Inorganic Chemistry

Article

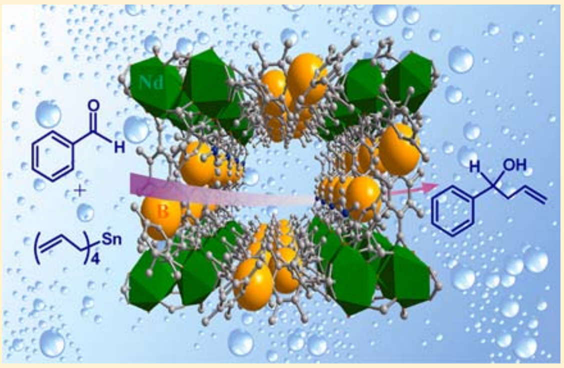
pubs.acs.org/IC

Porous and Robust Lanthanide Metal-Organoboron Frameworks as Water Tolerant Lewis Acid Catalysts

Yan Liu, Ke Mo, and Yong Cui*

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Supporting Information



ABSTRACT: Porous and robust 12-connected metal−organic frameworks (MOFs) were constructed by linking tetranuclear lanthanide (Ln) carbonate clusters with organoboron-derived tricarboxylate bridging ligands. The high-connectivity Ln-MOFs feature remarkable thermal and hydrolytic stability and a large number of isolated Lewis acid B(III) and Ln(III) sites on the pore surfaces. The Nd-MOF assisted with sodium dodecylsulfate was found to be highly effective, recyclable, and reusable heterogeneous catalyst for the carbonyl allylation reaction, the Diels−Alder reaction, and the Strecker-type reaction in water. The transformations were cocatalyzed by Nd(III) and B(III) Lewis acids, with activities much higher than those of the individual organoboron and lanthanide counterparts and their mixture. This work highlights the potential of generating highly efficient water-tolerant solid catalysts via heterogenization of different weak and/or mild Lewis acids in confined spaces of robust MOFs.

INTRODUCTION

Lewis acid catalysts have attracted much attention in organic synthesis because of their versatile catalytic activities in carbon−carbon/nitrogen bond forming reactions.[1] Of particular interest is the development of water-tolerant Lewis acids for organic reactions in water that allow environmentally friendly processes under mild conditions.[2] Even more desirable is to perform organic reactions in water using heterogeneous Lewis acids that are insoluble, easily separable from products.[3] With this purpose, for example, polymer and inorganic oxide-supported lanthanide triflates (homogeneous Lewis acids) have been developed as solid acids for various organic transformations in aqueous media.[4,5] While many solids including zeolites and metal oxides have Lewis acid sites, these are generally inactive sites for reactions in water because of the formation of Lewis acid−base adducts by the coordination of water to the acid sites.[3]

Metal−organic frameworks (MOFs) have emerged as promising crystalline materials for diverse applications.[6,7] In particular, MOFs have great potential in heterogeneous catalysis for their catalysis-friendly features such as large surface areas, extensive porosity, and readily accessible cavities with ordered catalytically active functionalities.[8] The main drawbacks of MOFs as solid catalysts compared to zeolites are their rather lower thermal and chemical stability (hydrolysis sensitive nature), a fact that may undoubtedly limit their practical applications.[8] Whereas numerous MOFs are known to contain a large percentage of coordinatively unsaturated metal ions capable of catalyzing reactions in organic media, one has not been identified as a water-tolerant Lewis acid catalyst.[9,10] In fact, only a few MOFs are found to exhibit high porosity combined with water stability.[11,12] The search for MOF-based catalysts capable of withstanding harsh working conditions remains a long-term challenge. In this regard, Ln-based MOFs with high-connectivity may be the ideal compounds to achieve this target since strong Ln-O bonds can resist hydrolysis, and Ln^{3+} ions have rather flexible coordination spheres and may create coordinatively unsaturated open sites.[10] Tricoordinate organoboron(III) compounds sterically protected by bulky aryl groups are potential Lewis acids with activity in water owing to the vacant $2p_\pi$ orbital on boron[13] and have been employed to make electron deficient MOFs.[14] We report here the synthesis of two porous and robust 12-connected MOFs that combine Lewis acid sites of tricoordinate organoboron(III) derivatives and Ln(III) ions and their applications in heterogeneous Lewis acid catalysis for organic reactions in water, with the activities significantly exceeding their organic and inorganic counterparts.

EXPERIMENTAL SECTION

General Information. All of the chemicals are commercially available, and were used without further purification. The neodymium trimesate metal−organic framework [Nd(trimesate)] was synthesized and activated according to the literature.[10e] Elemental analyses of C, H, and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400−4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. ^1H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at a resonance frequency of 100.63 MHz. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 °C min^{-1} on a STA449C

Received: March 11, 2013
Published: September 5, 2013

dx.doi.org/10.1021/ic400598x | *Inorg. Chem.* 2013, 52, 10286−10291

integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data.

Synthesis of Tris(*p*-carboxylic acid)tridurylborane (H_3L). To a solution of tris(bromoduryl)borane (3.88g, 6.0 mmol) in dry tetrahydrofuran (THF, 150 mL) was added dropwise a pentane solution of *t*-BuLi (1.1M, 33 mL, 36.5 mmol) at −78 °C. After stirring for 1 h, the reaction mixture was allowed to warm up to −60 °C and then dry CO_2 was aerated to the solution. After 1 h, the mixture was warmed up to room temperature and stirred overnight. The reaction mixture was quenched with water and was extracted with Et_2O. The combined organic layers were washed several times with brine, dried over $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by washing with hexane to afford the ligand H_3**L** (2.6g, 80%) as a white solid. ^1H NMR (DMSO-d_6, 400 MHz) δ: 2.04 (s, 18H), 1.90 (s, 18H). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 172.62, 149.28, 138.66, 136.24, 128.85, 20.00, 17.59. ESI-MS: m/z 541.4 (Calcd m/z 541.3 $[M\text{-}H]^+$).

Synthesis of MOFs. A mixture of $NdCl_3\cdot 6H_2O$ (0.01 mmol), H_3**L** (0.005 mmol), and K_2CO_3 (0.005 mmol) was placed in a small vial containing THF (1.0 mL), DMF (0.5 mL), and EtOH (0.5 mL). The vial was sealed, heated at 80 °C for two days, and allowed to cool to room temperature. The purple crystals of **1** suitable for XRD were collected by filtration, washed with diethyl ether, and dried in air. Compound **2** was synthesized in a similar procedure by using $La(NO_3)_3\cdot 6H_2O$. The single-crystal diffraction showed that the products have the formula $(Me_2NH_2)_2[Nd_4(CO_3)\mathbf{L}_4(DMF)_2(H_2O)_2]\cdot 2H_2O$ (**1**) and $(Me_2NH_2)_2[La_4(CO_3)\mathbf{L}_4(DMF)_4(H_2O)_2]\cdot 2H_2O$ (**2**), while microanalysis and TGA indicated that they partially lost guest molecules upon exposure to air.

1. Yield: 72%. IR (KBr, cm^{-1}): 3411(s), 2991(w), 2929(m), 1656(m), 1531(s), 1423(s), 1277(s), 1099(m), 1079(w), 1043(m), 1002(w), 979(m), 870(m), 854(m), 781(w), 675(m), 632(m). Elemental Analysis: Anal. (%). Calcd for $C_{143}H_{202}B_4N_4Nd_4O_{43}$: C, 52.28; H, 6.20; N, 1.71. Found: C, 51.90; H, 6.15; N, 1.69.

2. Yield: 67.9%. IR (KBr, cm^{-1}): 3411(s), 2991(w), 2929(m), 1653(m), 1548(s), 1417(s), 1276(s), 1099(m), 1076(w), 1040(m), 1004(w), 978(m), 869(m), 852(m), 790(w), 672(m), 632(m). Elemental Analysis: Anal. (%). Calcd for $C_{149}H_{208}B_4La_4N_6O_{41}$: C, 53.61; H, 6.28; N, 2.52. Found: C, 52.93; H, 6.21; N, 2.50.

X-ray Crystallography. Single-crystal XRD data for the compounds was collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Cu−Kα radiation (λ = 1.54178 Å) for **1** and Mo−Kα radiation (λ = 0.71073 Å) for **2** at 123 K. The empirical absorption correction was applied by using the SADABS program.[15] The structure was solved using the direct method, and refined by full-matrix least-squares on F^2.[16] All non-H atoms were refined anisotropically. Crystal data and details of the data collection are presented in Table 1, and the selected bond distances and angles are given in Supporting Information, Tables S2 and S3.

Na^+-Exchange Experiment. Freshly ground crystalline powder of **1** (20 mg) was placed in a saturated aqueous solution of NaCl (8 mL). Then, the mixture was heated in a 10 mL capped vial at 40 °C for 4 days. The exchanged product was then isolated by filtration, washed several times with water, acetone, and ether. Inductively coupled plasma (ICP) analysis on the exchanged sample revealed that the molar ratio of Nd to Na is 2:1. Elemental analysis result (%): C, 50.37; H, 5.81; N, 0.83. Thus, the ion-exchanged product can be formulated as $Na_2[Nd_4(CO_3)\mathbf{L}_4(DMF)_2(H_2O)_2]\cdot 10H_2O$ [Anal. (%). Calcd: C, 50.27; H, 5.83; N, 0.84]. Powder XRD experiments indicate that the framework and crystallinity of **1** are retained upon exchange of the cation.

General Procedure for the Allylation Reaction. To a suspension of the evacuated **1** (0.02 mmol) in water (2 mL) in a Schlenk tube was added SDS (sodium dodecyl sulfate, 0.20 mmol), aldehyde or ketone (1 mmol), and tetraallyltin (0.4 mmol). This mixture was stirred at room temperature for a certain period of time and then the solid catalyst was filtered and washed with water and EtOAc. The filtrate was extracted with EtOAc, and the combined organic layers were dried with Na_2SO_4. After filtration and concentration, the residue was purified by flash chromatography to afford the pure product. The characterization data for the products and the procedures for the Diels−Alder reaction and the Strecker reaction are given in the Supporting Information.

Table 1. Crystal Data and Structure Refinement for 1 and 2

	1	**2**
CCDC	861465	861466
empirical formula	$C_{143}H_{182}B_4Nd_4N_4O_{33}$	$C_{149}H_{196}B_4N_6La_4O_{35}$
f_w (g/mol)	3105.13	3230.00
T (K)	123(2)	123(2)
λ (Å)	1.54178	0.71073
cryst syst	orthorhombic	orthorhombic
space group	*Pnna*	*Pnna*
a (Å)	37.6140(15)	37.927(3)
b (Å)	27.2860(11)	27.1472(19)
c (Å)	18.2171(7)	18.4835(12)
V (Å^3)	18694.8(13)	19031(2)
Z	4	4
ρ_{calcd} (g/cm^3)	1.103	1.127
μ (mm^{-1})	8.795	0.940
F(000)	6367	6640
R(int)	0.1086	0.1378
GOF (F^2)	1.012	1.015
R1/wR2 ($I > 2\sigma(I)$)	0.0832/0.1812	0.0609/0.1566
R1/wR2 (all data)	0.1147/0.1949	0.1201/0.1973

■ RESULTS AND DISCUSSION

The ligand H_3L was synthesized in 80% yield by treating tris(*p*-bromoduryl)borane with *tert*-butyllithium and CO_2 at low temperature and was characterized by ^1H and ^{13}C NMR and ESI-MS. Single crystals of $(Me_2NH_2)_2[Ln_4(CO_3)\mathbf{L}_4(DMF)_m(H_2O)_2]\cdot nH_2O$ (**1**: Ln = Nd, m = 2, n = 12; **2**: Ln = La, m = 4, n = 6) were obtained in excellent yields by heating a mixture of $LnCl_3\cdot 6H_2O$, H_3L, and K_2CO_3 in DMF, THF, and EtOH at 80 °C for 2 days. The formulations were supported by the results of microanalysis, IR spectroscopy, and thermogravimetry (TGA).

A single-crystal XRD study performed on **1** reveals an anionic 3D open metal−organic network. **1** crystallizes in the orthorhombic space group *Pnna*, with half of a formula unit in the asymmetric unit. The basic building block for **1** is a tetranuclear $[Nd_4\mu_4\text{-}CO_3]$ cluster. The four metal ions are bridged by a central CO_3^{2-} in a μ_4-η^2:η^2:η^2 fashion to form a quadrangle. The atoms of the carbonate ligand and the four metal centers are almost coplanar with a crystallographic C_2 axis passing through the center. A total of 12 carboxylate groups spans the metal ions from above and below the quadrangle plane. Besides the μ_4-CO_3^{2-} anion, the Nd centers are further coordinated by one chelated and five bidentate carboxylate groups of six **L** ligands forming a dodecahedron or by one chelated and three bidentate carboxylate groups of three **L** ligands, one dimethylformamide (DMF), and one water molecule forming a tricapped trigonal prism. The **L** ligand takes two different coordination modes; one is *exo*-pentadentate (one monodentate and two bis-monodentate bridging carboxylate groups) and the other is *exo*-hexadentate (three bis-monodentate bridging carboxylate groups). The central B atom of each **L** is completely trigonal planar with three duryl groups arranging in a propeller-like fashion. The

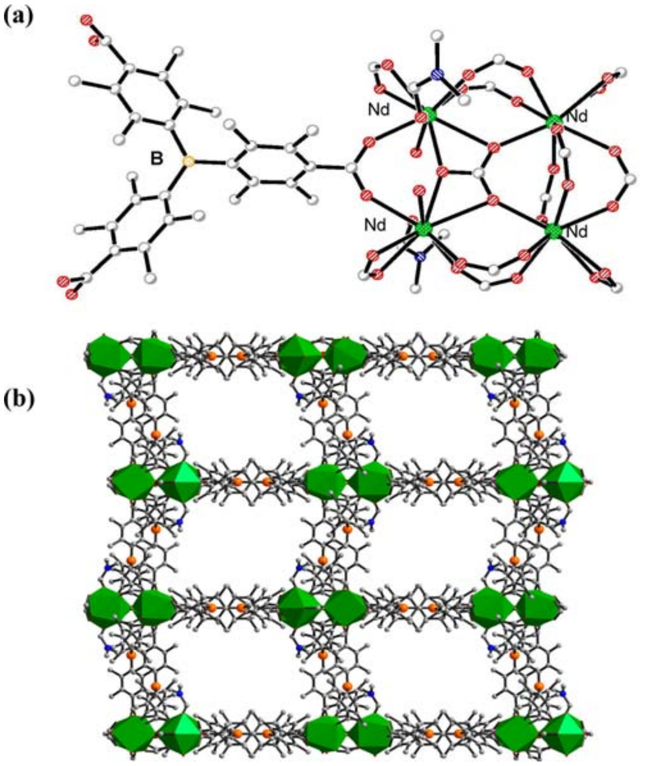


Figure 1. (a) $[Nd_4(\mu_4\text{-}CO_3)]$ cluster with one **L** ligand. (b) A view of the 12-connected 3D framework of **1** along the *c*-axis [Nd green, B yellow, N blue, O red, C gray; the Nd centers are drawn as polyhedra in (b)].

dihedral angles between the boron and the duryl planes range from 43.6 to 59.8°.

Each Nd_4 cluster in **1** is thus linked by 12 **L** ligands, and each **L** ligand is linked to 3 Nd_4 cores forming a unique 3D framework with 1D square-shaped channels of $\sim 1.2 \times 0.8$ nm^2 cross-section along the *c*-axis, which are filled with charge balancing cations $Me_2NH_2^+$ and guest molecules DMF and water. The channel surfaces are uniformly lined with hydrophobic organoboron units and weakly coordinated water and DMF molecules. Although more than 10 different kinds of coordination modes have been reported for the carbonate anion, this particular $\mu_4\text{-}CO_3^{2-}$ bridge mode has only been observed in a limited number of complexes.[17] Tetrametallic clusters bridged by CO_3^{2-} anions have never been encountered in a MOF before. The network topology can be described as a two-nodal (3,12)-connected topology with the point symbol of $(4^{20}.6^{28}.8^{18})(4^3)_4$ whose topological type is 3,12T2 (binary ttd) when the Nd_4 cluster is treated as one 12-connected node and **L** as another 3-connected node. Although high connectivity MOFs are of significance, 12-connected MOFs are still uncommon.[18] Complex **2** is isostructural to **1** and also adopts a (3,12)-connected network structure built from $[La_4(\mu_4\text{-}CO_3)]$ clusters linked by the **L** ligands. Calculations using PLATON show that both **1** and **2** have about ~40% of the total volume available for guest inclusion.[19]

The porous Ln-MOFs are thermally and chemically robust. TGA showed the free and coordinated water and DMF molecules of **1** could be removed at 100 and 220 °C, and the framework is thermal stable up to ~310 °C. The thermal stability of **1** has also been demonstrated using variable-temperature PXRD (VT-PXRD) experiments [Supporting Information, Figure S6(c)], which show that the framework is stable at least up to 290 °C and that is consistent with the TGA result.

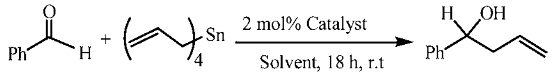
The permanent porosity of **1** and **2** was demonstrated by N_2 adsorption measurements, which showed that they exhibited type I isotherm characteristic N_2 adsorption at 77 K with a Brunauer–Emmett–Teller (BET) surface area of 585 m^2/g and 582 m^2/g, respectively. Examination of the chemical stability of **1** was performed by heating the sample in boiling benzene, methanol, and water for 7 days (conditions that reflect potential extreme industrial requirements), and no obvious change in the powder XRD patterns was found after these treatments. The sample of **1** after soaking in water for 7 days has a BET surface area of 403 m^2/g, further confirming its framework stability and permanent porosity. Moreover, the cation $H_2NMe_2^+$ in **1** can be completely replaced by Na^+ by heating the sample in an aqueous solution of NaCl at 50 °C for 3 days, as confirmed by inductively coupled plasma analysis (ICP) and elemental analysis. The exchanged material (**1**-Na) remains highly crystalline. Note that existing Ln-MOFs are thermally stable in air up to approximately 400 °C, but their stabilities in water are weak and need to be improved. The enhanced structure and thermal stability of **1** is consistent with its high connectivity network, robust Nd_4 cluster nodes bridging by carbonate dianions, and strong Nd–O bonds involving carboxylate groups.[10,16]

The exceptional hydrolytic stability and metric attributes of **1** have prompted us to explore its utilization as a water-resistant solid acid catalyst. The activity of **1** was first examined in the allylation reactions of carbonyl compounds with tetraallyltin, which are among the most fundamental and important carbon–carbon bond-forming reactions in organic synthesis. We chose the reaction of benzaldehyde with tetraallyltin as a model reaction for optimization of the reaction conditions. The reaction proceeded smoothly in the presence of 2 mol % of **1** and 20 mol % SDS in water at room temperature for 18 h, providing the corresponding homoallylic alcohol in 99% yield. The La-MOF **2** showed a similar activity to **1** in the allylation of benzaldehyde (Table 2, entry 8).

When only MOF **1** was used as a catalyst in water, only a trace amount of the product was detected after 18 h. A controlled experiment showed that water itself could not catalyze the reaction (Table, entry 11). The anionic surfactant SDS alone also gave the product in a low yield (18%). The addition of SDS, which can solubilize hydrophobic organic reactants and/or form emulsion in water,[3a] to the reaction system results in a remarkable increase in the catalytic performance of **1** (Table 2, entry 7). A lower catalyst loading (<2%) can be used, but prolonged reaction time was required. While excellent yield was obtained in water, lower yields were observed in organic solvents including dichloromethane, acetonitrile, benzene, and methanol. In all cases, the reaction mixture was clean as only the starting materials and the products were observed by thin layer chromatography during the reaction. Thus, the reaction rate was much faster in water than in organic solvents, and the utilization of water as the solvent was essential in this allylation reaction using **1**/SDS as a catalyst (Table 2, entries 9 and 10).

With the optimized reaction conditions established, we next examined the substrate scope of this transformation. As shown in Table 3, both aromatic and aliphatic aldehyde reacted smoothly with tetraallyltin to give the desired alcohols in good to high yields (Table 3, entries 1–5 and 8). For the unsaturated

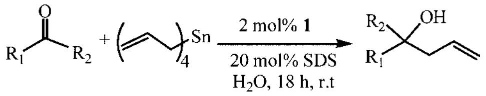
Table 2. Examination of Reaction Conditions[a]



entry	solvent	catalyst	SDS [mol %]	yield [%][b]
1	CH_3CN	**1**	0	77
2	MeOH	**1**	0	72
3	CH_2Cl_2	**1**	0	60
4	DMF	**1**	0	35
5	toluene	**1**	0	trace[c]
6	H_2O	**1**	0	trace[d]
7	H_2O	**1**	20	99
8	H_2O	**2**	20	97
9	DMF	**1**	20	41
10	MeOH	**1**	20	76
11	H_2O	/	20	trace[e]
12	H_2O	SDS	20	18[f]
13	H_2O	$NdCl_3$[g]	20	45
14	H_2O	B(*p*-duryl-Br)$_3$[g]	20	58
15	H_2O	H_3**L**[f]	20	68
16	H_2O	$NdCl_3$ + H_3**L** (1:1)[g]	20	52
17	H_2O	**1**-Na	20	99
18	H_2O	Nd(trimesate)[g]	20	33

[a] Reaction conditions: tetraallyltin (0.4 mmol), aldehyde/ketone (1 mmol), solvent (2 mL), catalyst (0.02 mmol). [b] Isolated yield. [c] Determined by thin layer chromatography. [d] A 1:1 mixture of toluene and water also gave a trace amount of product. [e] No catalyst. [f] SDS (0.24 mmol). [g] 8 mol % loading.

Table 3. Catalytic Allylation Reactions Using 1/SDS in Water[a]



entry	R_1	R_2	yield [%][b]
1	Ph	H	99
2	*p*-$NO_2C_6H_4$	H	98
3	*p*-MeC_6H_4	H	90
4	$Ph(CH_2)_2$	H	91
5	$PhCH{=}CH_2$	H	96
6	$Ph(CH_2)_2$	Me	46[c]
7	$PhCH{=}CH_2$	Me	81[c]
8	biphenyl	H	80
9	coronenyl	H	17

[a] Reaction conditions: tetraallyltin (0.4 mmol), aldehyde/ketone (1 mmol), water (2 mL), **1** (0.02 mmol), SDS (0.2 mmol). [b] Isolated yields. [c] Reaction time: 48 h.

aldehyde (entry 5), only the 1,2-addition product was obtained, and none of the product from a potentially competitive 1,4-addition pathway was observed. We also tested the allylation of ketones (entries 6 and 7), which are in general less reactive than aldehydes in addition reactions, and the desired 1,2-addition adducts were obtained in moderate or good yields at room temperature after 48 h. In the reaction with *α*,*β*-unsaturated ketone, the 1,2-addition reaction proceeded exclusively, and no 1,4-addition took place (entry 7). Therefore, with tetraallyltin in water, the allylation catalyzed by **1**/SDS displayed exclusive chemoselectivity toward both aldehydes and ketones.

Control experiments showed that $NdCl_3{\cdot}6H_2O$, the ligand H_3**L**, and its precursor tris(bromoduryl)borane (8 mol % catalyst loading in each case) all could act as catalysts for the benzaldehyde allylation in water in the presence of SDS, though the product yields are much lower than **1** (Table 2, entries 13–15). Moreover, tricoordinated organoborane derivatives showed higher activity than $NdCl_3$, while MOF **1** exhibited up to 47% higher activity in terms of yield than a 1:1 mixture of $NdCl_3{\cdot}6H_2O$ and H_3**L** (Table 2, entry 16). The profiles of the allylation of benzaldehyde in the presence of **1**/SDS, $NdCl_3$/SDS, and H_3**L**/SDS were studied (Figure 2). It was found that the initial rates of the $NdCl_3$- and H_3**L**-catalyzed reactions were comparable to the MOF-catalyzed reaction in water, but the former almost lost their activities after ~10 h. By contrast, the MOF-based catalyst exhibited close to constant reactivity over 18 h. The allylation of benzaldehyde was also carried out with the cation exchanged sample **1**-Na and the robust MOF Nd(trimesate) reported by Zou et al., which contains 1D channels (7.0 × 7.0 Å^2) with open Nd clusters.[10e] **1**-Na showed almost the same activity as **1**, suggesting that the cation has little influence on the activity of the framework, whereas Nd(trimesate) showed much lower activity, with 33% yield after 18 h using 8 mol % catalyst loading. Taken together, the above results suggested that the allylation reaction was cocatalyzed by the lanthanide and boron Lewis acids synergistically. The assembly of organoboron and lanthanide ions into a robust MOF can not only avoid their deactivation during reactions and but also create confined spaces with a high density of two types of accessible surface Lewis acid sites,[8] leading to a property that is not a simply linear sum of those of the pure components. Further study to elucidate the reaction mechanism is in progress.

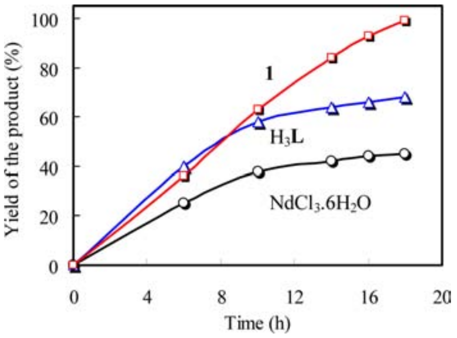


Figure 2. Plots of yields versus time for the allylation of benzaldyhyde in water catalyzed by **1**/SDS, H_3**L**/SDS, and $NdCl_3$/SDS (8 mol % catalyst and 20 mol % SDS for the latter two cases). The yields were isolated yields.

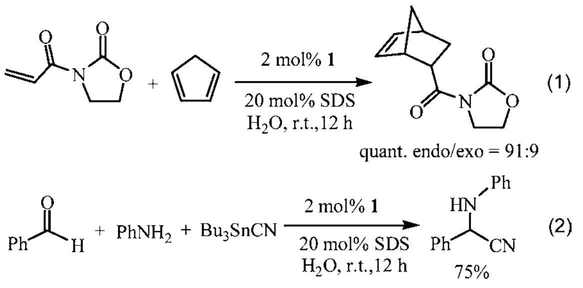
Importantly, removal of **2** by filtration after only 6 h shut down the allylation of benzylaldehyde, affording only 30% total conversion upon standing for 36 h. The solution NMR during the allylation of benzylaldehyde was recorded, which indicates the absence of ligand from the solution. These results demonstrate that no effective homogeneous catalyst species exists in the reaction solution, indicating the heterogeneous nature of the catalyst system. When a sterically more demanding substrate coroneyl aldehyde was used (Table 3, entry 9), only 17% yield was observed, which was much lower than 50% yield obtained with a 1:1 mixture of $NdCl_3{\cdot}6H_2O$ and H_3**L**, presumably because this aldehyde cannot easily gain access to the active sites within **1** because of its large diameter.

This point is also suggested by the fact that ground and unground particles of **1** (~200 nm in size) exhibited similar catalytic activities in the allylation of benzyaldehyde after 18 h. It is thus likely that the catalytic reactions are heterogeneous and may occur within the MOF.

Upon completion of the allylation of benzylaldehyde, the solid catalyst **1** could be recovered by simple filtration and can be reused at least three times without any significant loss of its catalytic activity (~99, 97, and 91% yields for 1−3 cycles). PXRD indicated the framework structure and surface area of **1** remained almost unchanged after three cycles. Inductively coupled plasma-atomic mass spectrometry (ICP-AMS) analysis of the product solution indicated little loss of the Nd ion (~0.1%) from the structure per cycle, either as molecular species or as particles too small to be removed by filtration through Celite. The activity observed for MOF **1** catalyzed allylation of benzylaldehyde is comparable to those found for $Sc(OTf)_3$ (5 mol % loading, 94% yield and 8 h),[3c] the Sc-exchanged surfactant (10 mol % loading, 82% yield and 12 h),[4e] and the organic polymer-supported Sc(III) catalyst (3.2 mol % loading, 92% yield and 12 h),[4a] as well as the Ti-exchanged zeolite ZSM-5 (35 wt % loading, 82% yield and 1 h)[5d] and metal oxide $Nb_2O_5 \cdot nH_2O$ (catalyst/substrate 21:50 (w/w), 23% yield and 1 h).[5a] To our knowledge, this represents the first example of a MOF that can be used as a Lewis acid catalyst in aqueous medium.[8c,10,20]

We have also demonstrated the applicability of the catalytic **1**/SDS system in other important synthetic reactions. As shown in Scheme 1, in the presence of 2 mol % of **1** and 20 mol % SDS, 3-acryloyl-1,3-oxazolidin-2-one reacted with cyclopentadiene at room temperature for 12 h in water to afford the corresponding Diels−Alder product quantitatively (endo/exo = 91/9)]. The Strecker-type reaction of benzaldehyde, aniline, and tributyltin cyanide was performed. The reaction proceeded smoothly in the presence of 2 mol % of **1** and 20 mol % SDS in water to afford the corresponding α-amino nitrile derivative in 75% yield (room temperature, 12 h). In both cases, the isolated product yields are much higher than those of the 1:1 catalyst mixture of $NdCl_3$ and H_3**L** (53% and 46% yields for the Diels−Alder and the Strecker reaction, respectively). These results illustrate the generality of the **1**/SDS system in catalyzing carbon−carbon/nitrogen bond-forming reactions in water. Note that the observed quantitative and 75% yields for the above reactions are comparable with yields obtained for lanthanide/scandium triflates and their polymer-supported solids.[3d,4a,b]

Scheme 1. Diels-Alder Reaction and Strecker-Type Reaction Catalyzed by 1/SDS in Water



CONCLUSIONS

We have synthesized two 12-connected 3D porous MOFs built of polynuclear Ln clusters linked by organoboron tricarboxylate ligands. The high-connectivity Ln-MOFs containing tetranuclear lanthanide carbonate clusters feature remarkable thermal and chemical stability and internal accessible B(III) and Ln(III) Lewis acid sites. The Nd-MOF/SDS system was verified to be highly effective, recyclable, and reusable solid acids for various organic reactions in water, establishing that its catalytic activity is much higher than those of the individual organic and inorganic counterparts. The heterogenization of different types of Lewis acids in confined spaces of robust MOFs may provide a new paradigm for the development of novel and synthetically useful catalysts. We are currently exploring the general applicability of the dual catalyst design concept based on framework structures.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yongcui@sjtu.edu.cn. Tel: +86-21-54747687. Fax: +86-21-54741297.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by NSFC-21025103 and 21371119, "973" Program (2014CB932102 and 2012CB8217) and Shanghai Science and Technology Committee (10DJ1400100 and 12XD1406300).

REFERENCES

(1) (a) Yamamoto, H., Ed.; *Lewis Acid in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2000. (b) North, M.; Usanov, D. L.; Young, C. *Chem. Rev.* **2008**, *108*, 5146.

(2) (a) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095. (b) Butle, R. N.; Coyne, A. G. *Chem. Rev.* **2010**, *110*, 6302.

(3) (a) Kobayashi, S.; Manabe, K. *Acc. Chem. Res.* **2002**, *35*, 209. (b) Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641. (c) Kobayashi, S.; Wakabayashi, T.; Oyamada, T. *Chem. Lett.* **1997**, 831. (d) Kobayashi, S.; Busujima, T.; Nagayama, S. *Chem. Commun.* **1998**, 19.

(4) (a) Nagayama, S.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 567. (b) Reetz, M. T.; Giebel, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2498. (c) Gu, W.; Zhou, W.; Gin, D. L. *Chem. Mater.* **2001**, *13*, 1949. (d) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2003**, *125*, 10486. (e) Hachiya, I.; Kobayashi, S. *J. Org. Chem.* **1993**, *58*, 6958.

(5) (a) Nakajima, K.; Baba, Y.; Noma, R.; Kitano, M.; Kondo, J. N.; Hayashi, S.; Hara, M. *J. Am. Chem. Soc.* **2011**, *133*, 4224. (b) Corma, A.; Llabrés i Xamena, F. X.; Prestipino, C.; Renz, M.; Valencia, S. *J. Phys. Chem. C* **2009**, *113*, 11306. (c) Moliner, V.; Román-Leshkov, Y.; Davis, M. E. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6164. (d) Bhuyan, B. K.; Borah, A. J.; Borah, K. J.; Phukan, P. *Tetrahedron Lett.* **2011**, *52*, 2649.

(6) (a) Tranchemontagne, D. J.; Mendoz-Cortes, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257. (b) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.

(7) (a) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330. (b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (c) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (d) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, V.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705. (e) Tanabe, K. K.; Cohen, S. M. *Chem. Soc. Rev.* **2011**, *40*, 498. (f) Chen, S. X.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115. (g) Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. *Acc. Chem. Res.* **2005**, *38*, 273. (h) Xuan, X.; Zhu, C.; Liu, Y.; Cui, Y. *Chem. Soc. Rev.* **2012**, *41*, 1677.

(8) (a) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (b) Lee, J.-Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (c) Corma, A.; Garcia, H.; Xamena, F. X. L. i. *Chem. Rev.* **2010**, *110*, 4606. (d) Liu, Y.; Xuan, W.; Cui, Y. *Adv. Mater.* **2010**, *22*, 4112.

(9) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Horike, S.; Dincă, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 5854. (c) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 4204. (d) Gedrich, K.; Heitbaum, M.; Notzon, A.; Senkovska, I.; Frölich, R.; Getzschmann, J.; Mueller, U.; Glorius, E.; Kaskel, S. *Chem.—Eur. J.* **2011**, *17*, 2099.

(10) (a) Evans, O. R.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2001**, *123*, 10395. (b) Gándara, F.; Puebla, E. G.; Iglesias, M.; Proserpio, D. M.; Snejko, N.; Monge, M. A. *Chem. Mater.* **2009**, *21*, 655. (c) Snejko, N.; Cascales, C.; Gomez-Lor, B.; Gutiérrez-Puebla, E.; Iglesias, M.; Ruiz-Valero, C.; Monge, M. A. *Chem. Commun.* **2002**, *38*, 1366. (d) Han, J. W.; Hill, C. L. *J. Am. Chem. Soc.* **2007**, *129*, 15094. (e) Gustafsson, M.; Bartoszewicz, A.; Martín-Matute, B.; Sun, J.; Grins, J.; Zhao, T.; Li, Z.; Zhu, G.; Zou, X. *Chem. Mater.* **2010**, *22*, 3316. (f) Lin, Z.; Zou, R.; Xia, W.; Chen, L.; Wang, X.; Liao, F.; Wang, Y.; Lin, J.; Burell, A. K. *J. Mater. Chem.* **2012**, *22*, 21076. (g) Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2008**, *130*, 6718. (h) Ma, S.; Wang, X.-S.; Yuan, D.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4130. (i) Chen, Y.; Ma, S. *Rev. Inorg. Chem.* **2012**, *32*, 8.

(11) (a) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci.* **2006**, *103*, 10186. (b) Huang, X.-C.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557. (c) Biswas, S.; Grzywa, M.; Nayek, H. P.; Dehnen, S.; Senkovska, I.; Kaskel, S.; Volkmer, D. *Dalton Trans.* **2009**, 6487.

(12) (a) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surble, S.; Dutour, J.; Margiolaki, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6296. (b) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040. (c) Ahnfeldt, T.; Guillou, N.; Gunzelmann, D.; Margiolaki, I.; Loiseau, T.; Fërey, G.; Senker, J.; Stock, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 5163. (d) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. J. *J. Am. Chem. Soc.* **2008**, *130*, 13850.

(13) (a) Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131. (b) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6335.

(14) (a) Liu, Y.; Xu, X.; Zheng, F.; Cui, Y. *Angew.Chem., Int. Ed.* **2008**, *47*, 4538. (b) Liu, Y.; Xuan, W.; Zhang, H.; Cui, Y. *Inorg. Chem.* **2009**, *48*, 10018. (c) Liu, Y.; Xu, X.; Xia, Q.; Yuan, G.; He, Q.; Cui, Y. *Chem. Commun.* **2010**, *46*, 2608. (d) Blight, B. A.; Guillet-Nicolas, R.; Kleitz, F.; Wang, R.-Y.; Wang, S. *Inorg. Chem.* **2013**, *52*, 1673.

(15) Sheldrick, G. M. *SADABS, program for empirical absorption correction of area detector data*; University of Göttingen: Göttingen, Germany, 1996.

(16) Sheldrick, G. M. *SHELXTL NT, Program for Solution and Refinement of Crystal Structures*, Version 5.1; University of Göttingen: Göttingen, Germany, 1997.

(17) (a) Fondo, M.; García-Deibe, A. M.; Bermejo, M. R.; Sanmartín, J.; Llamas-Saiz, A. L. *Dalton Trans.* **2002**, 4746. (b) Rodríguez, M.; Llobet, A.; Corbella, M.; Müller, P.; Usón, M. A.; Martell, A. E.; Reibenspies, J. *Dalton Trans.* **2002**, 2900.

(18) (a) Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. C.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 1560. (b) Ahnfeld, T.; Guillou, N.; Gunzelmann, D.; Margiolaki, I.; Loiseau, T.; Férey, G.; Senker, J.; Stock, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 5163. (c) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850. (d) Li, D.; Wu, R.; Zhou, X.-P.; Zhou, R.; Huang, X.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175. (e) Zhang, X. M.; Fang, R.-Q.; Wu, H.-S. *J. Am. Chem. Soc.* **2005**, *127*, 7670. (f) Jia, J.; Lin, X.; Wilson, C.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Walker, G.; Cussen, E. J.; Schroder, M. *Chem. Commun.* **2007**, 84. (g) Sumida, K.; Hill, M. R.; Horike, S.; Dailly, A.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 15120. (h) Robinson, S. A. K.; Mempin, M.-V. L.; Cairns, A. J.; Holman, K. T. *J. Am. Chem. Soc.* **2011**, *133*, 1634.

(19) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(20) Dewa, T.; Saiki, T.; Aoyama, Y. *J. Am. Chem. Soc.* **2001**, *123*, 502.