MOF-Based Catalysts

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Engineering a Metal–Organic Framework Catalyst by Using Postsynthetic Modification**

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Metal–organic frameworks (MOFs) are porous, crystalline materials that have gathered increasing attention owing to their high surface areas, uniform pores, and chemical tunability.[1–6] The ability to synthesize a wide range of MOFs has made them attractive materials for applications in gas sorption, separations, and catalysis.[7–12] Recently, postsynthetic modification (PSM) of MOFs has been shown to be a general, practical approach for incorporating a wide range of functional groups into MOFs.[13] We[14–19] and others[20–31] have shown that topologically diverse MOFs can be customized by PSM with many different types of functional groups. Herein, PSM is shown to be a novel route to obtain active, stable, and recyclable MOF-based catalysts.

Previous reports have described the use of PSM to introduce metal-binding sites into MOFs. The treatment of several different MOFs with succinic anhydride has resulted in materials containing free (i.e. uncoordinated) carboxylic acid groups.[19,29] In one of these reports, it was demonstrated that the carboxylate-bearing MOF could coordinate Cu^{2+} ions from solution.[29] In another study, an isoreticular metal–organic framework (IRMOF-3) was treated with salicylaldehyde, generating salicylimine (salen) chelators within the MOF lattice with approximately 13 % conversion.[22] The salicylimine sites were metallated with $[V(O)(acac)_2H_2O]$ (acac = acetylacetonate) and the resulting MOF was shown to oxidize cyclohexene in the presence of *t*BuOOH. This prior study nicely demonstrated that PSM could generate active metal sites into a MOF; however, the system was limited by low activity and reusability, probably a result of framework collapse. In a very recent report, a similar imine condensation was reported between 2-pyridinecarboxyaldehyde and UMCM-1-NH_2.[31] UMCM-1-NH_2, a MOF synthesized from BTB (4,4′,4′′-benzene-1,3,5-triyl-tribenzoate), NH_2-BDC (2-amino-1,4-benzenedicarboxylic acid), and $Zn(NO)_3$, was selected because of its large open channels that allow for facile diffusion of reagents.[18] The modified MOF, containing iminopyridine moieties was successfully metallated with $[PdCl_2(CH_3CN)_2]$, but no enhanced chemical functionality or reactivity was reported for the palladium-containing material. Herein, a complete demonstration of the introduction of isolated, reactive metal sites using two different chelating ligands and two different metal ions is presented. Furthermore, one of these metallated frameworks is shown to be an active, robust, and reusable MOF-based catalyst.

3-Hydroxyphthalic anhydride and 2,3-pyrazinedicarboxylic anhydride were selected as reagents for generating competent metal binding sites within a MOF. As previously mentioned, UMCM-1-NH_2 has large pores and a very high surface area (BET ca. 3900 $m^2\,g^{-1}$) capable of accommodating not only substituents introduced by PSM, but also substrates for catalytic transformations.[18] Under mild reaction conditions (see Supporting Information) UMCM-1-NH_2 was successful transformed with 3-hydroxyphthalic anhydride and 2,3-pyrazinedicarboxylic anhydride into two new MOFs designated UMCM-1-AMsal and UMCM-1-AMpz, respectively (Scheme 1). ^{1}H NMR spectra of digested samples (dissolved in DMSO/DCl) indicated approximately 35 % modification for UMCM-1-AMsal and approximately 50 % modification in UMCM-1-AMpz (Figure 1, Supporting Information Figure S1). The ^{1}H NMR spectroscopy and mass spectrometry data also confirm that these anhydrides give products that do not cyclize to give imide products, but rather form substituents with free carboxylate groups (Supporting Information, Figure S1); this is consistent with reports of PSM using other cyclic anhydrides.[19,29] Thermal gravimetric analysis (TGA) and powder X-ray diffraction (PXRD) confirm the modified MOFs have comparable thermal stability and crystallinity to the parent UMCM-1-NH_2, thus showing that metal chelating groups can be introduced without disrupting the framework (Supporting Information, Figure S2). BET surface area measurements (dinitrogen) indicated both modified materials had surface areas of approximately 3600 $m^2\,g^{-1}$ (Supporting Information, Table S1).

UMCM-1-AMsal and UMCM-1-AMpz were examined for their ability to bind metal ions. $[Fe(acac)_3]$ and $[Cu(acac)_2]$ were chosen as metal sources because of their solubility in $CHCl_3$ and for the distinct color changes expected upon chelation with salicylate and pyrazine carboxylate ligands, respectively. Addition of $[Fe(acac)_3]$ to UMCM-1-AMsal resulted in an immediate color change from pale yellow to dark red. Likewise, UMCM-1-AMpz instantly became bluish green in the presence of $[Cu(acac)_2]$. TGA and PXRD analysis of the iron and copper containing products UMCM-1-AMFesal and UMCM-1-AMCupz, respectively, confirmed that metallation did not compromise the thermal stability or structural integrity of the MOFs (Figure 2, Supporting Information, Figure S2). BET surface area measurements

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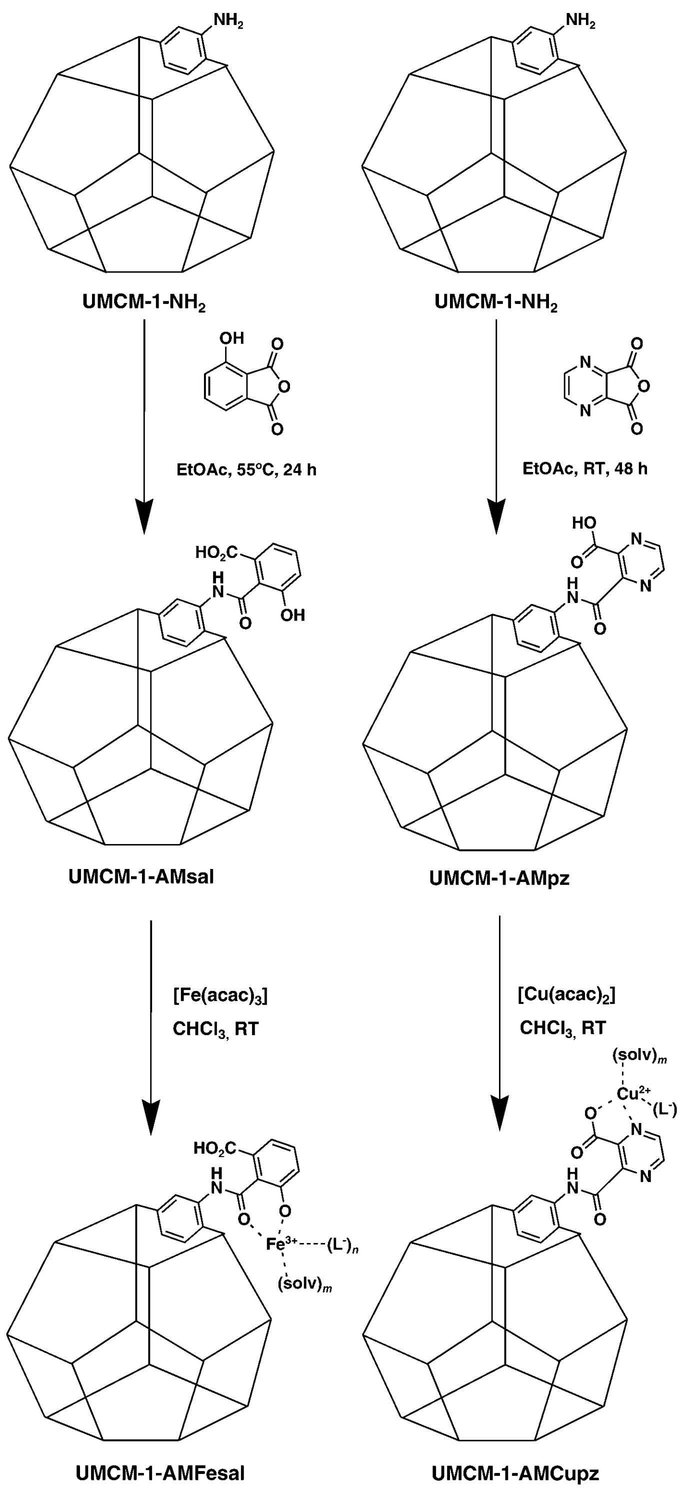


Scheme 1. Synthesis of UMCM-1-AMFesal (left) and UMCM-1-AMCupz (right).

also showed that the metallated MOFs remained highly porous (ca. 3600 $m^2 g^{-1}$ for UMCM-1-AMFesal and ca. 3400 $m^2 g^{-1}$ for UMCM-1-AMCupz, Supporting Information, Table S1).

The metallation detected between the chelator-modified MOFs and Fe^{3+} or Cu^{2+} was not detected with unmodified UMCM-1-NH_2. Diffuse reflectance electronic spectroscopy on crystalline samples of UMCM-1-NH_2, UMCM-1-AMsal, and UMCM-1-AMpz did not show any significant transitions beyond 400 nm. Treatment of UMCM-1-NH_2 with either [Fe(acac)$_3$] or [Cu(acac)$_2$] generated negligible changes in the reflectance spectra (Figure 3, Supporting Information, Figure S3); however, UMCM-1-AMFesal showed a distinct band centered around 500 nm (Figure 3), while UMCM-1-AMCupz had a band at approximately 700 nm (Supporting Information, Figure S3). These spectroscopic features are consistent with Fe^{3+} salicylate and Cu^{2+} pyrazine carboxylate compounds.[32,33] Selective metallation of the modified MOFs was further confirmed by using atomic absorption (AA) analysis. Analysis of UMCM-1-NH_2 confirmed that uptake of

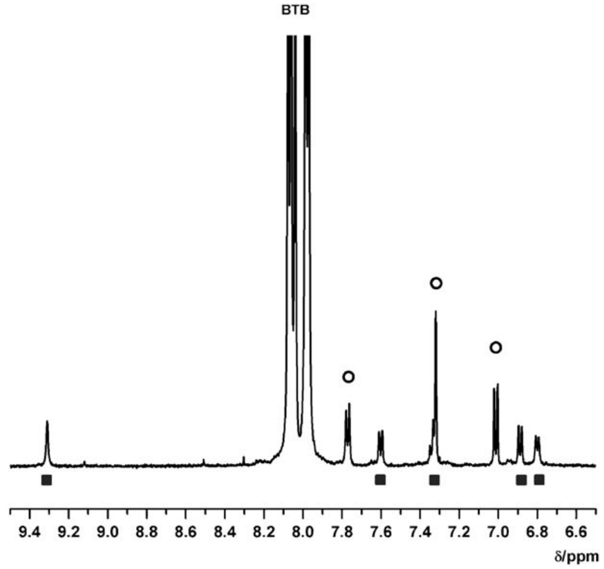


Figure 1. ^{1}H NMR spectra of digested UMCM-1-AMsal (ca. 35% modified). Unmodified NH_2-BDC (○), modified NH_2-BDC (■). An additional resonance for the modified ligand is obscured by the large BTB peaks.

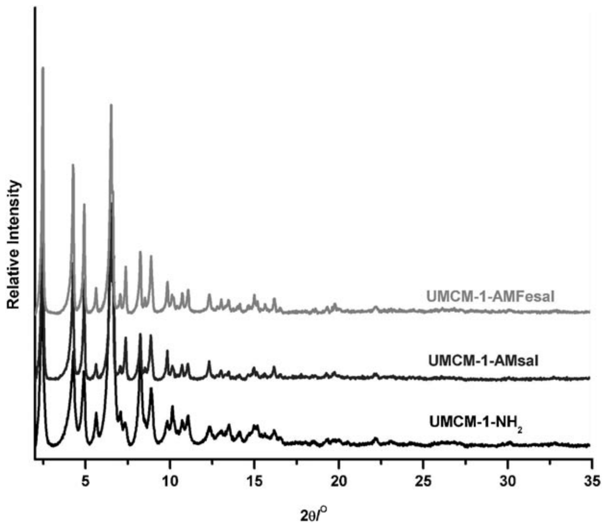


Figure 2. PXRD analysis of UMCM-1-NH_2 (bottom), UMCM-1-AMsal (middle), and UMCM-1-AMFesal (top).

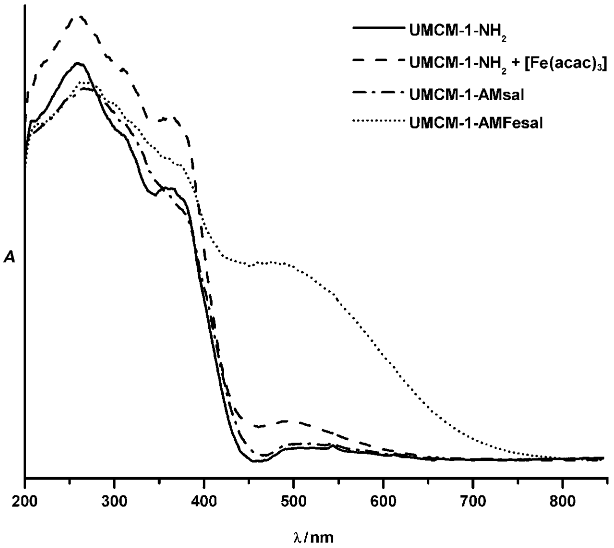
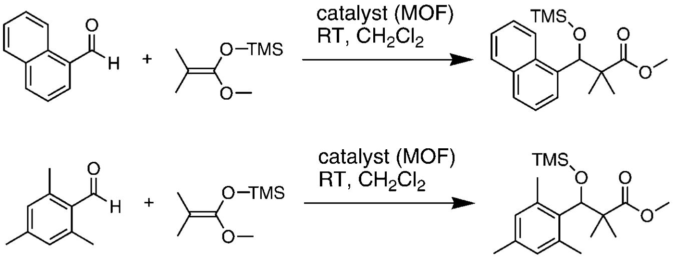


Figure 3. Diffuse reflectance solid-state UV/Vis spectra of UMCM-1-NH_2 (——), UMCM-1-NH_2 treated with [Fe(acac)$_3$] (–––), UMCM-1-AMsal (–•–•), and UMCM-1-AMFesal (••••).

either Fe^{3+} or Cu^{2+} ions was less than 0.06 wt %. In contrast, UMCM-1-AMFesal was found to contain 0.77 wt % of Fe^{3+}, and UMCM-1-AMCupz was found to have 1.76 wt % of Cu^{2+} ions (Supporting Information, Table S2). Based on the number of modified sites (see above), about 50 % of the chelator sites are metallated in UMCM-1-AMFesal and UMCM-1-AMCupz (assuming a 1:1 metal:ligand ratio). These experiments clearly show that metallation was selective for the MOFs that had undergone PSM with chelating moieties.

Having successfully introduced Lewis acidic Fe^{3+} sites into the MOF, the ability of this material to act as a solid-state catalyst was explored. UMCM-1-AMFesal was used to catalyze the Mukaiyama-aldol reaction, an important carbon–carbon bond forming reaction. The Mukaiyama-aldol reaction can be conducted under mild conditions and facilitated by Lewis acids at low temperatures and in solvents compatible with the UMCM family of MOFs.[34] Reaction mixtures contained 0.014 mmol (0.0001 mmol of Fe^{3+}) of UMCM-1-AMFesal, 0.1 mmol of aldehyde (mesitaldehyde or 1-naphthaldehyde), and 0.2 mmol 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (Scheme 2). Catalysis with UMCM-1-AMFesal was performed at room temperature in CH_2Cl_2 for 24 h, in order to compare our results with a reported MOF catalyst.[35] Control reactions were prepared under identical conditions, but included UMCM-1-NH_2, UMCM-1-NH_2 treated with [Fe(acac)$_3$], UMCM-1-AMsal, or no MOF at all, instead of UMCM-1-AMFesal. To determine the reaction yield, the supernatant solution of each reaction mixture was analyzed by ^1H NMR spectroscopy (Supporting Information, Figure S4, Figure S5). After 24 h, the control reactions all gave less than 10 % conversion and in the presence of UMCM-1-NH_2 treated with [Fe(acac)$_3$], approximately 27 % conversion was achieved in the first round of catalysis, but this sharply dropped off upon recycling (Table 1). In contrast, UMCM-1-AMFesal showed approximately 58 % conversion in 24 h at room temperature with both aldehydes over three catalytic cycles. By comparison, a recently reported MOF-based catalyst reported conversions as high as 63 % with benzaldehyde and 24 % with *tert*-butylbenzaldehyde, but after 99 h in the presence of 0.2 mmol Mn^{2+} ions.[35] The results reported herein give comparable yields in less than one-third the time and approximately 2000-fold less metal loading. Size selectivity was observed with UMCM-1-AMFesal, as the reaction of either aldehyde with a larger silyl enol, namely (1-*tert*-butylvinyloxy)trimethylsilane, showed no turnover after 24 h (Supporting Information, Figure S6), providing evidence that catalysis takes place within the pores of the MOF.



Scheme 2. Mukaiyama-aldol reactions with 1-naphthaldehyde (top) and mesitaldehyde (bottom) that were catalyzed by UMCM-1-AMFesal.

Table 1: Results from Mukaiyama-aldol reactions with UMCM-1-AMFesal catalyst and control reactions (after 24 h).

Aldehyde	MOF (UMCM-1)	Cycle 1 [%]	Cycle 2 [%]	Cycle 3 [%]	Overall [%]
naphthaldehyde	no MOF	<1	n.d.	n.d.	n.d.
	-NH_2	<10	n.d.	n.d.	n.d.
	-AMsal	<10	n.d.	n.d.	n.d.
	NH_2 + [Fe(acac)$_3$]	27	15	14	19 ± 7
	-AMFesal[a]	70 ± 11	56 ± 12	52 ± 12	58 ± 14
mesitaldehyde	no MOF	<1	n.d.	n.d.	n.d.
	-NH_2	<5	n.d.	n.d.	n.d.
	-AMsal	<5	n.d.	n.d.	n.d.
	NH_2 + [Fe(acac)$_3$]	<5	n.d.	n.d.	n.d.
	-AMFesal[b]	53 ± 18	55 ± 5	65 ± 8	58 ± 12

[a] Based on four trials. [b] Based on three trials. n.d. = not determined.

It is important to note that removal of UMCM-1-AMFesal by filtration resulted in no further reaction, confirming that the MOF and not some soluble species was responsible for the observed catalysis. In addition, UMCM-1-AMFesal is quite robust as a catalyst, retaining full activity over three cycles (Table 1). Stability of the catalyst was further verified by PXRD, which showed that UMCM-1-AMFesal remained crystalline (Supporting Information, Figure S7). AA analysis also indicated very little leaching of the catalytic metal ions from the structure after three catalytic cycles as well, with over 80 % of the Fe^{3+} ions retained (Supporting Information, Table S2).

The findings detailed herein show that PSM can be used to introduce chelating sites into a MOF, that these sites can be metallated with divalent or trivalent transition metals, and that the resulting materials can be used as robust catalysts for carbon–carbon bond forming reactions. UMCM-1-NH_2 was successfully modified with two different metal binding groups that were metallated with Fe^{3+} and Cu^{2+} ions to yield UMCM-1-AMFesal and UMCM-1-AMCupz. UMCM-1-AMFesal was found to be catalytically active for the Mukaiyama-aldol reaction, over multiple catalytic cycles without loss of activity or crystallinity. The properties of UMCM-1-AMFesal met and exceed the performance one of the best MOF-based catalysts reported to date. Clearly, the full potential for the use of PSM for metal binding in MOFs has yet to be fully explored, and studies on modulating MOFs for selective gas sorption, molecular sensing, and other applications are ongoing.

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