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Evaluation of Heterogeneous Metal-Organic Framework Organocatalysts Prepared by Postsynthetic Modification

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Abstract

A metal-organic framework (MOF) containing 2-amino-1,4-benzenedicarboxylate (NH_2-BDC) as a building block is shown to undergo chemical modification with a set of cyclic anhydrides. The modification of the aluminum-based MOF known as MIL-53(Al)-NH_2 (MIL = Matérial Institut Lavoisier) by these reagents is demonstrated by using a variety of methods, including NMR and ESI-MS, and the structural integrity of the modified MOFs has been confirmed by TGA, PXRD, and gas sorption analysis. Reaction with these cyclic anhydrides produces MOFs that display carboxylic acid functional groups within their pores. Furthermore, it is shown that maleic acid functionalized MIL-53(Al)-AMMal can act as a Brønsted acid catalyst and facilitate the methanolysis of several small epoxides. Experiments show that MIL-53(Al)-AMMal acts in a heterogeneous manner and is recyclable with consistent activity over at least three catalytic cycles. The findings presented here demonstrate several important features of covalent postsynthetic modification (PSM) on MOFs, including: 1) facile introduction of catalytic functionality using simple organic reagents (e.g. anhydrides); 2) the ability to utilize and recycle organocatalytic MOFs; 3) control of catalytic activity through choice of functional group. The findings clearly illustrate that covalent postsynthetic modification represents a powerful means to access new MOF compounds that serve as organocatalytic materials.

Introduction

Metal-organic frameworks (MOFs) are crystalline materials composed of metal ions or metal cluster nodes connected by organic ligands.[1-3] The ability to design MOFs with varying pore volumes and surface areas[4,5] has made these materials attractive for applications in gas storage.[6-12] However, MOFs have shown promise in a diverse set of technologies including separation,[13,14] drug delivery,[15-17] and catalysis.[18] Throughout the last several years, several groups have shown that MOFs can act as heterogeneous catalysts in a variety of reactions such as alkene oxidation,[19 20] aldol condensations,[21,22] hydrogenation,[23-25] and epoxide ring opening.[26,27] Compared to homogeneous reactions, the use of heterogeneous catalysts simplifies the reaction work-up by requiring only filtration to separate the catalyst from the product for reuse.

The alcoholysis of epoxides is a well-studied reaction that is promoted by a variety of homogeneous and heterogeneous acid catalysts. Historically, the methanolysis of epoxides is achieved by using sulfuric acid.[28] Heterogeneous catalysts based on polymers or silica-based materials have also been widely studied for the methanolysis of epoxides.[29,30] With respect to MOFs, Baiker and co-workers utilized a bipyridine Cu(II) based MOF Cu(bpy)

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Supporting Information **Available**. Figures S1-S22. This material is available free of charge via the Internet at http://pubs.acs.org.

$(H_2O)_2(BF_4)_2$(bpy) for the methanolysis of epoxides demonstrating high activity and selectivity.[31] However, further investigation of this system revealed that the excellent catalytic properties were due to the structural rearrangement of the MOF and subsequent release of multicopper clusters upon exposure to methanol.[32] Rosseinsky and co-workers cleverly developed catalytically active chiral aspartate MOFs.[27] With the careful addition of HCl the MOFs could be protonated at a carboxylate group bound to the Cu(II) or Ni(II) metal centers, thereby introducing Brønsted acid sites. While the Brønsted acid functionalized materials showed modest activity and enantioselectivity in the methanolysis of small epoxides, the recyclability and robustness of these catalytic materials was not described.

Our group and others have recently demonstrated the practical use of postsynthetic modification (PSM) to produce functionalized systems by targeting the organic linking group or secondary building unit of pre-fabricated MOFs.[33] We have become increasingly interested in the use of PSM to develop MOFs as catalytic materials. Several recent studies from our laboratory have focused on the generation of metal ion sites within a MOF to generate Lewis acid catalytic centers.[34,35] A recent study utilized coordinative postsynthetic modification with pyridyl L-proline onto the open metal coordination sites of MIL-101 (MIL = Material Institut Lavoisier).[22] Through this approach MIL-101 was transformed into a catalytically active homochiral material that was competent for asymmetric aldol reactions between aldehydes and ketones. While the material displayed high catalytic activities and enantioselectivity, its catalytic properties diminished over time on account of leaching of the pyridyl groups after repeated use. The experiments here focus on the heterogeneous acylation of the pendant amino group of MOFs employing 2-amino-1,4-benzenedicarboxylate (NH_2-BDC) as an organic building block. Covalent PSM of these systems provides an opportunity to develop MOFs with stable and reusable organocatalytic functionality. Herein, we demonstrate the utilization of carboxylic acid functionalized MOFs as a solid state Brønsted acid catalyst for the ring opening of small epoxides by methanol. The findings described here demonstrate that these modified MOFs act as a heterogeneous catalysts that can be reused after regeneration without loss of activity.

Experimental Methods

General

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). MIL-53(Al)-NH_2[36] and MIL-53(Al)-AM1[37] were synthesized and activated as described previously.

Synthesis

Synthesis of 4-((2,5-bis(methoxycarbonyl)phenyl)amino)-4-oxobut-2-enoic acid (DMT-AMMal)—Maleic anhydride (17.4 g, 177 mmol) was added to a solution of dimethyl amino terephthalate (1.06 g, 5.1 mmol) in ~125 mL of $CHCl_3$. The solution was stirred for 24 h at room temperature. The solvent was removed by rotary evaporation. The brown solid was washed with ~100 mL of ethyl acetate, filtered, and washed with ~100 mL of $CHCl_3$. The product was dried at ~85 °C. Yield = 27%. ^{1}H NMR (500 MHz, d^6-DMSO): δ 10.75 (s, 1 H), 8.7 (s, 1H), 7.96-7.6 (d, 2H), 6.5-6.34 (d, 2H), 3.8 (s, 6H). ESI-MS *m/z* 306.07 $[M-H]^-$.

Synthesis of 4-((2,5-bis(methoxycarbonyl)phenyl)amino)-4-oxobutanoic acid (DMT-AMSuc)—Succinic anhydride (17.9 g, 177 mmol) was added to a solution of dimethyl amino terephthalate (1.06 g, 5.1 mmol) in ~125 mL of $CHCl_3$. The solution was

stirred for 24 h at room temperature. The solvent was removed by rotary evaporation. The brown solid was washed with ~100 mL of ethyl acetate filtered and washed with ~100 mL of $CHCl_3$. The product was dried at ~85 °C. Yield = 67%. ^{1}H NMR (500 MHz, d^6-DMSO): δ 12.19 (s, 1H), 10.54 (s, 1 H), 8.7 (s, 1H), 7.96-7.6 (d, 2H), 3.8 (s, 6H), 2.6-2.5 (d, 4H). ESI-MS *m/z* 308.00 $[M-H]^-$.

MIL-53(Al)-AMMal—In a typical reaction, residual DMF was removed from microcrystalline MIL-53(Al)-NH_2 (~60 mg) by heating at 150 °C for 5 h. The activated MIL-53(Al)-NH_2 (~50 mg 0.2 mmol-NH_2) was treated with a 5 mL solution of CH_3CN containing the anhydride (12 mmol) and heated at 80 °C for 24 h. After the reaction was complete the sample was rinsed with CH_3CN (3×6 mL), centrifuged, and dried at 80 °C for up to 2 h resulting in 43±4% (-AMMal), 39±4% (-AMSuc), and 34±4% (-AMCrot) conversion.

Characterization of MILs

^{1}H NMR Digestion and Analysis—Approximately 10 mg of microcrystalline MIL was digested by sonication in one of two digestion cocktails: a) 400 μL D_2O and 200 μL of NaOH 40 wt. % of D_2O; or b) 570 μL of d_6-DMSO and 30 μL of HF. After complete dissolution of the crystals, the solution was used to collect a ^{1}H NMR spectrum. ^{1}H NMR spectra were recorded on a JEOL ECA spectrometer (500 MHz).

ESI-MS Analysis—Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer and the data were analyzed using the Xcalibur software suite in negative ion mode. MIL samples were digested by sonicating the materials in a mixture of 10 μL of HF and 1.0 mL of CH_3CN.

Thermal Gravimetric Analysis—Approximately 10-20 mg of modified MIL samples were dried at 150 °C for 5 h and used for TGA measurements. Samples were analyzed under a stream of dinitrogen using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 °C/min.

PXRD Analysis—PXRD data were collected at ambient temperature on a Bruker Advance D8 diffractometer at 40 kV, 40 mA for *K*α (λ = 1.5418 Å) with a scan speed of 3 sec/step, a step size of 0.02° in 2θ, and a 2θ range of 5-45°. Approximately 15 mg of microcrystalline MIL samples were dried at 150 °C for at least 2 h before PXRD analysis. The experimental backgrounds were corrected using the Jade 5.0 software package.

FT-IR Analysis—Approximately 5-10 mg of modified MIL was dried at 150 °C for at least 2 h before FT-IR analysis. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR spectrometer with a diamond ATR.

Catalysis

Catalysis Experiments—In a typical reaction, the MIL microcrystalline solids (*ca.* 0.20 mmol equiv of BDC ligand) were pre-dried for ~5 h were and added to a CD_3OD solution (2 mL) containing the epoxide substrate (0.40 mmol). The reaction was allowed to stand for 2 d at 25 °C. At the end of the reaction, *ca.* 0.8 mL aliquot was taken from the mixture and used for ^{1}H NMR measurements. Note that the chemical formula for each MOF that was examined for catalysis are as follows: MIL-53(Al)-NH_2 = Al(OH)($C_8H_5NO_4$), MIL-53(Al)-AM1 = Al(OH)($C_{10}H_7NO_5$), MIL-53(Al)-AMCrot = Al(OH)$(C_8H_5NO_4)_{0.66}(C_{12}H_9NO_5)_{0.34}$, MIL-53(Al)-AMSuc = Al(OH)$(C_8H_5NO_4)_{0.6}(C_{12}H_9NO_7)_{0.4}$, and MIL-53(Al)-AMMal = Al(OH)$(C_8H_5NO_4)_{0.57}(C_{12}H_7NO_7)_{0.43}$.

Catalyst Recycling—After the completion of a reaction with epoxide, the CD_3OD solution was decanted and the MIL solids were washed with $CHCl_3$ (3×6 mL, isolated by centrifugation between washes) before soaking in 10 mL of pure $CHCl_3$ for three days, with fresh $CHCl_3$ added every 24 h. After three days of soaking the solids were stored in the last $CHCl_3$ solution until needed. Samples treated this way were showed a large reduction in activity, which required regeneration as described below.

Catalyst Regeneration—The $CHCl_3$ storage solution was decanted away from the inactive MOF catalysts (see Catalyst Recycling above) and the solids was dried at 55 °C for up to 2 h. To the dried MOFs, ~13 mL of a 0.1 M HCl solution was added and allowed to stand for ~18 h. The solids were centrifuged and washed with H_2O (3×6 mL) and dried at 100 °C for at least 2 h prior to use.

Results and Discussion

Modification of MIL-53-NH_2 with Anhydrides

In order to develop a heterogeneous MOF catalyst, a chemically robust framework was selected for compatibility with the protic solvents of the ring opening reaction conditions. The MIL-53(Al) framework is chemically stable to many protic solvents and acidic environments, unlike zinc(II)-carboxylate MOFs (IRMOF-3 derivatives),[38] which degrade under these reaction conditions described below (data not shown). Recently MIL-53(Al)-NH_2, a MIL-53(Al) analogue incorporating NH_2-BDC, was synthesized and could be postsynthetically modified with formic acid.[36] PSM of MIL-53(Al)-NH_2 was attempted with a variety of anhydrides (Scheme 1). The use of maleic and succinic anhydride generated carboxylic acid functionalized MIL-53(Al)-AMMal and MIL-53(Al)-AMSuc with modest conversions of ~43% and ~40%, respectively (Figure 1). The percent conversions were determined by ^1H NMR analysis of digested materials, as previously described.[37,39] Specifically, conversion was determined by comparing the relative integration areas of the singlet aromatic resonance (corresponding to the C3-position) of the modified to the unmodified NH_2-BDC ligands (Figure 1). Fourier transform infrared spectroscopy (FTIR) on MIL-53(Al)-AMMal and MIL-53-(Al)-AMSuc showed new stretches around 1720 cm^{-1} characteristic of carbonyl functionalities. In addition, the N-H stretches at 3500 to 3387 cm^{-1}, associated with the amine of the NH_2-BDC ligand, were notably diminished (Figure S1-S2). MIL-53(Al)-NH_2 treated under identical reaction conditions with crotonic and acetic anhydride resulted in MIL-53(Al)-AMCrot and MIL-53(Al)-AM1 modified with ~34% and ~95% conversion.[37] As expected, the N-H stretches associated with the NH_2-BDC ligand in the FTIR spectrum of MIL-53(Al)-AM1 disappeared, while a new vibration at 3361 cm^{-1} emerged, corroborating the nearly quantitative conversion to an amide (Figure S1). In addition, electrospray ionization mass spectroscopy (ESI-MS) of modified materials (digested in an HF/CH_3CN solution) confirmed PSM of the NH_2-BDC ligands (Figures S3-S6). The structural and thermal properties of the modified MILs were found to closely resemble that of MIL-53(Al)-NH_2 as evidenced by powder X-ray diffraction (PXRD) (Figure S7) and thermogravimetric analysis (TGA) (Figure S8).

Catalytic Properties of MIL-53-(Al)-AMMal and MIL-53(Al)-AMSuc

Having demonstrated that MIL-53(Al)-NH_2 could be modified with cyclic anhydrides without degradation of the framework, the ability of these solid-state Brønsted acid materials in the methanolysis of *cis*-2,3-epoxybutane was explored. In order to confirm the origin of catalysis (i.e. Brønsted acid catalysis), control experiments with the structural surrogates MIL-53(Al)-NH_2, MIL-53(Al)-AM1, and MIL-53(Al)-AMCrot were performed in parallel (Scheme 2). The MOF solids (~0.08 mmol of carboxylate group) were pre-dried for ~5 h and were then added to a CD_3OD solution containing the epoxide (0.40 mmol). After two

days under ambient conditions, ^{1}H NMR revealed that the epoxide essentially underwent complete (>95%) turnover with MIL-53(Al)-AMMal, but there was no conversion with MIL-53(Al)-AMSuc or any of the control materials (Figure 2). These results strongly suggested that the carboxylate groups in MIL-53(Al)-AMMal were essential to catalyze the methanolysis of *cis*-2,3-epoxybutane.

The MIL-53-(Al)-AMMal system maintained its structural integrity after completion of the methanolysis reaction as evidenced by PXRD (Figure S9). To confirm that MIL-53(Al)-AMMal was acting in a heterogeneous manner, aliquots of the reaction mixture were taken after undergoing partial conversion and monitored by ^{1}H NMR over the course of several days for up to one week. The methanolysis of *cis*-2,3-epoxybutane is indeed a heterogeneous reaction, as the signals associated with product formation did not change after removal of the MIL catalysis (Figure S10).

The observation that MIL-53(Al)-AMSuc did not show good catalytic activity when compared with MIL-53(Al)-AMMal was particularly intriguing. While MIL-53(Al)-AMSuc contains approximately the same number of free carboxylate groups, it does not show catalytic activity above that observed with the control materials studied (Scheme 2, Figure 2). The disparity in catalytic activity likely originates from the difference in the acidity of the carboxylic acids. Unlike the succinic acid functionality, the maleic acid contains a conjugated C=C double bond, which can stabilize the conjugate base resulting in higher acidity. By comparison, propionic acid has a pK_a of 4.87, while its conjugated analogue, acrylic acid, has a pK_a of 4.25, more than a half a log unit lower. Consistent with the MOF findings, homogenous experiments for the methanolysis of *cis*-2,3,-epoxybutane using maleic and succinic modified dimethyl amino terephthlate ligands (DMT-AMMal, and DMT-AMSuc) gave similar results (Figure S11), with the DMT-AMMal ligand promoting the reaction much more effectively than DMT-AMSuc (21% compared to 2%, respectively).

In order to establish the recyclability of MIL-53(Al)-AMMal, the reaction mixtures were removed and extensively washed with CD_3OD. The solid catalyst then underwent a second catalytic reaction employing the same reaction conditions. Unfortunately, the recycled catalyst showed a significant reduction in activity (95% compared to 10%) (Figure S12). Given that the MOF is exposed to a large excess of methanol during catalysis, it was suspected that esterification of the carboxylic acid moieties could be responsible for the reduction in activity of subsequent catalytic reactions. Attempts to spectroscopically (FTIR, ^{1}H NMR) confirm esterification of MIL-53(Al)-AMMal after catalysis were unsuccessful. However, prolonged exposure of MIL-53(Al)-AMMal to methanol prior to the first catalytic cycle significantly hampered its ability to perform the methanolysis of *cis*-2,3,-epoxybutane. For example, freshly synthesized MIL-53-AMMal samples were treated with CD_3OD (2 mL) and allowed to stand at ambient conditions for 2, 4, and 7 days. These pre-treated samples were utilized as catalysts in the methanolysis of *cis*-2,3,-epoxybutane, but ^{1}H NMR revealed a decrease in product formation as a consequence of prolonged exposure to CD_3OD (Figure S13). Based on ^{1}H NMR integration, conversion from these pretreated MIL-53-AMMal samples for 2, 4, and 7 days were 43, 33, and 2%, respectively. These findings support the hypothesis that esterification of the carboxylate moieties is responsible for the reduced catalytic properties of MIL-53-AMMal after the first round of catalysis.

We reasoned that if the carboxylate groups of MIL-53(Al)-AMMal were undergoing esterification then hydrolysis should re-establish the activity of the solid state Brønsted acid catalyst. To test this hypothesis, inactive MIL-53(Al)-AMMal that had been through one catalytic cycle was soaked 0.1 M HCl (13 mL) overnight, followed by washing with H_2O (3×6 mL) and drying at 100 °C. Treatment with HCl successfully restored the catalytic

activity of MIL-53(Al)-AMMal (Figure S13). Due to the robust nature of the MIL-53(Al) system, treatment with HCl does not degrade the structural integrity of MIL-53(Al)-NH_2 or MIL-53(Al)-AMMal (Figure S14). The catalytic properties of inactive MIL-53(Al)-AMMal (turnover <2%), pretreated with CD_3OD for a week, showed complete restoration of activity upon treatment with HCl. We confirmed that the renewed catalytic activity is not the result of residual HCl, as a control reaction involving MIL-53(Al)-NH_2, MIL-53(Al)-AM1, and MIL-53(Al)-AMSuc treated identically with HCl led to insignificant catalytic activity (<2%, Figure S15). These findings suggest that the observed reduction in reactivity of MIL-53(Al)-AMMal is likely due to ester formation, which can be reversed upon hydrolysis with acid. With acidic treatment, MIL-53(Al)-AMMal provides a robust and recyclable solid-state catalyst. In this study, MIL-53(Al)-AMMal was found to undergo at least three catalytic cycles with consistent activity (Figure 3).

Attempts were made to determine the minimum catalyst loading for these reactions. MIL-53(Al)-AMMal samples containing 0.08 mmol of the catalytic group (maleic acid functionality) were introduced to solutions containing 8, 0.8, and 0.4 mmol of *cis*-2,3-epoxybutane, which corresponds to 1, 10, and 20% catalyst loadings. ^{1}H NMR of these reaction mixtures after two days under ambient conditions showed that the methanolysis reactions with 1, 10, and 20% catalyst loading led to 10%, 90%, and ~95% turnover, respectively (Figure S16). Therefore, under the present reaction conditions, at least 10% loading was required to obtain high conversions within two days.

Given the modest success in facilitating the methanolyis of *cis*-2,3,-epoxybutane, the catalytic scope of MIL-53(Al)-AMMal in the transformation of different epoxides was investigated. Under identical conditions, MIL-53(Al)-AMMal initiates the methanolysis of several epoxides (Table 1). MIL-53(Al)-AMMal promotes the methanolysis of cyclopentene oxide, cyclohexene oxide, styrene oxide, and *trans*-stilbene oxide, while the asymmetric 1,2-epoxyhexane is not activated by the catalyst (Figures S17-S21). It is unclear why the latter substrate is not efficiently turned over by the MIL-53(Al)-AMMal catalyst. Size exclusion from the MIL pores does not explain this result as the sterically more crowded cyclohexene oxide, styrene oxide, and *trans*-stilbene oxide are converted with MIL-53(Al)-AMMal as a catalyst. The only apparent feature of 1,2-epoxyhexane is its asymmetric structure, although it is unclear why this feature would inhibit catalytic turnover, as it does not appear to inhibit the reaction with styrene oxide. Nonetheless, consistent with this finding, (*R*)-(+)-propylene oxide was a significantly poorer substrate for MIL-53(Al)-AMMal than *cis*-2,3,-epoxybutane, giving a yield of only 59% (Figure S22).

Conclusions

In summary, the findings presented in this study demonstrate that covalent postsynthetic modification is a viable method for synthesizing MIL-based catalysts. In contrast to our earlier studies, which used Lewis acid metal sites for catalysis, the studies presented here incorporate Brønsted acid, organocatalytic groups into a MOF. MIL-53(Al)-NH_2 was treated with maleic anhydride producing a carboxylic acid functionalized material. The carboxylic acid groups residing in the framework were utilized as Brønsted acid catalytic sites for the methanolysis of epoxides. While MIL-53(Al)-AMMal facilitated the ring opening of several epoxides, another carboxylate functionalized MIL possessing a weaker acidic group, MIL-53(Al)-AMSuc, did not perform the same catalysis. The methanolysis reaction was found to be genuinely heterogeneous, but required regeneration with exogenous acid for recovery as a reusable catalyst. Presently, our data do not provide clear evidence whether catalysis is occurring in the interior or only on the surface of the MOFs. In addition, not all epoxide substrates were effectively turned over by MIL-53(Al)-AMMal, and the origins of this apparent selectivity require further investigation. Ongoing efforts will focus on

developing catalytic materials capable of asymmetric ring opening reactions as well as other organocatalytic transformations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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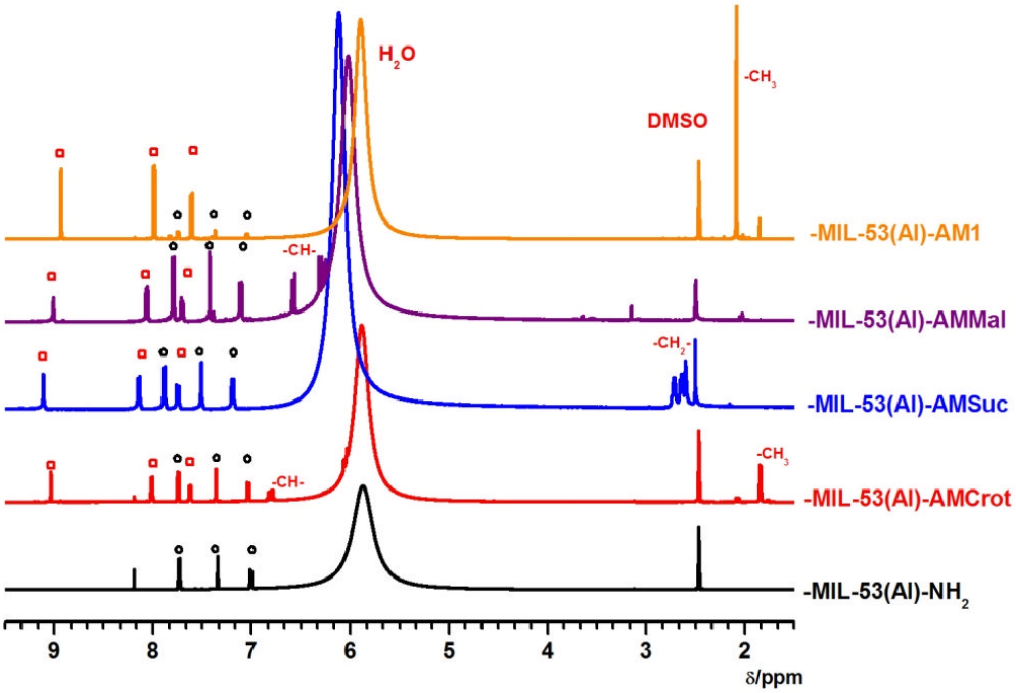


Figure 1.

^{1}H NMR spectra of modified MIL-53(Al)-NH_2 samples digested in HF/d_6-DMSO. Red squares and black circles represent signals of aryl protons in modified and unmodified NH_2-BDC, respectively. All other peaks associated with modifications or solvent are labeled explicitly in red.

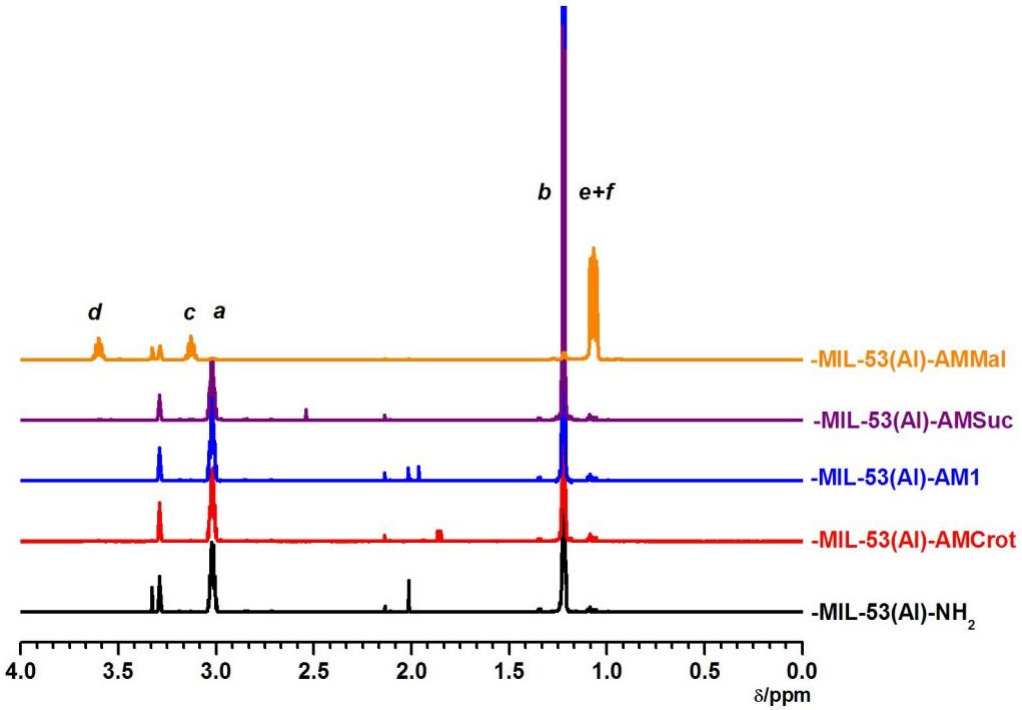


Figure 2.
^{1}H NMR of catalytic reaction aliquots employing MIL-53(Al)-AMMal (green), MIL-53(Al)-AM1 (blue), MIL-53(Al)-AMCrot (red), and MIL-53(Al)-NH_2 (black).

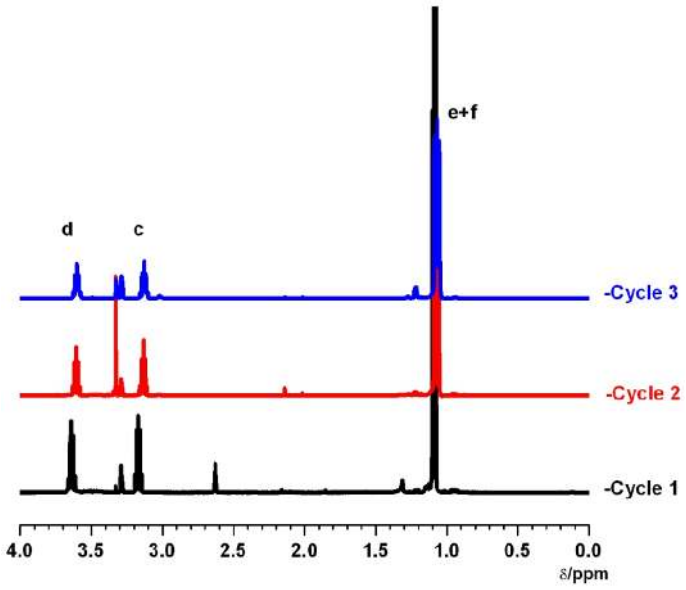
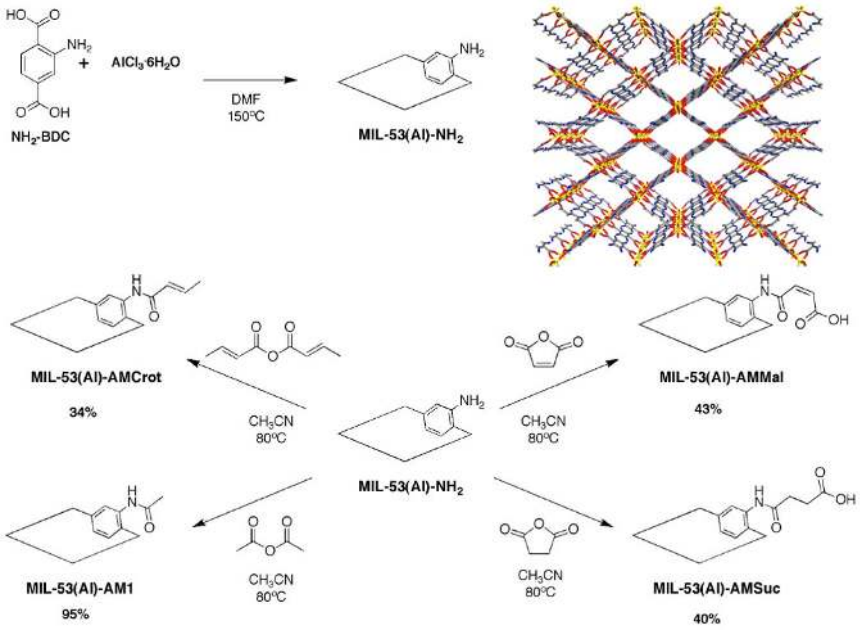


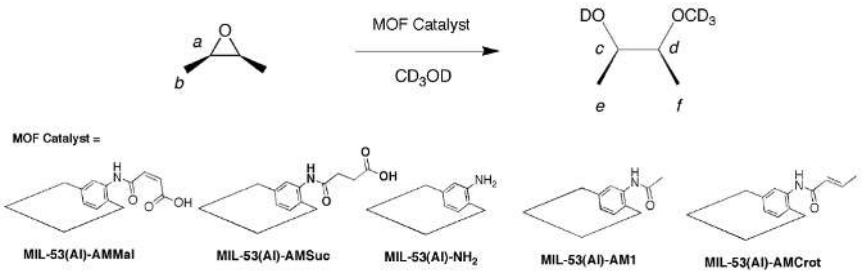
Figure 3.

^{1}H NMR spectra of three consecutive reactions of the methanolysis of *cis*-2,3,-epoxybutane utilizing MIL-53(Al)-AMMal showing essentially quantitative conversion (black), ~97% conversion (red), and 90% conversion (blue). The MIL was regenerated with HCl between each reaction cycle.



Scheme 1.

Synthesis (top left) and structure (top right) of MIL-53(Al)-NH_2. Postsynthetic modification reactions performed on MIL-53-(Al)-NH_2 relevant to this study (bottom).

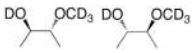
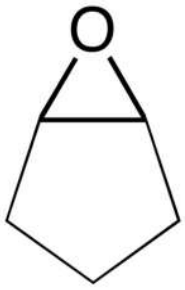
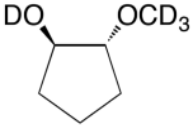
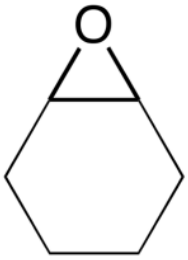
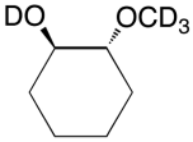
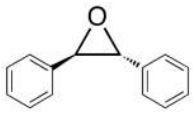
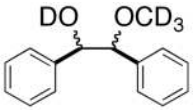
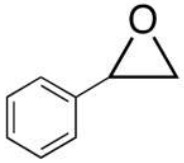
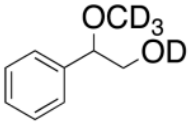


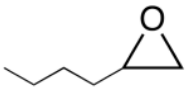
Scheme 2.

Attempted methanolysis of *cis*-2,3-epoxybutane with carboxylate functionalized MIL-53(Al)-AMMal and MIL-53(Al)-AMSuc. Letters *a*~*f* represent the protons associated with starting material and the ring opening product. Also listed are structural analogues MIL-53(Al)-NH_2, MIL-53(Al)-AM1, MIL-53(Al)-AMCrot that were used for control reactions.

Table 1

Methanolysis of epoxides with MIL catalysts. MIL catalysts (*ca.* 0.08 mmol based on free carboxylate groups) were added to a CD_3OD solution (2 mL) containing the epoxide substrate (*ca.* 0.40 mmol) and the reaction was allowed to stand for 2 days at 25 °C. The conversions are based on at least three independent trials.

Reagent	Product	Catalyst	Conversion [%]
cis-2,3,-epoxybutane		MIL-53(Al)-AMMal	95 ± 2
		MIL-53(Al)-AMSuc	<2
		MIL-53(Al)-AMCrot	<2
		MIL-53(Al)-AM1	<2
		MIL-53(Al)-NH_2	<2
Cyclopentene oxide		MIL-53(Al)-AMMal	44 ± 4
			
Cyclohexene oxide		MIL-53(Al)-AMMal	100 ± 2
			
trans-stilbene oxide		MIL-53(Al)-AMMal	37 ± 4
			
Styrene oxide		MIL-53(Al)-AMMal	100 ± 2
			
1,2-epoxyhexane	No reaction	MIL-53(Al)-AMMal	No reaction

Reagent	Product	Catalyst	Conversion [%]
			
(*R*)-(+)-propylene oxide		MIL-53(Al)-AMMal	59± 4