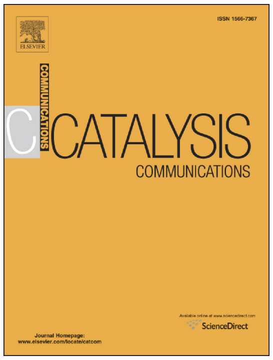

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A Urea-containing Metal-Organic Framework as a Multifunctional Heterogeneous Hydrogen Bond-Donating Catalyst

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Abstract

A urea-containing metal-organic framework (MOF) was synthesized from a V-shaped dicarboxylate ligand and Cu(II) ions. As the undesirable self-aggregation of the urea moiety has been prohibited in the framework, this MOF can act as a heterogeneous hydrogen bond-donating (HBD) catalyst, which accelerates the cyanosilylation reaction of aldehydes, the Henry reaction of aldehydes, and the methanolysis reaction of epoxides. It also displays a significantly enhanced catalytic activity when compared with its homogeneous urea counterpart and analogous MOF structures.

Keywords: Hydrogen bond-donating catalyst, Heterogeneous catalysis, Metal-organic frameworks, Urea

1. Introduction

Hydrogen bond-donating (HBD) catalysis has been recognized as an effective approach for the synthesis of various highly valuable intermediates for pharmaceutical and agricultural industries because HBD catalysts are capable of binding selectively and activating reactive substrates during the reaction process *through* hydrogen bonding or other noncovalent interactions [1-4]. In the past decades, n c reactions including Friedel–Crafts (F–C) reactions, Mannich reaction, Strecker reaction, etc. [5-8]. Among these catalysts, urea has been widely utilized as a catalytic moiety owing to its chelating hydrogen bonding *through* acidic N-H sites [9,10]. However, the intrinsic self-assembly of urea molecules caused by the intermolecular interactions of hydrogen bonding always leads to a potential deterioration in catalytic reactivity [11,12]. Thus, it is necessary to introduce enhanced catalyst loading or elongated reaction time or external toxic additives to achieve high yield in a certain homogeneous catalytic system [13,14]. In contrast to the conventional approach of enhancing the reactivity of urea-based catalysts, various supports have been exploited to break the self-association of urea moieties in catalysis. For instance, the Lin group demonstrated that mesoporous silica nanosphere materials could serve as support for a urea-based catalyst to achieve superior catalytic behavior in some important chemical transformations compared with their corresponding precursors [15,16]. The Portnoy group has developed a urea-based organocatalyst supported by a porous organic polymer. This organocatalyst has been established as an efficient catalyst for promoting nitro-Michael addition [17]. Additionally, metal-organic frameworks (MOFs), emerging as new support materials for heterogeneous catalysis, are gaining increasing interest owing to their unique features of high porosity, structural tunability, excellent stability, and well-defined catalytic sites [18-22]. For example, Roberts and co-workers first synthesized one MOF-based catalyst bearing a urea moiety, which is highly active in the F–C reactions between pyrroles and nitroalkenes. Subsequently, a few MOF-based HBD catalysts derived from urea-, thiourea-, or squaramide-functionalized molecules were prepared through direct synthesis or post-synthetic modification. These MOF catalysts also displayed high efficiency in catalyzing F–C reactions [23-30]. In spite of a growing interest in such solid catalysts, studies on multifunctional MOF-based HBD catalysts remain limited. In this work, a urea-containing MOF was synthesized and utilized as a highly efficient HBD catalyst to promote the cyanosilylation reaction of aldehydes, the Henry reaction of aldehydes, and the methanolysis reaction of epoxides. Additionally, this urea-based MOF catalyst exhibits a broad substrate scope and excellent recyclability.

2.1 Synthetic chemistry

In this work, the urea-containing MOF (**1**) was synthesized from a V-shaped dicarboxylate ligand (**L1**-H_2) with urea moiety according to a previously reported procedure (Scheme 1) [31]. For the comparison of catalytic activity, MOF **2** was readily obtained from a solvothermal reaction of copper nitrate and ligand **L2**-H_2. MOF **1** and **2** both possessed a similar two-dimensional framework. The structures of both MOFs were confirmed by the results of single-crystal X-ray diffraction analysis (Scheme 1 and Figs. S1-2).

2.2 Catalytic procedure

As shown in the structure of MOF **1** (Scheme 1 and Fig. S1), the guest DMF molecules remained in the framework through hydrogen bonding to urea moieties. Therefore, the active urea N-H sites in the channels of **1** were blocked. To remove the guest DMF molecules within the cavities, **1** was treated with anhydrous MeOH and CH_2Cl_2, followed by placing in vacuum for two hours at 100 °C. The activated MOF **1** was named as **1a**. General procedure for cyanosilylation reaction: 1.5 mol% **1a** (catalyst loading based on aldehydes) was added to a solution of indicated aldehyde (0.10 mmol), TMSCN (0.12 mmol), and dry MeOH (0.5 mL). The resulting mixture was stirred at 60 °C. For Henry reaction: a reaction mixture consisting of 1.5 mol% **1**a (based on aldehydes), indicated aldehyde (0.10 mmol), and $MeNO_2$ (1.0 mmol) was stirred at 60 °C. For methanolysis reaction of epoxides: a reaction mixture consisting of 1.5 mol% **1**a (based on epoxides), indicated epoxide (0.10 mmol), and dry MeOH (0.5 mL) was stirred at 60 °C. The three reactions were carried out for 24 hours, and the yields were determined by ^{1}H NMR.

3. Results and discussion

To the best of our knowledge, the intrinsic unwanted self-association behavior of the urea moieties is quite common in homogeneous catalysis. This phenomenon usually hampers their catalytic performance. It can be clearly seen that the self-association of the urea-containing ligand **L1**-H_2 (Scheme 2a) was successfully restricted when it was immobilized on the MOF structure. Therefore, MOF **1** can serve as a potential HBD catalyst. Cyanosilylation of various aldehydes using trimethylsilyl numerous biologically active products. As such, we would like to examine the effectiveness of the urea-containing MOF **1** in the cyanide reaction.

It is found that 1.5 mol% activated **1** (**1**a) can effectively catalyze the cyanosilylation reaction of benzaldehyde under optimized conditions to afford a corresponding product with 97% NMR yield (entry 1 in Table 1). To confirm that the main reactivity was contributed by the catalytic sites coming from the isolated urea moieties on the MOF structure, three control experiments were carried out. (i) The free ligand **L1**-H_2 was first utilized as a homogeneous catalyst to run the same reaction, and only 24% yield was obtained (entry 2 in Table 1) even at 3.0 mol% catalyst loading (twice the urea units in **1**a). The obviously low catalytic activity can be ascribed to the unwanted dimerization of **L1**-H_2 *through* intermolecular hydrogen-bonding interactions, resulting in the loss of active free ligand (Scheme 2a). (ii) Considering the presence of coordination-saturated copper sites in MOF **1** that may play some role in the catalysis, MOF **2**, sharing a similar structure with **1** but without urea moiety on its framework, was synthesized and used as a catalyst to catalyze the same reaction (Scheme 1 and Fig S2). This control experiment showed that MOF **2** gave only a 34% yield (the equal loading of copper as that in **1**a, entry 3 in Table 1), which implied that dicopper units in MOF **1** made some contribution to the cyanosilylation reaction of benzaldehyde. (iii) It is noted that a significant decrease in catalytic performance occurred when the pristine crystals of **1** were used as a catalyst (entry 4 in Table 1). This result presumably could be explained by the fact that the dual N-H sites in the MOF structure were blocked by guest DMF molecules *through* strong hydrogen-bonding interactions (Scheme 1 and Fig S1). On the basis of the above discussions, enhancement of the catalytic activity of **1a** should be mainly attributed to the isolated and unblocked urea functional groups immobilized on the MOF structure, in which the carbonyl group of aldehydes could be activated by the acidic dual N-H group of the urea units (Scheme 2b) [1].

The substrate tolerance of catalyst **1a** was further examined with various aromatic aldehydes. In the presence of **1a**, a wide range of aromatic benzaldehyde derivatives bearing both electron-donating and e d generate corresponding products in excellent yields ranging from 84% to 97% (entries 5-9 in table 1). Taken together, the above results suggest that **1a** could be used as a highly efficient HBD catalyst in the cyanosilylation reaction of multiple aldehydes. To the best of our knowledge, this is the first example of a urea-based MOF catalyst with high performance in cyanosilylation reaction. This excellent result encourages us to extend the applications of **1**a to other catalytic reactions.

We then attempted to apply this MOF catalyst to the Henry reaction. The reaction was performed between aldehydes and nitromethane by using 1.5 mol% catalyst **1**a. An optimum result was that benzaldehyde and its derivatives bearing electron-poor groups reacted with nitromethane efficiently to give β-nitro alcohols in 80-95% yields (entries 1-2, 6-9 of Table 2). Three control experiments were additionally carried out to determine the role of the open and isolated urea sites in this catalysis. Free ligand **L1**-H_2, **2**, and pristine **1** afforded only 36%, 9%, and 10% yields (entries 3-5 in Table 2), respectively, when they were used as catalysts in the Henry reaction of 4-nitrobenzaldehyde with nitromethane. The significant catalytic performance of **1a** in catalyzing the Henry reaction of aldehydes again implied that it is a highly efficient HBD catalyst.

To further investigate the versatility of this HBD MOF catalyst, the alcoholysis of epoxides to various alkoxy alcohols, an important reaction for pharmaceutical and agrochemical industries, was also tested with this MOF catalyst. As far as we know, studies of this reaction catalyzed by urea-containing MOFs to date are scarce [32]. In this work, the alcoholysis of epoxides was performed at 60°C for 24 h, in which methanol was used as both a nucleophile and a solvent. To our delight, **1a** can effectively catalyze the methanolysis of phenyl glycidyl ether to afford the product of 1-methoxy-3-phenoxypropan-2-ol with an excellent yield of 96% (entry 1 in Table 3). When the reaction was performed using **L1**-H_2, **2**, and pristine **1** as the catalysts, significantly lower yields were observed (entries 2-4 in Table 3). From the control experiments, we expected that the MOF-containing urea moieties can activate the oxygen atom of the epoxide to achieve higher catalytic activity (Scheme glycidyl ether, and 2-naphthyl glycidyl ether. In these reactions, **1**a could give the corresponding products a yield of 80-90%. Again, these results demonstrated the high utility of **1**a as an HBD catalyst.

Moreover, the heterogeneity and the recyclability of this HBD MOF catalyst were investigated. Upon completion of the methanolysis of phenyl glycidyl ether under the typical condition, solid catalyst **1**a can be easily recovered with quantitative mass from the reaction mixture through centrifugation and washed with excessive MeOH. Subsequently, the recovered catalyst **1**a could be reused for another four runs without any obvious loss of catalytic activity (ca. 96%, 93%, 92%, 91%, and 92% yields for runs 1-5, respectively). In addition, a comparison of the PXRD patterns of the recovered solid catalysts **1**a and the pristine crystal of **1** clearly showed that no significant changes occurred (Fig S3). These results suggest that this urea-containing MOF is a versatile HBD heterogeneous catalyst with high catalytic performance.

4. Conclusions

In summary, a urea-containing MOF was synthesized from a V-shaped urea-functionalized ligand. The MOF possesses catalytically active dual N-H groups that allow for the activation of the carbonyl compound. This HBD MOF catalyst demonstrated excellent activity in the cyanosilylation reaction, the Henry reaction of aldehydes, and the methanolysis of epoxides. Further, the HBD MOF catalyst can be easily recovered and reused without any apparent loss of catalytic activity. Our study, therefore, provides a highly efficient heterogeneous HBD catalyst functionalized with urea moieties in the MOF structure. This approach can be further extended for a variety of important organic transformations.

Acknowledgments

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Declaration of interest: None.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at https://doi.org/ xx.xxxx /j. catcom. xxxx.xx.xxx.

References

[1]. P. R. Schreiner, *Chem. Soc. Rev.*, 2003, 32 (5), 289-296.

[2]. M. S. Taylor; Jacobsen, E. N., *Angew. Chem., Int. Ed.*, 2006, 45 (10), 1520-1543.

[3]. A. G. Doyle; Jacobsen, E. N., *Chem. Rev.*, 2007, 107 (12), 5713-5743.

[4]. W. Zheng; Fu, Y.; Liu, L.; Guo, Q., *Acta Phys.-Chim. Sin.*, 2007, 23 (7), 1018-1024.

[5]. Y. Nishikawa, *Tetrahedron Lett.*, 2018, 59 (3), 216-223.

[6]. T. J. Auvil; Schafer, A. G.; Mattson, A. E., *Eur. J. Org. Chem.*, 2014, 2014 (13), 2633-2646.

[7]. D. Roca-Lopez; Marques-Lopez, E.; Alcaine, A.; Merino, P.; Herrera, R. P., *Org.Biomol. Chem.*, 2014, 12 (25), 4503-4510.

[8]. S. Xu; Zhu, H.; Li, Z.; Wei, F.; Gao, Y.; Xu, J.; Wang, H.; Liu, J.; Guo, T.; Guo, K., *Eur. Polym. J.*, 2019, 112, 799-808.

[9]. Y. Takemoto, *Org.Biomol. Chem.*, 2005, 3 (24), 4299-4306.

[10]. M. S. Taylor; Jacobsen, E. N., *Angew. Chem., Int. Ed.*, 2006, 45 (10), 1520-1543.

[11]. R. Custelcean, *Chem. Commun.*, 2008, (3), 295-307.

[ ), 1668-1676.

[13]. Z. G. Zhang; Bao, Z. B.; Xing, H. B., *Org.Biomol. Chem*., 2014, 12 (20), 3151-3162.

[14]. R. P. Herrera; Sgarzani, V.; Bernardi, L.; Ricci, A., *Angew. Chem., Int. Ed*., 2005, 44 (40), 6576-9.

[15]. S. Huh; Chen, H.-T.; Wiench, J. W.; Pruski, M.; Lin, V. S. Y., *Angew. Chem., Int. Ed*., 2005, 44 (12), 1826-1830.

[16]. H.-T. Chen; Trewyn, B. G.; Wiench, J. W.; Pruski, M.; Lin, V. S. Y., *Top Catal*., 2010, 53 (3-4), 187-191.

[17]. L. Tuchman-Shukron; Portnoy, M., *Adv.Synth. Catal.*, 2009, 351 (4), 541-546.

[18]. J. Liu; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C. Y., *Chem. Soc. Rev.*, 2014, 43 (16), 6011-61.

[19]. L. Jiao; Wang, Y.; Jiang, H.-L.; Xu, Q., *Adv. Mater*., 2018, 30 (37), 1703663.

[20]. A. H. Chughtai; Ahmad, N.; Younus, H. A.; Laypkov, A.; Verpoort, F., *Chem. Soc. Rev*., 2015, 44 (19), 6804-6849.

[21]. Y.-B. Huang; Liang, J.; Wang, X.-S.; Cao, R., *Chem. Soc. Rev*., 2017, 46 (1), 126-157.

[22]. G. Yuan; Jiang, H.; Zhang, L.; Liu, Y.; Cui, Y., *Coordin. Chem. Rev*., 2019, 378, 483-499.

[23]. X.-W. Dong; Liu, T.; Hu, Y.-Z.; Liu, X.-Y.; Che, C.-M., *Chem. Commun*., 2013, 49 (70), 7681-7683.

[24]. Y. Luan; Zheng, N.; Qi, Y.; Tang, J.; Wang, G., *Catal. Sci. Technol.*, 2014, 4 (4), 925-929.

[25]. C. M. McGuirk; Katz, M. J.; Stern, C. L.; Sarjeant, A. A.; Hupp, J. T.; Farha, O. K.; Mirkin, C. A., *J. Am. Chem. Soc*., 2015, 137 (2), 919-925.

[26]. X.-J. Wang; Li, J.; Li, Q.-Y.; Li, P.-Z.; Lu, H.; Lao, Q.; Ni, R.; Shi, Y.; Zhao, Y., *CrystEngComm.*, 2015, 17 (25), 4632-4636.

[28]. Z. Ju; Yan, S.; Yuan, D., *Chem.Mater*., 2016, 28 (7), 2000-2010.

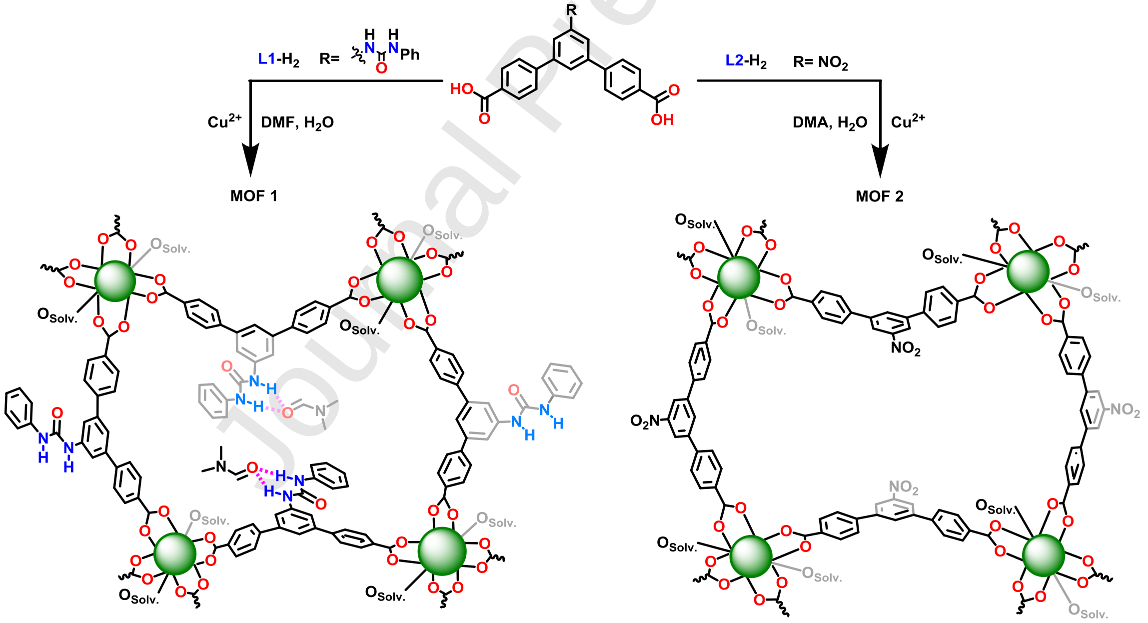
[29]. X. Zhang; Zhang, Z.; Boissonnault, J.; Cohen, S. M., *Chem. Commun*., 2016, 52 (55), 8585-8.

[30]. P. C. Rao; Mandal, S., *Chemcatchem*., 2017, 9 (7), 1172-1176.

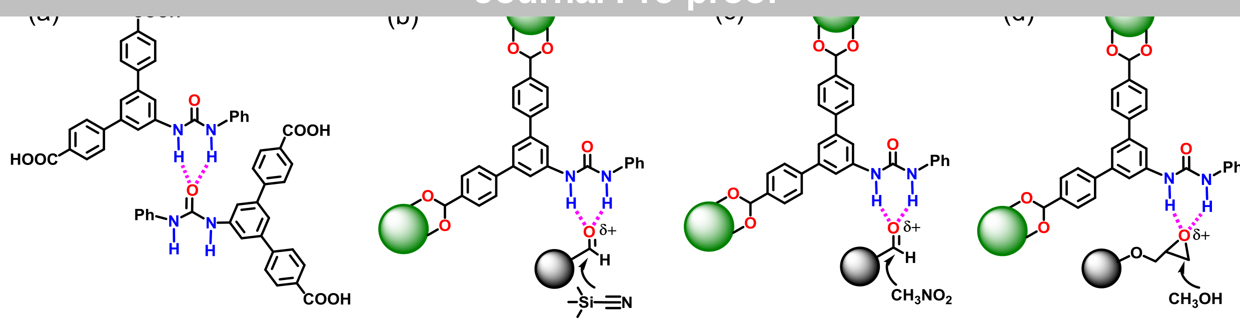
[31]. C. Zhu; Mao, Q.; Li, D.; Li, C.; Zhou, Y.; Wu, X.; Luo, Y.; Li, Y., *Catal. Commun*., 2018, 104, 123-127.

[32] A. A. Tehrani; Abedi, S.; Morsali, A.; Wang, J.; Junk, P. C., *J. Mater. Chem. A*, 2015, 3 (40), 20408-20415.

Figure Captions:

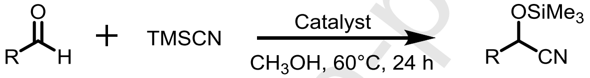


Scheme 1. Synthesis and structures of **1** and **2**.



Scheme 2. Self-association of urea-containing ligand, **L1**-H_2, in homogeneous catalysis (a) and substrate activation by the urea unit through hydrogen bonding for cyanosilylation reaction (b), Henry reaction (c), and methanolysis reaction (d), when urea has been immobilized in MOF.

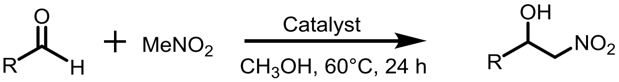
Table 1 Results of cyanosilylation reaction catalyzed by different catalysts [a]



Enty	R	Cat.	Cat. Load. (mol%) [b]	Conversion (%) [e]
1	Ph	**1**a	1.5	97
2	Ph	**L1**-H_2	3.0[c]	24
3	Ph	**2**	1.5[d]	34
4	Ph	**1**	1.5	36
5	4-Me-Ph	**1**a	1.5	94
6	4-Cl-Ph	**1**a	1.5	97
7	4-OMe-Ph	**1**a	1.5	84
8	4-CN-Ph	**1**a	1.5	93
9	2-naphtyl	**1**a	1.5	97

[a] For reaction details, see Experimental Section. [b] Catalyst loading based on aldehyde. [c] Twice the urea units in **1**a. [d] The same loading of copper as that of **1**a. [e] Calculated by ^1H NMR.

Table 2 Results of the Henry reaction catalyzed by different catalysts [a]



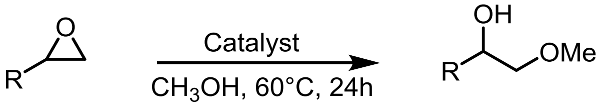
Enty	R	Cat.	Cat. Load. (mol%) [b]	Conversion (%) [e]
1	Ph	**1**a	1.5	83
2	4-NO_2-Ph	**1**a	1.5	95
3	4-NO_2-Ph	**L1**-H_2	3.0[c]	36
4	4-NO_2-Ph	**2**	1.5[d]	9
5	4-NO_2-Ph	**1**	1.5	10
6	3-NO_2-Ph	**1**a	1.5	91
7	2-NO_2-Ph	**1**a	1.5	93
8	4-CN-Ph	**1**a	1.5	90
9	4-Br-Ph	**1**a	1.5	80

[a] For reaction details, see Experimental Section; the reaction time is 24 h. [b] Catalyst loading is based

o

NMR.

Table 3 Ring-opening reactions of various epoxides with MeOH [a]



Enty	R	Cat.	Cat. Load. (mol%) [b]	Conversion (%) [e]
1	CH_2OPh	**1**a	1.5	96
2	CH_2OPh	**L1**-H_2	3.0[c]	22
3	CH_2OPh	**2**	1.5[d]	6
4	CH_2OPh	**1**	1.5	12
5	$CH_2O(p\text{-}BrC_6H_4)$	**1**a	1.5	80
6	$CH_2O(p\text{-}MeC_6H_4)$	**1**a	1.5	84
7	$CH_2O(p\text{-}OMeC_6H_4)$	**1**a	1.5	90
8	CH_2O(2-naphtyl)	**1**a	1.5	88

[a] For reaction details, see Experimental Section. [b] Catalyst loading based on epoxide. [c] Twice the urea units in **1**a. [d] The same loading of copper as that of **1**a. [e] Calculated by ^1H NMR.

- Two 2D metal-organic frameworks (MOFs) were readily synthesized and characterized.
- This urea-containing MOF is a superb hydrogen-bond-donating (HBD) catalyst.
- Three types of important reactions could be efficiently catalyzed.
- This HBD catalyst showed a superb catalytic activity and excellent recyclability.

Graphical abstract