford HB(C$_6$F$_5$)$_2$(Mes)/DABCO−pair anchored MIL-101 (Cr), which is denoted as MIL-101(Cr)-FLP-H$_2$. (Scheme S2) MIL-101(Cr)-FLP-H$_2$ (1.0 mmol FLP per 1 g MIL-101(Cr) or 0.34 FLP per unsaturated Cr site) was used in the following characterizations.

Figure 1. (a) $^{11}$B NMR spectrum of MIL-101(Cr)-FLP-H$_2$ and FLP; (b) IR spectra of MIL-101(Cr), FLP, and MIL-101(Cr)-FLP-H$_2$.

$^{11}$B NMR measurements were carried out to investigate the FLP with activated hydrogen that is anchored on the pore wall of MIL-101(Cr)-FLP-H$_2$. As shown in Figure 1a, the $^{11}$B NMR spectrum of the mixture of B(C$_6$F$_5$)$_2$(Mes) and DABCO shows a peak at 66.1 ppm, indicative of an extremely weak interaction between LA and LB. After reacting LA with MIL-101(Cr)-LB in toluene under 10 bar H$_2$ atmosphere and at room temperature for 24 h, the solid-state $^{11}$B NMR measurement gave a distinct peak at -22.4 ppm, which is comparable to that of the homogeneous [H(DBACO)]·[HB(C$_6$F$_5$)$_2$(Mes)] (d=22.5 ppm) and related [HB(C$_6$F$_5$)$_2$(Mes)]LB system (d=22.1 ppm), thus confirming the formation of the presumed ammonium hydridoborate of FLP. Furthermore, the peaks from the solid state $^{13}$F NMR spectrum (Figure S1) of MIL-101(Cr)-FLP-H$_2$ are consistent with the formation of a tetracoordinate anionic borate, further confirming the existence of FLP ammonium hydridoborate within the MOF. The porosity and phase purity of MIL-101(Cr)-LB and MIL-101(Cr)-FLP-H$_2$ were investigated by N$_2$ gas sorption at 77 K and powder X-ray diffraction (PXRD) measurements, respectively. As shown in Figure S2, the PXRD patterns of MIL-101(Cr)-LB and MIL-101(Cr)-FLP-H$_2$ are in good agreement with the calculated ones and those of the pristine MIL-101(Cr), indicating the retention of the framework’s structural integrity during the stepwise loading process. The N$_2$ sorption studies (Figure S3) indicated that in comparison with pristine MIL-101(Cr), there is a steady decrease in the BET surface area (from 2724 to 2196 and 1112 m$^2$/g) and reduction in pore sizes (Figure S4, SS and S6) for MIL-101(Cr)-LB and MIL-101(Cr)-FLP-H$_2$ due to the LB and FLP molecules grafted onto the pore wall of MIL-101(Cr).

The Fourier transform infrared (FT-IR) spectroscopy analysis was employed to verify the association of FLP and MIL-101(Cr) framework. The spectrum of MIL-101(Cr)-FLP-H$_2$ shows the characteristic peaks from LB and LA (Figure S7). As shown in Figure 1b, the presence of a new band at high wavenumbers (3000–3030 cm$^{-1}$) is due to the methyl C–H stretching vibrations of LA, and the new band around 1466 is owing to the aliphatic C–H stretching vibrations of LB. The above notable new bands of MIL-101(Cr)-FLP-H$_2$ further suggest the existence of the FLP-H$_2$ inside the MOF.$^{15}$

The coordination interaction between FLP and the open Cr(III) sites in MIL-101(Cr) was investigated by X-ray photoelectron spectroscopy (XPS) spectra of MIL-101(Cr) and MIL-101(Cr)-FLP-H$_2$. As presented in Figure S8 and S9, the Cr(2p) spectrum of MIL-101(Cr)-FLP-H$_2$ is notably different from the Cr(2p) spectrum of MIL-101(Cr). The Cr (2p$_{1/2}$) and Cr (2p$_{3/2}$) peaks of MIL-101(Cr)-FLP-H$_2$ are shifted by ca. 0.58 eV toward higher binding energies, compared to those of MIL-101(Cr). Such shifts indicate an change in the electron density of Cr(III), which can be attributed to the interaction between Cr and DABCO. The survey spectrum of MIL-101(Cr)-FLP-H$_2$ indicates the existence of the F and N elements of the FLP molecule within the MOF (Figure S10). The morphology of MIL-101(Cr)-FLP-H$_2$ was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 2a and 2b, the SEM and TEM images exhibited regular octahedral crystals of MIL-101(Cr)-FLP-H$_2$ with an average diameter of ~100 nm. To investigate the distribution of FLP-H$_2$ in MIL-101(Cr)-FLP-H$_2$, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) elemental mapping analyses were conducted. As presented in Figure 2c, the Cr, F, and N elements are evenly distributed inside the octahedral crystal of MIL-101(Cr)-FLP-H$_2$, suggesting the integration of FLP inside the pores of the MOF. These results indicated that the LP was homogeneously distributed in the MIL-101(Cr) pores without the presence of accumulation in particular regions.
To investigate the optimal loading amount for catalyzing the imine reduction reactions, we prepared a series of MOF-FLP with different FLP uptake amounts, (MIL-101(Cr)-FLP-H₂-1 (0.5 mmol FLP per 1 g MIL-101(Cr)) and MIL-101(Cr)-FLP-H₂-2 (0.75 mmol FLP per 1 g MIL-101(Cr))). The loading amount of FLP in the above samples was quantified with ¹H NMR by decomposing MOF-FLP in 10 wt% NaOH deuterium oxide solution (Figure S11, S12 and S13). The catalytic performances of the MIL-101(Cr)-FLP-H₂ catalysts were evaluated by exposing N-tert-butyl-1-phenylmethanamine (1a) to 20 mg catalyst in toluene, resulting in the reduction to N-Benzyl-tert-butylamine (1b) at 10 bar H₂ atmosphere and room temperature after 48 h. As presented in Table S2, along with the increase of FLP loading amount, the catalytic yield for the above reaction increased. The MOF-FLP with the lowest amount of FLP, MIL-101(Cr)-FLP-H₂-1, only gave 36% yield, whereas the highest uptake amount of FLP loaded MIL-101(Cr)-FLP-H₂ exhibited complete conversion. Therefore, MIL-101(Cr)-FLP-H₂ was chosen for the following catalysis studies. The control experiments using pristine MIL-101(Cr), MIL-101(Cr)-LB, and MIL-101(Cr)/LA were conducted, however no reduction product was detected in the reaction solvent even after 72h, suggesting MIL-101(Cr), MIL-101(Cr)-LB, and MIL-101(Cr)/LA are inactive for the imine reduction reaction.

Imine compounds with different substituting groups were employed to investigate the catalytic property of heterogeneous MIL-101(Cr)-FLP-H₂. As shown in Table S3, the reaction yields catalyzed by MIL-101(Cr)-FLP-H₂ from related imine compounds are 68% for N-Benzylideneaniline (2a), 91% for N-Benzylidene-1-phenylmethanamine (3a), and 58% for acridine (4a). The catalysis results reveal that the steric effect close to the N atoms can affect the catalytic performance. The steric effect could be presumably owing to the confinement effect imparted by the porous structure of the MOF, which restricts the accessibility of the C=N double bonds to the FLP active centers that are anchored on the pore walls of the MOF. Along with the increase in size of the imine substrate, the reduction reaction yield decreased. The reaction yield catalyzed by MIL-101(Cr)-FLP-H₂ for 5a is 21% and none of the product could be observed for 6a even after 72 h. Considering the existence of the coordinated FLP on the window, the size of the window (with diameters of 1.0 nm) is smaller than the diameter of 6a molecule (with diameters of 1.3 nm), thus the large imine molecule could not enter into the pores of MIL-101(Cr)-FLP-H₂. Therefore, the observed size selectivity performance of MIL-101(Cr)-FLP-H₂ can be attributed to the restriction of the window structure in the framework.

Table 1. The catalysis studies for hydrogenation of α, β-unsaturated imine compounds

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
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<tr>
<td>1</td>
<td>7a</td>
<td>7b</td>
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</tr>
<tr>
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<td>100%</td>
</tr>
<tr>
<td>7</td>
<td>12a</td>
<td>12b</td>
<td>93%</td>
</tr>
</tbody>
</table>

*Reaction conditions: 20 mg (10 mol% FLP) MIL-101(Cr)-FLP-H₂, 0.13 mmol substrate, 3 mL toluene, room temperature, 48 h. **Reaction conditions: 10 mol% FLP, 0.13 mmol 7b, 3 mL toluene, room temperature, 48 h.

Considering the interesting catalytic performance of MIL-101(Cr)-FLP-H₂ in the above imine reduction reactions, we decided to examine MIL-101(Cr)-FLP-H₂ for selective catalytic hydrogenation of the α, β-unsaturated imine compounds directly using hydrogen gas, which has barely been explored in both homogeneous and heterogeneous systems.12 Interestingly, for the substrate 7a, both imine and alkene double bonds were reduced in the case of homogeneous FLP, and no 7b can be observed after the catalytic reaction. However, the heterogeneous MIL-101(Cr)-FLP-H₂ shows a yield of 87% 7b for 7a under the same reaction conditions. This excellent selectivity could be attributed to the hydrogen bonding between the N atoms of the imines and the -OH groups from the framework and/or the interaction between the N atoms of the imines and remaining open metal sites.16 The α, β-unsaturated imine compounds with different substituted groups were employed to further investigate the chemoselective catalysis performance of the heterogeneous MIL-101(Cr)-FLP-H₂. As presented in Table 1, the reaction yields catalyzed by MIL-101(Cr)-FLP-H₂ from the related α, β-unsaturated imine compounds are 100% for 8a, 91% for 9a, 81% for 10a, 100% for 11a, and 93% for 12a. The high yields of these products highlight that MIL-101(Cr)-FLP-H₂ can serve as a porous FLP catalyst with excellent catalytic performance in the chemoselective hydrogenation reactions, which has not been achieved previously for any FLP-based catalyst.
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On the basis of the reported homogenous FLP catalyzed hydrogenation reactions and the solid-state 19F NMR of MIL-101(Cr)-FLP-H2 results, the tentative catalysis mechanism of MIL-101(Cr)-FLP-H2 catalyzed imine reduction reactions is proposed as illustrated in Figure S14. The process is initiated by the reaction between MIL-101(Cr)-FLP-H2 and the imine substrate. The [HBMes(CrF3)2] reduces the imine substrate and then converts to BMes(CrF3)2, while the MIL-101(Cr)-[LBH]+ converts to MIL-101(Cr)-LB. Subsequently, the MIL-101(Cr)-LB and BMes(CrF3)2 react with hydrogen to regenerate the MIL-101(Cr)-FLP-H2 and complete the catalysis cycle.

Density functional theory (DFT) calculations were employed to understand the tentative mechanism of the chemoselective hydrogenation of α, β-unsaturated imine compounds. As shown in Figure 3, the unsaturated Cr(III) sites and the hydroxyl group in Cr2O(OH)(COO)3H2O trimers of MIL-101 can serve as “active” sites that interact with the C=N group of 7a molecule. The calculated adsorption energy of 7a over the unsaturated Cr(III) sites and the hydroxyl group in Cr2O(OH)(COO)3H2O trimers is -33.77 and -34.83 kJ mol⁻¹, respectively; that is, binding between the trimers and 7a through N-HO and N-Cr is thermodynamically favored, with the interaction between 7a and hydroxyl group in Cr2O(OH)(COO)3H2O trimers being slightly stronger (Figure S15 and S16). Therefore, different from the homogenous catalyst, the MOF catalyst can selectively reduce the C=N bond in α, β-unsaturated imine compounds. These results support the experimental observation that the –OH groups and remaining open Cr(III) sites in MIL-101(Cr) preferentially interact with the C=N group (rather than the C=C group) of 7a thus to activate it, giving rise to the improved selectivity for the formation of product 7b.

In industrial processes, the recyclability and long-term stability of the catalyst are of utmost importance. Based on this consideration, we investigated the stability and recycling performance of MIL-101(Cr)-FLP-H2. MIL-101(Cr)-FLP-H2 can be readily recycled with great catalytic performance, and the yield of the catalysis reaction can maintain 100% percent even at the fifth recycling experiment (Figure S17). The 1H NMR data of the decomposed MIL-101(Cr)-FLP-H2 in 10 wt% NaOH deuterium oxide solution after five cycles of catalytic reaction matches the original MIL-101(Cr)-LB, thus reinforcing the idea that the LB portion of FLP is competently bound to the Cr(III) sites. The robustness of the catalyst was further confirmed by the well-retained crystallinity and pore structure in MIL-101(Cr)-FLP-H2 after the catalytic reaction, as evidenced by PXRD and N2 adsorption studies, respectively (Figure S18 and S19).

In summary, we demonstrated the successful incorporation of a frustrated Lewis pair (FLP) into the MOF, MIL-101(Cr) with a tailored pore environment featuring open metal sites and hydroxyl groups in the SBUs. Such tailored pore environment stabilizes the FLP through strong coordination interaction between LB and MOF thereby rendering it with excellent recyclability as well as interesting catalytic activity for catalytic reduction of imines with direct utilization of hydrogen gas under moderate pressure. Moreover, the hydroxyl groups and open metal sites from the tailored pore environment within the MOF promote the anchored FLP with great performance in the chemoselective hydrogenation of α, β-unsaturated imines through the preferential interaction between C=N group (rather than the C=C group) and the –OH group and remaining open Cr(III) site in catalyst, as indicated by DFT calculations. Our work not only lays a foundation to develop MOF-FLP as a new generation of efficient chemoselective heterogeneous catalyst, but also paves a new avenue for the design of precious metal-free chemoselective catalysts.

Acknowledgements

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Keywords: Frustrated Lewis Pair • MOF • heterogeneous • chemoselective catalysis • hydrogenation


The FLP anchored MOF that features activation groups including open metal sites and hydroxyl groups has been synthesized, and it can serve as a highly efficient heterogeneous catalyst to selectively reduce the imine bond in α, β-unsaturated imine substrates to afford unsaturated amine compounds by directly using hydrogen gas under moderate pressure.