Size-Selective Lewis Acid Catalysis in a Microporous Metal-Organic Framework with Exposed Mn²⁺ Coordination Sites

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The extraordinary combination of chemical tunability and high internal surface area has generated widespread interest in metal-organic frameworks.[1] One of the more prominent applications pursued for these materials has been their possible use in high-density hydrogen storage.[2] Here, efforts to increase the enthalpy of H_2 adsorption have led to a number of microporous frameworks bearing coordinatively unsaturated metal centers.[3] Importantly, such crystalline solids with well-defined pores and surface-isolated Lewis acid sites could also potentially serve as size- or shape-selective heterogeneous catalysts, in a manner similar to zeolites.[4] Reports of catalytic studies in metal-organic frameworks have, however, been relatively scarce.[5,6] While these have included some significant successes in enantioselective catalysis,[5a,b] there has been little focus thus far on probing selectivity with substrates of comparable size to the pore dimensions.[5d] With this in mind, we undertook investigations of the catalytic activity of the recently discovered sodalite-type compound $Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$ (1; H_3BTT = 1,3,5-benzene-tristetrazol-5-yl),[3e] wherein Mn^{2+} ions exposed on the surface of the framework might serve as potent Lewis acids. Herein, we show that compound 1 indeed catalyzes the cyanosilylation of aromatic aldehydes and ketones, as well as the more demanding Mukaiyama−aldol reaction. Moreover, in each case, a pronounced size-selectivity effect consistent with the pore dimensions is observed.

Compound 1 is a thermally stable microporous solid exhibiting a cubic network of 7 and 10 Å pores that affords a BET surface area of 2100 m²/g (see Figure 1).[3e] The 10 Å pore system is readily accessible and presents a surface lined with two different types of Mn^{II} sites. Site I has one chloride and four bridging tetrazolate ligands, with a sixth methanol ligand that projects into the pore present only 83% of the time. Site II is bound by just two tetrazolate ligands and accounts for one-ninth of the total manganese in the compound. Both types of coordinatively unsaturated metal centers are well-positioned to interact with guest molecules that enter the framework pores, suggesting that 1 should function as an active heterogeneous catalyst for Lewis acid promoted reactions.

To compare the catalytic activity of 1 with that of other metal-organic frameworks, we first probed the cyanosilylation of carbonyl-functionalized organic substrates. This reaction provides a convenient route to cyanohydrins, which are key derivatives in the synthesis of fine chemicals and pharmaceuticals.[7] Notably, catalysis of the transformation had previously been explored using metal-organic frameworks, but only relatively low conversion rates were observed.[6] Our experiments employed a 1:2 molar ratio of selected aromatic aldehydes and cyanotrimethylsilane in dichloromethane at room temperature. As shown in Table 1, a loading of 11 mol % of solid 1 led to a 98% conversion of benzaldehyde after 9 h. This represents a significant improvement over the best prior result for metal-organic frameworks: a yield of 69% obtained after 16 h of exposure to a series of lanthanide bisphosphonates.[6b] Importantly, removal of 1 by filtration after only 4 h completely shut down the reaction, affording only 40% total conversion upon standing for 20 h. This demonstrates that no homogeneous catalyst species exists in the reaction solution. In addition, infrared spectroscopy of the
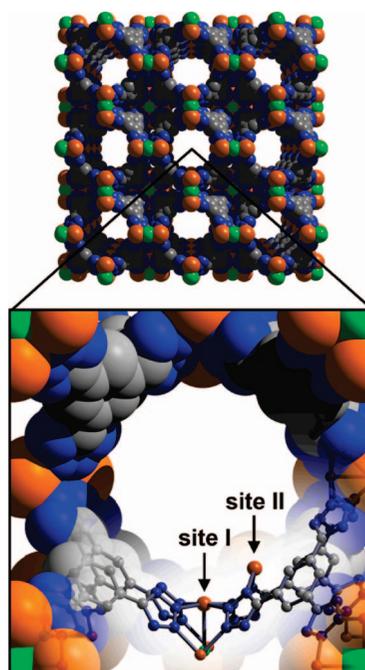

Figure 1. A portion of the crystal structure of **1** showing the two different types of Mn^{II} sites exposed within its three-dimensional pore system of 10 Å wide channels.[3e] Orange, green, gray, and blue spheres represent Mn, Cl, C, and N atoms, respectively; H atoms and bound MeOH molecules are omitted for clarity. Site I is five-coordinate, while site II is only two-coordinate; the separation between them is 3.420(8) Å.

Table 1. Results for the Cyanosilylation of Carbonyl Substrates in the Presence of **1**[a]


entry	Ar	R	time (h)	yield (%)[b]
1	phenyl	H	9	98
2	1-naphthyl	H	9	90
3	4-phenoxyphenyl	H	9	19
4	biphenyl	H	9	18
5	phenyl	CH_3	24	28
6	biphenyl	CH_3	24	1

[a] Reaction conditions: Me_3SiCN (3 mmol), aldehyde/ketone (1.5 mmol), CH_2Cl_2 (5 mL), **1** (0.04 g, 0.006 mmol), room temperature, under N_2. [b] Determined by ^1H NMR based on the carbonyl substrate.

catalyst impregnated with an aliquot of the reaction solution revealed two C−O stretches at 1698 and 1686 cm⁻¹. These correspond to free and Mn^{II}-bound benzaldehyde, respectively, confirming that activation of the substrate occurs at the unsaturated Mn^{II} sites within **1**.

To probe whether activation of the carbonyl species occurs inside the pores or on the surface of the solid catalyst, substrates of increasing dimension were tested. Unlike the lanthanide bisphosphonates, which exhibit lamellar structures that can swell to

Table 2. Results for the Mukaiyama−Aldol Reaction in the Presence of **1**[a]
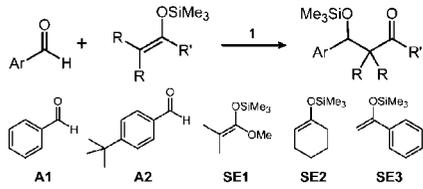
entry	aldehyde	silyl enolate	time (h)	solvent	yield (%)[b]
1	**A1**	**SE1**	99	CH$_2$Cl$_2$	63
2	**A2**	**SE1**	99	CH$_2$Cl$_2$	24
3	**A1**	**SE2**	99	CH$_2$Cl$_2$	<1
4	**A1**	**SE3**	99	CH$_2$Cl$_2$	<1
5[c]	**A1**	**SE1**	6	DMF	8[d]
6[c]	**A1**	**SE1**	6	DMF	51

[a] Reaction conditions: silyl enolate (2 mmol), aldehyde (1 mmol), solvent (5 mL), **1** (0.04 g, 0.006 mmol), room temperature, under N$_2$. [b] Determined by ^{1}H NMR based on the aldehyde. [c] Reaction at −45 °C. [d] No catalyst added.

accommodate a wide range of substrates,[6b] a significant size-selectivity effect is observed with **1**. As evident from Table 1, the molecular dimensions of 1-naphthaldehyde, 9.7 × 8.4 Å^2,[8] allow it to diffuse swiftly through the pores, such that its conversion to the corresponding cyanosilylate reaches 90% after 9 h. In contrast, the conversion yields for 4-phenoxybenzaldehyde and 4-phenyl-benzaldehyde, with molecular dimensions of 13.3 × 7.3 and 13.1 × 6.7 Å^2, respectively, are reduced to below 20% under similar conditions. Given the expectation of comparable reactivity, this suggests that the 10 Å wide pore systems in **1** are too small to readily accommodate the transition state geometry required for activating these substrates. A size-selectivity effect is also apparent in the conversion of selected ketones. Due to their innate reduced reactivity, ketones typically give lower yields than aldehydes under similar conditions. Thus, while conversion of acetophenone to the cyanosilylated product reached only 28% after 24 h, conversion of 4-acetylbiphenyl, a larger ketone with dimensions 13.9 × 6.7 Å^2, was still below 1% after 24 h. Together with recent reports on the oxidation of sulfides[5d] and the Knoevenagel condensation,[5e] this represents one of the first demonstrations of size-selective catalysis in a metal-organic framework.

Encouraged by the high yields observed for the cyanosilylation reactions, we tested the catalytic activity of **1** toward a transformation typically requiring stronger Lewis acids. The Mukaiyama−aldol reaction involves the reaction of an aldehyde (**A**) with a silyl enolate (**SE**) and is one of the most fundamental tools for the selective formation of carbon−carbon bonds.[9] Significantly, this reaction is catalyzed only by very active Lewis acid catalysts,[10] and previous attempts to employ metal-organic frameworks as catalysts proved unsuccessful.[6c] In a test reaction, a solution of benzaldehyde (**A1**) in CH$_2$Cl$_2$ was treated with methyltrimethylsilyldimethylketene acetal (**SE1**) in the presence of 16 mol % of **1**. As shown in Table 2, the observed yield at room temperature was 63% after 99 h, which is comparable with yields obtained for cation-exchanged ZSM-5 or Y-zeolites.[11] In **1**, however, an unprecedented size-selectivity was realized, with the use of 4-*tert*-butylbenzaldehyde (**A2**) reducing the conversion to only 24% and reactions of benzaldehyde with the larger silyl enolates **SE2** and **SE3** resulting in no conversion.

To test the activity of the Mn^{II} sites in the presence of coordinating solvents, the Mukaiyama−aldol reaction was also performed in *N,N*-dimethylformamide (DMF). DMF and certain polar solvents are known to act as Lewis bases that can accelerate the Mukaiyama−aldol reaction at room temperature, even in the absence of Lewis acids.[12] Indeed, for the reaction of **A1** with **SE1** in neat DMF at 25 °C, we observed yields of up to 80% after only 1 h. The rate

was greatly retarded at −45 °C, however, affording only an 8% conversion for the same reaction after 6 h. Notably, addition of **1** accelerated the reaction considerably at this lower temperature, with a conversion of 51% being observed after 6 h. This indicates that the Mn^{II} centers are active even in the presence of a highly coordinating solvent such as DMF. In fact, the 51% conversion is much higher than the 16% conversion observed in dichloromethane after 6 h at 25 °C. Although further mechanistic investigations would be necessary to elucidate the cause of this conversion enhancement, we tentatively ascribe it to a cumulative effect wherein the Mn^{II} centers activate the carbonyl substrate and DMF molecules activate the silyl enolate through loose association with the Si−O bond.

The foregoing results demonstrate that the microporous metal-organic framework **1**, featuring a high concentration of Lewis acidic Mn^{II} sites on its internal surfaces, can catalyze both the cyanosilylation of aromatic aldehydes and the Mukaiyama−aldol reaction in a size-selective fashion. Further studies will focus on modifying **1** toward enantioselective versions of these and other reactions, as well as on investigating the differences arising upon exchange of Mn^{II} for other reactive metal centers.[3f,g]

Supporting Information Available: Experimental procedures, plots demonstrating catalyst recyclability and conversion ratios, an IR spectrum of **1** after absorbing benzaldehyde, powder X-ray diffraction data for as-synthesized and postreaction samples of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Férey, G. *Chem. Soc. Rev.* **2007**, *37*, 191.

(2) (a) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494. (b) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176. (c) Collins, D. J.; Zhou, H.-C. *J. Mater. Chem.* **2007**, *17*, 3154.

(3) (a) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506. (b) Chen, B. L.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745. (c) Peterson, V. K.; Liu, Y.; Brown, C. M.; Kepert, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 15578. (d) Forster, P. M.; Eckert, J.; Heiken, B. D.; Parise, J. B.; Yoon, J. W.; Jhung, S. H.; Chang, J. S.; Cheetham, A. K. *J. Am. Chem. Soc.* **2006**, *128*, 16846. (e) Dincă, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (f) Dincă, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419. (g) Dincă, M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 11172.

(4) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111.

(5) (a) Hu, A.; Ngo, H. L.; Lin, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 6000. (b) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (c) Cho, S. H.; Ma, B. Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563. (d) Dybtsev, D. N.; Nuzhdin, A. L.; Chun, H.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 916. (e) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607. (f) Horcajada, P.; Surble, S.; Serre, C.; Hong, D. Y.; Seo, Y. K.; Chang, J. S.; Greneche, J. M.; Margiolaki, I.; Férey, G. *Chem. Commun.* **2007**, 2820.

(6) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Evans, O. R.; Ngo, H. L.; Lin, W. B. *J. Am. Chem. Soc.* **2001**, *123*, 10395. (c) Schlichte, K.; Kratzke, T.; Kaskel, S. *Microporous Mesoporous Mater.* **2004**, *73*, 81.

(7) (a) Higuchi, K.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2016. (b) Gregory, R. J. H. *Chem. Rev.* **1999**, *99*, 3649. (c) North, M. *Tetrahedron: Asymmetry* **2003**, *14*, 147.

(8) The dimensions given represent maximal cross-sections for the molecules, as determined using MOPAC 7.

(9) (a) Sasidharan, M.; Raju, S. V. N.; Srinivasan, K. V.; Paul, V.; Kumar, R. *Chem. Commun.* **1996**, 129. (b) Orlandi, S.; Mandoli, A.; Pini, D.; Salvadori, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2519. (c) Palomo, C.; Oiarbide, M.; Garcia, J. M. *Chem.—Eur. J.* **2002**, *8*, 37.

(10) (a) Aspinall, H. C.; Bickley, J. F.; Greeves, N.; Kelly, R. V.; Smith, P. M. *Organometallics* **2005**, *24*, 3458. (b) Trost, B. M.; Martinez-Sanchez, S. *Synlett* **2005**, 627. (c) Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. *Synlett* **2005**, 2445.

(11) (a) Sasidharan, M.; Kumar, R. *J. Catal.* **2003**, *220*, 326. (b) Garro, R.; Navarro, M. T.; Primo, J.; Corma, A. *J. Catal.* **2005**, *233*, 342.

(12) Mukaiyama, T.; Fujisawa, H.; Nakagawa, T. *Helv. Chim. Acta* **2002**, *85*, 4518.

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