ACS Catalysis

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Lewis Acid Activation of a Hydrogen Bond Donor Metal−Organic Framework for Catalysis

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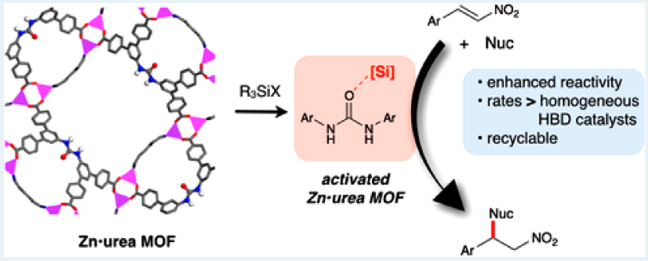
Supporting Information

ABSTRACT: A new metal−organic framework (MOF) composed of urea-containing tetracarboxylate struts was synthesized, and its hydrogen bonding capabilities were evaluated. The catalytic performance of this heterogeneous framework is enhanced through preactivation with silyl Lewis acids, leading to Friedel−Crafts reaction rates greater than those of common homogeneous hydrogen bond donors.



KEYWORDS: *metal−organic framework, catalysis, hydrogen bond donor, urea MOF, Lewis acid*

INTRODUCTION

Hydrogen bond donor molecules have become selective organocatalysts for a wide range of applications because of their tunable reactivity, rigid conformation, and stable functionality.[1] Their emergence as powerful tools for organic synthesis has led to novel H-bond donors with unique capabilities enabling new reactions and approaches.[2] Since Schreiner and Wittkopp reported seminal applications of H-bond-donating thioureas,[3] much effort has been directed toward increasing the potency of these unique organocatalysts.[4] The majority of this work has been focused on the development of new classes of H-bond donor catalysts including electronically and conformationally activated squaramides,[5] quinazolines,[6] aminobenzothiadiazines,[6] 2-aminobenzimidazoles,[7] 2-aminopyridiniums,[8] and silanediols.[9] Alternatively, dual catalytic activation with Brønsted[10] or Lewis acids[11] has also been shown to significantly enhance the inherent reactivity of simple (thio)urea scaffolds. Urea catalysts in particular are known for their high thermal and chemical stability, but their reactivity is often critically attenuated *by undesired catalyst oligomerization* (quenching).[12] Our recent efforts to prevent self-quenching by physically separating urea H-bond donors have shown that modest rate enhancements can be obtained by incorporating urea catalysts into metal−organic frameworks (MOFs).[13] However, obtaining high levels of reactivity from a heterogeneous MOF catalyst has proven to be a challenging endeavor because of restrictive pore sizes and the inherently low activity of urea catalysts.[14]

An alternative strategy for the installation of catalytic components into MOFs is postsynthetic modification, which allows the introduction of new functionality that could not otherwise be incorporated through de novo solvothermal synthesis. This approach has been used to incorporate ureas[15] and thioureas;[16] however, dependence upon this strategy has limited innovation toward novel MOF topologies, especially those with large pore sizes that do not require covalent postsynthetic modifications.[17] In addition, the treatment of MOFs containing "metalloligand" struts with catalytically active metals had also led to interesting new heterogeneous catalysts.[18] In this vein, Cohen and Tanabe demonstrated the incorporation of Cu, Fe, and In into MOF architectures to catalyze epoxide ring-opening reactions,[19] and Ma has reported the binding of Al(III) using Brønsted acid chelators.[20]

We imagined that the optimal combination of Lewis acid and hydrogen bond donor could produce a stable MOF catalyst with enhanced catalytic activity for new bond-forming reactions (Figure 1). A novel MOF architecture (NU-GRH-1) using urea functionalized tetracarboxylate struts (Scheme 1) emerged as a new scaffold for these studies. The unique bent geometry and unsymmetrical nature of these struts enabled the generation of a highly porous framework capable of accepting substrates larger than those of previous H-bond donor MOF reports.[13,15b,16] We report herein a Lewis acid activation approach of urea functionalized MOF scaffolds and their enhanced catalytic activity versus related homogeneous urea catalysts.

RESULTS

The synthesis of urea strut **6** began with commercially available bromide **1**, which was deaminated[21] to yield dibromide **2**. A Suzuki coupling with 4-acetylphenylboronic acid followed by reduction of the nitro functionality with Pd/C provided aniline **4**. Two equivalents of the aniline were combined with carbonyldiimidazole to provide urea **5**. A mild methyl ester

Received: February 10, 2016
Revised: April 11, 2016

DOI: 10.1021/acscatal.6b00424
ACS Catal. 2016, 6, 3248−3252

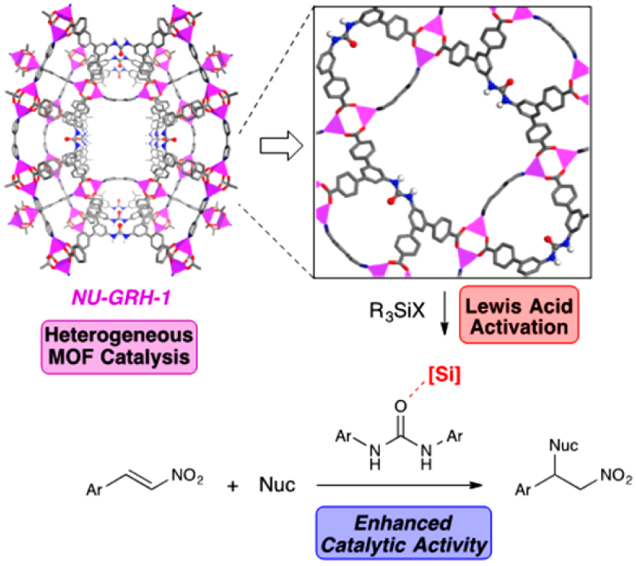
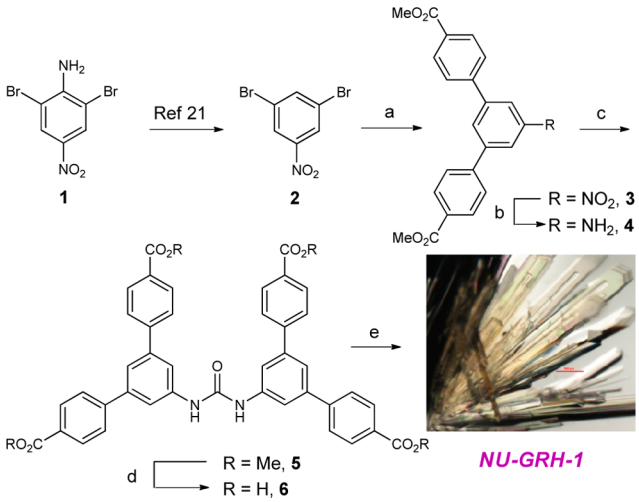


Figure 1. Enhanced hydrogen bonding catalyst strategy.

Scheme 1. Synthesis of NU-GRH-1[a]



[a](a) $Pd(OAc)_2$, 4-acetylphenylboronic acid, Na_2CO_3, PPh_3, THF, reflux, 18 h; (b) Pd/C, H_2, THF, rt, 6 h; (c) CDI, THF, reflux, 18 h; (d) $KOSiMe_3$, THF, reflux, 18 h; (e) $Zn(NO_3)_2[6(H_2O)]$, 4,4′-dipyridyl, DMF, 95 °C, 2 d.

cleavage using potassium trimethylsilanolate provided scalable yields of tetracarboxylate strut **6**. This synthetic protocol provides multigram quantities of the organic strut (>10 g) without the need for chromatographic purification (see Supporting Information for details). The solvothermal synthesis of NU-GRH-1 was carried out on gram scale with strut **6**, $Zn(NO_3)_2$, and 4,4′-dipyridyl (BPy)[22] yielding large, clear-to-pale yellow crystalline rods having the empirical formula $Zn_2(BPy)(\mathbf{6})$.

These MOF crystals were then subjected to single-crystal X-ray crystallographic analysis (Figure 2). NU-GRH-1 exists in the $P4_2/mnm$ space group and contains large oblong pores (widest aperture dimensions: 31.6 × 14.0 Å^2; distances measured between atoms) with the N−H bonds of the ureas pointing inward for catalysis. Powder X-ray diffraction spectra (PXRD) of bulk samples matched that of the simulated spectra generated from the cif file (see Supporting Information).

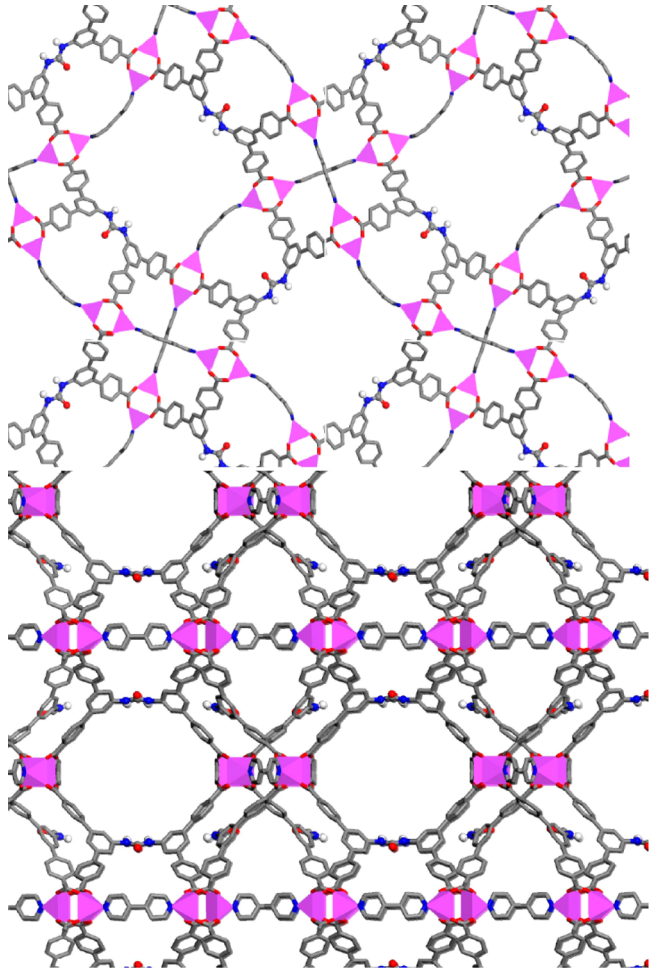


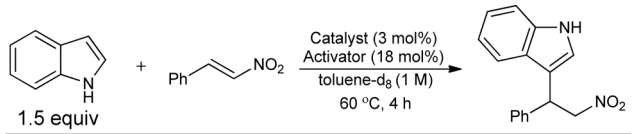
Figure 2. NU-GRH-1 crystal structure: (top panel) view along *c* axis; (bottom panel) view along *a* axis rotated 45°. Urea H atoms added for clarity.

Dipyridyl ligands within the H-bonding pores of NU-GRH-1 display substantial bending[23] (159.7°) potentially caused by the coordinate bond angles required for Zn metal chelation at both termini. Cambridge Structure Database (CSD) searches based on these angular parameters provided previously reported MOF structures supporting the validity of substantial dipyridyl bending using Zn,[24] Cd,[25] and Cu.[26] Notably, ligand bending in NU-GRH-1 *is 5° greater than any previously disclosed MOF structure*. Variations in the displacement parameters within the bent ligands versus the linear BPy ligands in NU-GRH-1 (ORTEP) further suggest the presence of bent pyridyl struts (see Supporting Information for detailed explanation).

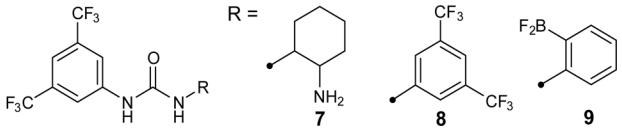
The urea functional groups positioned within NU-GRH-1 were first activated for catalysis by removing the Lewis basic DMF molecules bound to the urea N−H bonds. The solvent was exchanged daily with $MeNO_2$ at 50 °C over 1 week. The crystals were dried under vacuum, digested in 3% D_2SO_4/DMSO-d_6, and characterized by ^{1}H NMR spectroscopy, confirming a 1:1 strut-to-BPy ratio. We then employed NU-GRH-1 in a Friedel−Crafts (FC) reaction with *β*-nitrostyrene and indole as a simple benchmark to assess catalytic activity (Table 1). Our first attempts using dried NU-GRH-1 crystals surprisingly resulted in no reaction (data not shown). PXRD of the solvent-free MOF did not give sharp peaks consistent with the solvent-saturated MOF, suggesting collapse of the pores

DOI: 10.1021/acscatal.6b00424
ACS Catal. 2016, 6, 3248−3252

Table 1. Indole Friedel–Crafts Activator Screen



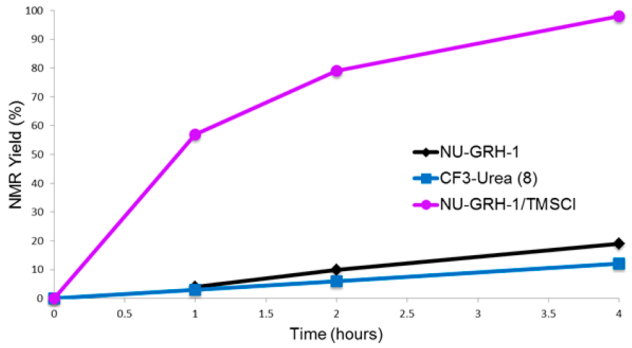
Entry	Catalyst	Activator[a]	Yield (%)[b]
1	5	-	<5
2	7	-	7
3	8	-	12
4	9	-	40
5	NU-GRH-1	-	19[c]
6	NU-GRH-1	$AlMe_3$	3
7	NU-GRH-1	$EtAlCl_2$	47
8	NU-GRH-1	$Ti(iOPr)_4$	17
9	NU-GRH-1	$B(OMe)_3$	49
10	NU-GRH-1	$BF_3{\bullet}OEt_2$	69
11	NU-GRH-1	TMS-Cl	98[c]
12	NU-GRH-1	TMS-OTf	99[d]
13	NU-GRH-1	TMSCl/DTBMP[e]	92
14	-	TMS-Cl	16[f]
15	5	TMS-Cl	20[f]
16	8	TMS-Cl	43[f]
17	NU-GRH-1	TMS-OH	16



[a]Used to preactivate MOF then removed by toluene wash prior to reaction. [b]NMR yields using 2-methylnapthalene as internal standard. [c]Average yield between three separate batches of NU-GRH-1. [d]Reaction complete in 1.5 h. [e]DTBMP (20 mol %) was used during MOF preactivation then removed via toluene wash prior to reaction. [f]TMS-Cl (18 mol %) was present during reaction. DTBMP = 2,5-di*tert*-butyl-4-methylpyridine.

after removal of solvent. To circumvent this problem, the as-synthesized crystals were collected with a brief filtration to remove excess solvent and used without any further drying. The wet MOF crystals displayed notable catalytic activity, especially when compared to modern homogeneous urea catalysts (Table 1, entries 1–4).

We then investigated strategies to enhance catalytic activity of NU-GRH-1 by pretreatment with a range of Lewis acids. NU-GRH-1 was soaked with a Lewis acid in toluene overnight at 23 °C, *at which point the Lewis acid solution was removed* and the crystals were thoroughly washed with toluene (5×). Boron, titanium, and aluminum-based Lewis acids all provided moderate rate enhancements (Table 1, entries 5–8). However, silicon-based Lewis acids provided the greatest increase of catalytic activity, with trimethylsilyl trifluoromethanesulfonate (TMS-OTf) being the most effective. Control experiments with TMS-OTf without MOF revealed a significant homogeneous background rate. Furthermore, we observed partial MOF degradation upon treatment with TMS-OTf leading to precipitous drops in reactivity when recycling the catalyst. Consequently, trimethylsilyl chloride (TMS-Cl) was chosen as the optimal additive moving forward (Figure 3, top panel).



# of Catalyst Cycles	1	2	3	4	5
NMR % Yield (@4 h)	>98	>98	>98	>98	>98

Figure 3. (Top panel) Relative rates of Friedel–Crafts catalysis. (Bottom panel) TMS-Cl preactivated NU-GRH-1 catalytic recyclability.

Notably, attempts to activate homogeneous urea **8** provided some rate enhancement (entry 16; Lewis acid was still present during reaction) but could not replicate the same increase observed with the MOF/TMS-Cl combination (entry 11; Lewis acid washed away prior to reaction). Additionally, this combination is a more active catalyst then strut **5** alone (entry 1) or **5** combined with TMS-Cl (entry 15).

MOF preactivation provides the benefit of washing away the remaining Lewis acid in solution when compared to standard homogeneous catalysts, thus preventing substrate degradation or complexation with strongly Lewis acidic metals. Moreover, NU-GRH-1/TMS-Cl showed robust recyclability (Figure 3, bottom). Over five consecutive catalytic cycles, NU-GRH-1/TMS-Cl maintained high reactivity, without any observable drop in reaction rate or yield (determined by ^{1}H NMR spectroscopy). The ^{1}H NMR spectra from unpurified reactions using recycled TMSCl-activated MOF did not show signals related to Si-Me (or Si-CH_3) to avoid confusion of the possible presence of TMS-OH or other such compounds.

Control experiments support the heterogeneous catalyst role of NU-GRH-1 in the FC reaction. The use of solely TMS-Cl (18 mol %) provides low levels of reactivity (Table 1, entry 14), which in combination with washing protocols to remove TMS-Cl from the NU-GRH-1 catalyzed reactions, supports the conclusion that the Lewis acid additive does not provide rate enhancement in solution independent of the MOF. Reactions that included 2,6-di*tert*-butyl-4-methylpyridine (DTBMP, 20 mol %) during preactivation showed only a minor decrease in reaction rate (Table 1, entry 13; see Supporting Information for rate profile), reducing the likelihood of residual Brønsted acid (presumably HCl) activating NU-GRH-1 or independently catalyzing the reaction.[27] Additionally, NU-GRH-1 in the presence of TMS–OH (Table 1, entry 17) shows no significant change in reaction rate compared to the unactivated framework.

DOI: 10.1021/acscatal.6b00424
ACS Catal. 2016, 6, 3248–3252

Filtration of the MOF after 1 h halted further product formation, indicating that the heterogeneous framework is the primary catalyst (Figure 4). Furthermore, activated NU-GRH-1 demonstrated superior reactivity in comparison to other common lewis acidic MOFs (MIL-100(Fe) and HKUST-1; see Supporting Information).

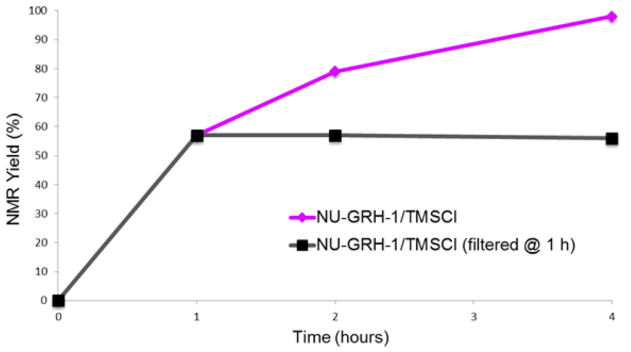
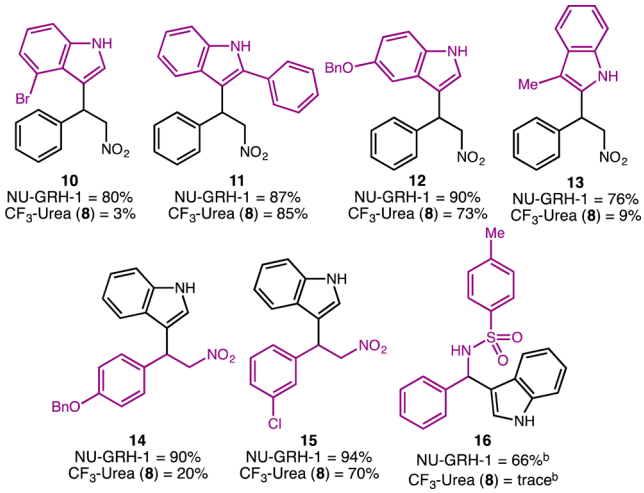


Figure 4. MOF filtration experiment.

Table 2. Substrate Scope[a]



[a]Isolated yields. Identical equivalencies to Table 1. Reactions heated at 60 °C for 24 h. [b]Reactions at 23 °C for 24 h and diluted to 0.5 M.

A substrate scope analysis was performed to probe the tolerance of NU-GRH-1 to larger substrates (Table 2). In all examples, NU-GRH-1 accepted expanded substrates and still provided faster rates than homogeneous urea **8**. Crushed MOF did not provide any change in rate, suggesting that reactions with large substrates are not exclusively catalyzed on the surface of the MOF. Less reactive substrates including 4-bromoindole (**10**), 3-methylindole (**13**), and *N*-tosyl imine (**16**) highlight the expanded reactivity profile of NU-GRH-1 relative to standard urea catalysts. These studies also expand upon our scope of nitrostyrene electrophiles to include imines with similarly satisfying results. A common notion is that the inherent entropic penalties resulting from substrate transport and active site accessibility in heterogeneous MOF catalysts render them less reactive than their homogeneous counterparts. However, these results suggest that new and enhanced reactivity is indeed possible with proper catalytic design and novel activation strategies.

There are multiple pathways that may account for catalyst activation. Our current understanding suggests an interaction between the silicon and urea carbonyl oxygen. The stability of this interaction may be increased via encapsulation within a heterogeneous framework. Direct urea silylation is unlikely given that little effect of in situ generated acid is observed in experiments employing exogenous base during preactivation. Furthermore, *N,O*-bis(trimethylsilyl)acetamide (a strong silylating reagent) provided no enhancement of catalytic activity when used to pretreat NU-GRH-1. Urea H-bond donors also have a propensity to bind anions (such as chloride)[28] which may provide a scenario in which NU-GRH-1 activates the Lewis acid. In this situation, catalytic activation would then occur at the electron-deficient silicon center. Attempts at single-crystal X-ray analysis of MOF/TMS-Cl combinations have thus far been unable to determine the mode of Lewis acid binding. Single-crystal data sets in combination with PXRD analysis indicate the overall topology of NU-GRH-1 remains intact and unaffected by TMS-Cl treatment. However, *both ICP-OES analysis and* ^{1}*H NMR spectroscopy of the TMS-Cl activated MOF indicate silicon is present after digestion of the material* (see Supporting Information for details). While the impact on catalysis is clear, the precise molecular interactions in the MOF·TMS-Cl combination responsible for the high levels of activity are still under investigation.

CONCLUSION

Lewis acid activation of ureas is feasible through specific design and judicious incorporation of hydrogen bond donor organocatalysts into a heterogeneous metal−organic structure. These activated MOF catalysts are recyclable and can display superior reactivity compared to their homogeneous urea counterparts. The novel MOF topology includes an unusual BPy conformation and contains large pores amenable to general catalysis. Continued investigations with these activated heterogeneous catalysts as well as new MOF strategies for catalysis with hydrogen bond donors are ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00424.

General experimental details, synthesis of NU-GRH-1, substrate characterization, ICP-OES and 1H NMR for detection of Si-based activators, PXRD, bent dipyridyl analysis, and single-crystal X-ray data (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank AbbVie for support of this work. Single-crystal and powder X-ray crystallographic experiments were carried out with support from Amy Sarjeant and Charlotte Stern (NU). We thank Prof. SonBinh Nguyen (NU) for helpful discussions.

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DOI: 10.1021/acscatal.6b00424
ACS Catal. 2016, 6, 3248−3252