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An In-based 3D metal-organic framework as heterogeneous

Lewis acid catalyst for multi-component Strecker reactions

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Abstract

A novel three-dimensional metal-organic framework (MOF) $\{[In_3(NIPH)_3 (HNIPH)(OH)_2] \cdot 4H_2O\}_n(1)$ (H₂NIPH = 5-nitroisophthalic acid) with one-dimensional channels was synthesized and structurally characterized. Importantly, it demonstrates excellent catalytic activity for the Strecker reactions of two or three components under mild conditions. Moreover, the catalytic recycling of 1 as a representative example was explored. It can be easily separated and reused for no less than five runs with more than 80% conversion yield in catalytic ability.

Keywords: metal-organic framework; structure; Strecker reactions; catalyst

1. Introduction

Metal-organic frameworks (MOFs) are crystalline hybrid materials consisting of discrete inorganic metal-containing nodes and multidentate organic ligands (linkers)[1-3]. As an emerging class of crystalline materials, MOFs have gained tremendous attention and become one of the fastest growing fields in both chemistry

and materials over the last two decades owing to their periodic structure and high thermal stability [4-11]. It has been known that various factors, such as temperature, solvent, additive templating, metal-to-ligand ratio, coordination geometries of metal centers, coordinated modes of organic ligands, etc., can impose a great influence on the self-assembly process, which is responsible for the variation of properties of MOFs significantly [12]. Over the last few years, it has been reported that MOFs can catalyze various organic reactions such as Cyanosilylation, Acetalization, Knoevenagel condensation reactions, Coupling reactions of CO_2 , Strecker reactions and so on [13-15].

Some functional MOFs have been developed as efficient heterogeneous catalysts capable of catalyzing various organic reactions for the following reasons: 1) the ordered porous structures can facilitate the accessibility of substrates to active sites; and 2) metal ions can serve as Lewis acid to activate substrates [16-20]. In this regard, the choices of metals and ligands are crucial to constructing MOFs of catalytic function. In³⁺ ions have rather flexible coordination spheres and usually adopt various coordination numbers, which affords active Lewis acid catalysis center for various organic reactions [21,22]. Moreover, 5-nitroisophthalic acid (H₂NIPH), closed to benzene-1, 3, 5 tricarboxylic acid (H₃BTC), has multiple coordination sites that may generate structures of higher dimensions [23]. Nitryl groups (-NO₂) coexisting in isophthalic acid probably act as a hydrogen bond acceptor and also take on some spatial effects in the formation of MOFs [24]. In some previous reports, it has been validated to be a proper polydentate bridging ligand for the formation of multidimensional MOFs [25-29]. In-based MOFs with high-connectivity may afford active Lewis acid catalysis centers to perform catalytic activities [30-32].

Strecker reactions are one of the most common ways for the syntheses of aminonitriles, which have been extensively employed as significant organic intermediates for α -amino acids, β -amino acids, other nitrogen-containing heterocycles etc. [33-35]. Thus, exploring efficient catalysts for Strecker reactions has become a topic of great significance. Over the past decades, a variety of efficient homogeneous and heterogeneous catalysts have been studied for Strecker reactions [36-39]. Compared to conventional homogeneous catalysts, heterogeneous catalysts have many advantages, including separation and catalyst reutilization, low toxicity, especially for MOFs [40,41]. Li et al. reported that copper(I)/copper(II)-salen MOF could be used as an efficient heterogeneous multifunctional catalyst for the synthesis of aminonitriles via asymmetric three-component Strecker reactions with 99% conversion rate [42]. Monge et al prepared a mesoporous In-MOF that can be reused for 10 repeated experiments without significant loss of activity [43].

In this article, a novel MOF $\{[In_3(NIPH)_3(HNIPH)(OH)_2]\cdot 4H_2O\}_n$ (1) was obtained based on H₂NIPH and structurally characterized. 1 shows a 3D porous framework with 1D channels. And catalytic performance of the obtained MOF was investigated toward Strecker reactions. For the catalytic process, metal In (III) site served as Lewis acid to activate aldimine or aldehyde, and the obtained MOF catalysts exhibited excellent catalytic performance for Strecker reactions under mild conditions. More importantly, 80% conversion rate of catalyst 1 was maintained after five consecutive runs.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were purchased from commercial sources without further purification. Powder X-ray diffraction (PXRD) data were obtained using SHIMADAZU XRD-6100 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Fourier-transform infrared (FT-IR) spectra was measured on a Nicolet Impact 410 spectrometer in the 4000-400 cm⁻¹ range using the KBr pellet method. Elemental analyses (C, H and N) were performed using an Elementar Vario EL cube CHNOS Elemental Analyzer. ¹H NMR spectra were recorded with a Bruker Avance 400 console at a frequency of 400 MHz. UV-vis absorption spectra were tested on a Perkin-Elmer Lambda 950 spectrophotometer.

2.2. Synthesis

{[In₃(NIPH)₃(HNIPH)(OH)₂]·4H₂O}_n (1): A mixture of H₂NIPH (0.0211 g, 0.1 mmol), InCl₃·4H₂O (0.1 M, 1 ml) was added to CH₃CN (4 ml), NaOH (1 M, 100 μ l) in a 23 ml Teflon-lined autoclave and then heated under autogenous pressure at 110 °C for three days, then cooled to room temperature under ambient conditions. The colorless block crystals were obtained by filtration and washed with distilled water, and dried in air. Yield: 70% for **1** (based on InCl₃·4H₂O). Elemental analysis (%) for **1**: Anal. Calc.: C, 29.84; H, 1.79; N, 4.38; Found: C, 29.91; H, 1.87; N, 4.27.

2.3. Single crystal X-ray crystallography

Crystallographic data for **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Mo K α (0.71073 Å) radiation at room

temperature. Structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by the SHELXTL-97 crystallographic software package [44]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to C atoms were placed in calculated positions and refined isotropically using a riding model with an Uiso(H) equivalent to 1.2 times of Ueq(C). Approximately 26.9 % of the unit cell volume comprises a large region of the disordered solvent which could not be modeled as discrete atomic sites. To resolve this issue, solvent molecules were removed by SQUEEZE subroutine in PLATON [45]. The final molecular formula of 1 was derived from crystallographic data combined with elemental and thermogravimetric analyses data. Crystal detailed data collection and refinement of 1 are summarized in Table S1.

Crystallographic data (excluding structure factors) for the structures of this work have been submitted to Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1560355 for **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

2.4. Catalytic experiment

Sample 1 was soaked in CH₃OH for 24 h at room temperature and then heated at 100 °C for 12 h under vacuum before the reaction to remove guest molecules from pores and surface. The basic framework of 1 was retained after activation. For the catalytic experiments, activated catalyst (0.0134 mmol), aldimine (0.14 mmol) and trimethylsilyl cyanide (TMSCN) (47 μ l) in CDCl₃ (2.4 ml) were sequentially added to a glass vial of 20 ml. The reaction mixtures were stirred at room temperature. The reactions were monitored by ¹H NMR spectroscopy and conversion yield was

determined from the ratio of the integral of the product signal in relation to the sum of integrals of all signals (aldehyde, aldimine and products).

3. Results and discussion

3.1. Structural description



Scheme 1. Coordination modes of H₂NIPH ligand in 1.



Fig. 1. (a) Coordination environments of In^{3+} ions in **1**. Hydrogen atoms are omitted for clarity. Symmetry mode: A = -x, y, 1-z; B = -0.5+x, 0.5-y, z. (b) 2D layer in **1**. (c) View of the 3D network along [001] direction. (d) Topology structure of **1**.

Single-crystal analysis reveals that **1** crystallizes in monoclinic space group C2/m. As shown in Fig. 1a, there are two kinds of metal atoms (In1 and In2) in the

asymmetric unit of **1**, in which the In2 atom resides at a crystallographic inversion center with an occupancy of 0.5. In1 ion is located in a octahedral geometry and coordinated by four carboxylate oxygen atoms (O5, O5A, O10, O10A) from four different NIPH²⁻ ligands and two oxygen atoms (O1, O1A) from two OH groups, in which O1, O1A, O5, O5A at the equatorial positions, O10 and O10A are at the axial positions with an O(10)-In(1)-O(10A) angle of 179.053(151)°. In2 atom also displays a slightly distorted octahedral coordination geometry, in which O1, O3, O7B, O12 atoms define the equatorial plane and two atoms O9A, O11 occupy vertex position. Apexes bond angle of O9A-In2-O11 is 170.266(148)°. In-O bond length varies from 2.111(4) Å to 2.234(4) Å. [symmetry codes: (A) -x, y, 1-z; (B) -0.5+x, 0.5-y, z].

In 1, InO₄ units are linked to each other through OH groups, giving an infinite bent -In-OH-In-OH-chain (Fig. S7). These chains are further alternately linked by NIPH²⁻ ligands with conformations I and III to yield a layer along *a* axis (Fig. 1b). HNIPH⁻ ligands adopting bridge modes II pillared these 2D layers, resulting in the formation of a single 3D network with 1D channels along *c* axis (Fig. 1c). From a topological perspective, the ligand could be regarded as a 2-connected node, and each In1 connecting two O1 atoms of OH groups can be considered as a two-connected node. Each In2 connecting two ligands and O1, O2 atoms can be seen as a four-connected node. Thus, the single 3D network can be described as a 2, 2, 4-connected network with a point symbol of $\{8^2.10^3.12\}_2$ $\{8\}_3$ (Fig. 1d).

 N_2 adsorption-desorption was performed with activated **1** given its 1D channels structural nature [Fig. S10]. Although **1** contains sufficient window dimension (6 Å) for diffusion of N_2 , it shows a low uptake [46-48].

3.2. Characterizations

Phase purity of as-synthesized **1** was confirmed by PXRD measurements, which is in agreement with the simulated one (Fig. S1). TGA was performed on **1** under air atmosphere with a heating rate of 10 °C min⁻¹ from 25 to 800 °C. **1** releases OH groups and free H₂O molecules (8.1 wt.%) over the temperature range of 25-100 °C (calc. 8.4 wt.%). Between 360 and 590 °C, **1** displays a continuous mass loss (55.2 wt.%), which corresponds to the loss of ligands in the framework (calc. 58.9 wt.%) (Fig. S6).

FT-IR spectrum of **1** shows the characteristic bands of nitro groups and carboxylic groups. In particular, nitro groups show absorption owing to asymmetric and symmetric N-O stretching modes. Asymmetric modes typically result in a strong band at 1532 cm⁻¹, symmetric modes absorption peaks at 1347 cm⁻¹ [49,50]. The absorption band appeared at 1630 cm⁻¹ was attributed to the C=O stretching vibration. The absorption bands at 1080 cm⁻¹ corresponded to the C-O stretching vibration [51] (Fig. S4), all of which are consistent with the results of single-crystal X-ray analysis.

Chemical stability of **1** was expected to play a critical role in its catalytic performance for the Strecker reactions. Herein, we evaluated the stability of **1** by immersing the samples in various organic solvents, including DMF, DMA, CH_3OH , C_2H_5OH , CH_2Cl_2 , and $CHCl_3$. PXRD patterns show that all experimental diffraction peaks agree well with the simulated counterparts (Fig. S2), indicating that the structure of **1** was retained after treatment with solvents.

3.3. Catalytic properties

Strecker reactions, as a class of important organic reactions for synthesis of amino acids, have aroused ample attention [52,53]. Strecker reactions are well known as Lewis acid or base catalyzed C-C bond formation. In the past decades, numerous

homogeneous catalysts, such as metal salts, metal-salen complexes, metal oxides, have been extensively utilized for Strecker reactions of aldimines [54-58]. Moreover, some MOFs with open metal sites have also shown high catalytic efficiencies for Strecker reactions in the presence of organic solvents [59-61]. A comparison of the catalytic performance of different MOF catalysts in Strecker reactions is shown in Table S2. Given the rich coordination unsaturated In³⁺ in **1**, the catalytic performance of the Strecker reactions was investigated with low catalyst loading and mild temperature conditions.

To evaluate the effectiveness of the fresh and activated **1** as catalysts, their catalytic activities were compared in Table S4. From the Table S4, we can conclude that the catalytic performance is significantly improved after activation.



Table 1. Strecker reaction of various aldimines catalyzed by activated 1^a.



24



11

66

^a Reaction conditions unless specified otherwise: aldimine (0.14 mmol), TMSCN (47 μ l), catalyst (0.0134 mmol), CDCl₃ (2.4 ml) at room temperature. ^b Yields were calculated by ¹H NMR with aldimines. ^c Same reaction conditions without catalyst **1**.

As shown in Table 1, initial reaction was performed at room temperature. Benzylidene-phenyl-amine reacted with TMSCN and gave rise to 96% conversion rate of Phenyl-phenylamino-acetonitrile after 24 h (Table 1, entry 2). Noticeably, when the reactions were carried out without catalysts, it is hardly to yield any target products (Fig. 2, Table 1, entry 1), indicating the high catalytic performance of activated **1** with respect to Strecker reactions.

Considering the high catalytic activity of activated **1** toward the Strecker reaction of aldimine with TMSCN, various aldimines with different substitution groups were further selected as reaction substrates. The electron-donating group (-OCH₃) gave higher yields whereas the electron-withdrawing group (-CF₃) decreased yields with respect to aldimine. Aldimine derivatives bearing electron-donating groups (-OCH₃) were converted to catalytic products with a higher conversion rate (92%) after 24 h (Table 1, entry 3).

When sterically more demanding substrate aldimines were used, conversion rates were obviously reduced (Table 1, entries 8 and 11), which may be ascribed to the fact that these aldimines cannot easily approach the active sites within **1** due to its larger bulkiness than the others.





Fig. 2. Conversion of benzylidene-phenyl-amine in the Strecker reaction catalyzed by 1 (green) and by the filtrate of 1 after 5 h of the reaction (red). Reaction conditions: aldimine (0.14 mmol), TMSCN (47 μ l), CDCl₃ (2.4 ml), Cat.1 (0.0134 mmol), room temperature.

To clarify the heterogeneity of the catalytic reaction, activated **1** was separated by filtration when product conversion rate reached 24% (5 h) and then the reaction continued on. A slight increase in product yield after 30 h (Fig. 2). Moreover, H₂NIPH ligand was not observed from UV-vis spectra of the filtrate, indicating that the present Strecker reaction was indeed heterogeneous (Fig. S8).

Table 2. Strecker reaction of three-component catalyzed by activated 1^a.



entry	aldehyde	amine	reaction time (h)	conversion yield (%) ^b
1	С Н	NH ₂	24	94
2	Н	H ₃ CO	² 7.5	93
3	Н	F ₃ C NH ₂	24	61
4	H ₃ CO H	NH ₂	24	44
5	H ₃ CO	H ₃ CO	H ₂ , 24	91
6	H ₃ CO	F ₃ C NH ₂	24	18
7	Н3С Н	NH ₂	24	51
8	нзс Н	H ₃ CO NH	² 24	57
9	F ₃ C H	NH ₂	24	91

10
$$\mathbf{F_{3}C}$$
 $\mathbf{NH_{2}}$ 24 19

^a Reaction conditions: aldehyde (0.14 mmol), aniline (0.14 mmol), TMSCN (47 μl), catalyst (0.0134 mmol), CDCl₃ (2.4 ml) at room temperature. ^b Yields were calculated by ¹H NMR with aldehydes.

three-component Strecker reactions also aroused great concerns. The Three-component Strecker reactions possess obvious advantages over binary reactions, for example, the separation and purification of intermediate products are omitted and the former method improves atom economy with broaden applicability [62]. Herein, the three-component Strecker reactions were successfully carried out based on a series of various aldehydes, amines and TMSCN by using one-pot protocol in the presence of activated 1 at room temperature and gave good yields as summarized in Table 2. Significantly, for the three-component Strecker reaction of aromatic aldehydes with an electron-donating group (i.e. -OCH₃, -CH₃), anilines and TMSCN, the catalytic conversion rate can only reach 44% and 51%, respectively (Table 2, entries 4 and 7). Moreover, amines such as 4-methoxyl-phenylamine were also utilized as substrates in the reactions. Notably, 4-methoxyl-phenylamine and aldehyde showed a much higher conversion (93%) rate and 91%) in comparison that to of 4-trifluoromethyl-phenylamine (61% and 18%), indicating that electron group types also have effects on the catalytic performance (Table 2, entries 2, 3 and 5, 6).

Stability and recyclability of activated **1** were further investigated by using benzaldehyde and aniline as substrate. After a 24 h catalytic reaction, activated **1** was isolated by filtration and washed with methanol and reused for the next reaction. More than 80% yield was retained even after five consecutive runs (Fig. S9). Moreover,

PXRD patterns before and after the catalytic reactions indicate that structure of activated **1** was maintained after recycle reactions (Fig. S3).

4. Conclusions

In summary, a stable 3D In-based 1 with 1D channels was produced with rich open Lewis acid sites. It exhibited higher catalytic activities as an efficient heterogeneous catalyst for the multi-component Strecker reactions under mild conditions. Importantly, activated 1 shows much higher catalytic activities to aldimine derivatives with electron-donating groups in comparison to those with electron-withdrawing groups in two-component Strecker reaction catalytic process. With increasing size of reaction substrates, conversion rates were suppressed obviously. Moreover, in the three-component Strecker reaction, catalyst 1 can be reused up to five times with comparable stability. The excellent catalytic activity and good stability demonstrate that 1 is an efficient heterogeneous catalyst for α -aminonitriles formation at room temperature.

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Graphical abstract and legend

An In-based 3D metal-organic framework as heterogeneous Lewis acid catalyst for multi-component Strecker reactions

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A novel three-dimensional metal-organic framework based on 5-nitroisophthalic acid ligand has been prepared under solvothermal condition. It can be as Lewis acid

catalyst and show good catalytic activity for the multi-component Strecker reactions. Especially, it can obtain more than 80% conversion yields after five consecutive runs.

Highlights

- In-base metal-organic framework (MOF) 1 has been successfully synthesized. 1 features a 3D framework with 1D channels.
- 2. 1 performs as Lewis acid catalyst on multi-component Strecker reactions.
- 3. 1 displays good catalytic activity for heterogeneous multi-component Strecker reactions with more than 80% conversion yields after five runs.