Bifunctional Gyroidal MOFs: Highly Efficient Lewis Base and Lewis Acid Catalysts

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Abstract: A family of gyroidal metal–organic frameworks (STUs) composited with transition metal ions and bi-imidazolate ligands (BIm) were prepared and applied as both Lewis base and acid catalysts. Benefiting from the intrinsic basicity of the ligands and the Lewis acidic sites of the open metal centres, the STUs materials show excellent catalytic activities as Lewis base for the Knoevenagel condensation reaction between various aldehydes and malononitrile, and as Lewis acid for cyanosilylation reactions. Among these STUs, STU-4 (Ni(BIm)) shows the best catalytic efficiency (conversions >99%) in both Knoevenagel condensation and cyanosilylation reactions under mild conditions, providing thus an advanced material for both Lewis base and Lewis acid catalysis.

Introduction

Knoevenagel condensation reaction between aldehydes or ketones with an activated methylene group-containing compound is one of the important routes to C–C coupling to synthesize α, β-unsaturated carbonyl compounds/heterocyclic compounds, which are common intermediates in pharmaceutical industry or biological applications.[1–4] This reaction features basic-catalyzed character,[5] also there are some studies reporting the acidic-basic synergistic functions.[6,7] The Knoevenagel reaction could be catalyzed by N-containing homogeneous catalysts like urea, amino acids and piperidine.[8,9] Some solid complex, such as metal oxides or ionic liquid immobilized mesoporous silica are also utilized for this basic-catalyzed reaction,[10–12] however, drawbacks of metal contamination of the products or leaching of the anchored catalyst usually hinder the application of these catalysts.

Constructed from organic linkers and metal nodes, Metal-organic frameworks (MOFs) have large surface area and pore volume, tunable characters of metallic nodes and organic linkers, high stability, and have been widely used as heterogeneous catalysts.[5,13–20] The active catalysis sites in MOFs are commonly the unsaturated coordinative metal nodes and the ligands or post-modified ligands.[21–23] Compared with the post-synthetic modification strategy, catalysis using intrinsic basicity in MOF is more convenient and simple. Both ligand and metal ion in MOFs can be served as active sites for catalysis. Thus, a MOF can bear several functions, for example, catalyzing multiple types of reactions and being a promising material.

In our previous studies, a series of MOFs with gyroidal surfaces were fabricated from solvothermal reactions of metal ions and the bi-imidazolate ligand (BIm), formulated as M(BIm) (M= Zn^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}, named with STUs 1–5, respectively).[24,25] These gyroidal MOFs have a normally five-coordinated metal center with four N coordinative sites from the imidazole rings, and the other from the hydrazine group (Figure 1). Although the application of STUs 1–5 in gas adsorption has been investigated,[25] the utilization as the catalysis is limited. Recently, our group reported the synthesis of bimetallic STU-2 (Cu^{2+} or Zn^{2+} modified STU-2) and explored their applications in Lewis-acid catalyzed cyanosilylation reaction. The catalytic active sites mainly come from the unsaturated coordinative Mn^{II} center, while Cu and Zn acted in stabilizing the

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/asia.201900853.

This manuscript is part of a special issue on Metal-Organic Frameworks and Their Applications. Click here to see the Table of Contents of the special issue.
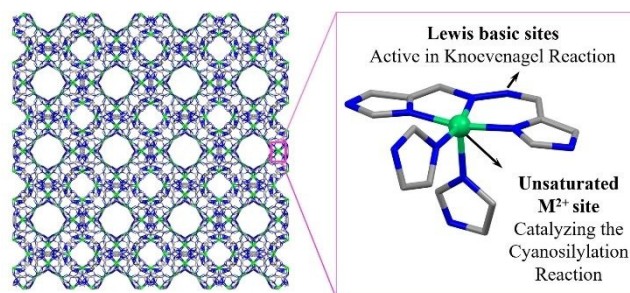
Figure 1. Structural illustration of STUs and their Lewis basic and acid sites. Color codes: C gray, M green, N blue.

framework structure of fragile STU-2.[26] However, the investigations on the basic-catalysis capacity for STUs materials have not been explored currently.

In this work, we firstly explored the basic catalysis activities of STU series in Knoevenagel condensation reaction, and the impacts of metal centers, solvents, aldehydes etc. on the catalytic activity. Based on the basic catalysis results and the potential unsaturated coordinative metal sites, we further selected the best-performing STU-4 as the catalyst for Lewis-acid catalyzed cyanosilylation reaction, for the purpose to obtain a bifunctional base and acid catalyst, expanding the catalysis application of STUs. STU-4 show excellent catalysis activities in both Knoevenagel condensation and cyanosilylation reactions, demonstrating an effective bifunctional catalyst for both Lewis base and Lewis acid catalyzed reactions.

Results and Discussion

Synthesis, characterization, and structure of STUs

Three kinds of STUs samples (STU-1, STU-3, and STU-4) were synthesized by using Zn^{2+}, Cu^{2+}, and Ni^{2+} metal salts and BIm (BIm = 1,2-bis((5H-imidazol-4-yl)-methylene)hydrazine) under solvothermal conditions, respectively, following our previously reported methods.[24, 25] The successful synthesis of STUs can be identified from their PXRD patterns, matching well with the simulated ones (Figure S1). Although STU series could be also ascribed to the big family of zeolitic imidazolate frameworks (ZIFs), the metal centers in these STUs adopt a five-coordinated geometry after activation (Figure 1), which were different from typical ZIFs constructed by tetrahedral metal centers and imidazolate ligands with varied substitution groups.[27] This special coordination mode endows STUs a distorted square pyramidal geometry, in which, metal ions coordinate with five nitrogen atoms from the imidazole rings and hydrazine group (Figure 1). Therefore, all the STUs had unsaturated coordination metal sites after activation and can be served as Lewis acid sites.[28] On the other hand, the nitrogen atoms in the hydrazine group of the BIm ligand without coordinating with metal center has weak basicity, which can be utilized in the base-catalyzed reaction.

Basic catalyzing Knoevenagel reactions

Benzaldehyde and malononitrile were selected as the reaction substrates for testing Knoevenagel condensation reaction (Scheme 1). The catalysis reaction of STU-1 (Zn(BIm)) was carried out in tetrahydrofuran (THF) with the reacting ratio of benzaldehyde and malonitrile being 1:2. As shown in Figure 2, the conversion was achieved to 62% in a reaction time of 1 h
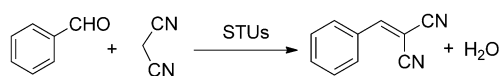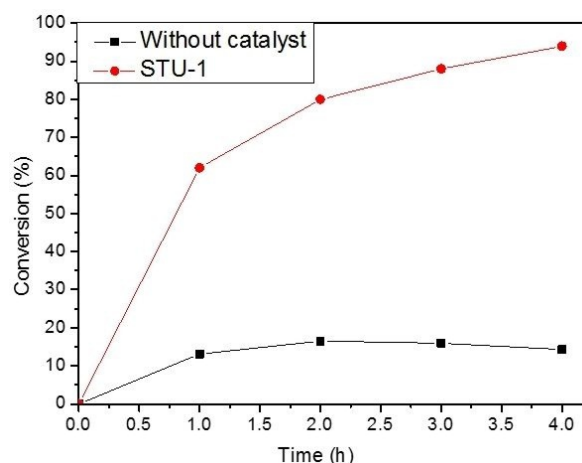

Figure 2. Knoevenagel condensation reaction conversion with and without STU-1 catalyst at 45 °C in THF.

at 45 °C and further elevated to 80% in 2 h. This conversation rate is much higher than the that of Co_2dobdc (Co-MOF-74, 4%, 70 °C, 2 h) ascatalyst, where the yield of only 32% was obtained in 24 h.[21] Under the same conditions, for other M-MOF-74 catalysts,[21] the yields were 39% (M = Cu^{2+}), 17% (M = Mg^{2+}), 13% (M = Zn^{2+}), and 69% (M = Ni^{2+}), respectively, much lower than that of STU-1. STU-1 not only showed a better catalytic activity than MOF-74, but also is superior than traditional common basic catalysts of zeolites and mesoporous silica.[23, 29] For example, the yield for NH_2-SBA-15 was 70% at 80 °C in 16 h.[23] The conversion for STU-1 gradually increased to 94% in 4 h, which is comparative with Ba_2(BTC)(NO_3) catalyst with much higher temperature and reaction time (yield: 97%, 110 °C, 24 h).[30]

To optimize the catalysis, the effects of different reaction parameters (such as the temperature, catalyst amount, molar ratio of the substrates, metal centers in STUs, solvents, aldehyde categories) on the catalytic activity were explored in details. The reaction conversion for 4 h was increased rapidly from 58% to 94%, while temperature was increased from 30 to 45 °C (Figure 3 a). A higher temperature of 60 °C only had a minor impact on the catalytic activity of STU-1. Therefore, the temperature of 45 °C was used for the further investigation. The amount of catalyst was not optimized in detail, but the decrement of amount to 2 mol% will tenderly reduce the catalytic conversion (Figure 3 b). We also studied the effect of molar ratio of benzaldehyde and malononitrile on the conversion. As demonstrated in Figure 3 c, a molar ratio of 1:1 gives a low conversion, and once increasing the amount of malononitrile, the conversion was also enhanced. The difference is not very obvious among these of 1:2, 1:3, and 1:4, which is different from a typical ZIF material ZIF-8,[31] in which the conversion was much higher at shorter reaction time, while using larger amount of malononitrile substrate. To explore the metal effect on catalytic activity, STU-1, STU-3, and STU-4 were utilized for catalyzing the Knoevenagel condensation reaction. All STUs could effectively catalyze this reaction, as shown in Figure 3 d, which manifests that the main catalytic sites are the Lewis
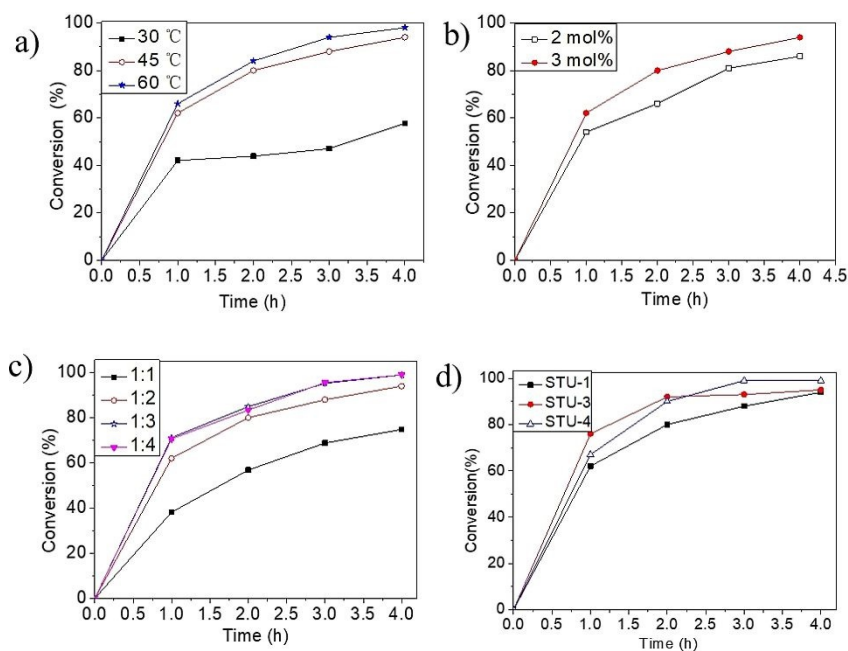

Scheme 1. Knoevenagel condensation reaction between benzaldehyde with malononitrile by using STUs as catalysts.

Figure 3. Effects of (a) temperature, (b) catalyst amount, (c) molar ratio of benzaldehyde and malononitrile, and (d) different metal ions based STUs on the Knoevenagel condensation reaction conversion.

base sites, not the metal centers. To be clearly identified, we found the following rough order of reaction conversion: STU-4 > STU-3 > STU-1, which can also be observed in literature.[21]

The solvent effect on the Knoevenagel condensation reaction are extremely important, although it also depends on the characters of the catalysts.[31] To study the influence of solvents on the reaction conversion between benzaldehyde and malononitrile, five kinds of solvents with different dielectric constants (ε): DMF (37.6), EtOH (24.3), THF (7.6), chloroform (4.8) and ethyl acetate (4.3) were employed. The catalytic results were demonstrated in Figure 4a. It was commonly known that the dielectric constant reflected solvent polarity.[2] The larger dielectric constant for solvent molecule always gives with the bigger solvent polarity. Herein, when DMF and EtOH act as solvents, with a much bigger polarity than the others, higher conversions of nearly 99% at 45 °C for 1 h were obtained. In contrast, THF owned a much lower dielectric constant of 7.6, a conversion of 65% was observed. For chloroform and ethyl acetate, the same conversion of 32% was found, which is probably due to their small and close polarities as compared to DMF and ethanol. These results demonstrate that the conversion of this Knoevenagel condensation reaction will be enhanced in relatively polar solvent, while decreased obviously in less polar solvent, consistent with that reported in literature.[6, 32, 33] However, the dielectric constant/polarity of the solvent was not the decisive factor towards the catalytic ability. Although ethanol has a lower dielectric constant than DMF, STU-1 could also catalyze this reaction very efficiently in it. This may be due to the amphiprotic property of ethanol and the moderate acidity of benzaldehyde. Ethanol may cause the electrophilic polarization of the carbonyl group in benzaldehyde, thus improving the catalytic activity.[2, 34] Interestingly, the Knoe-
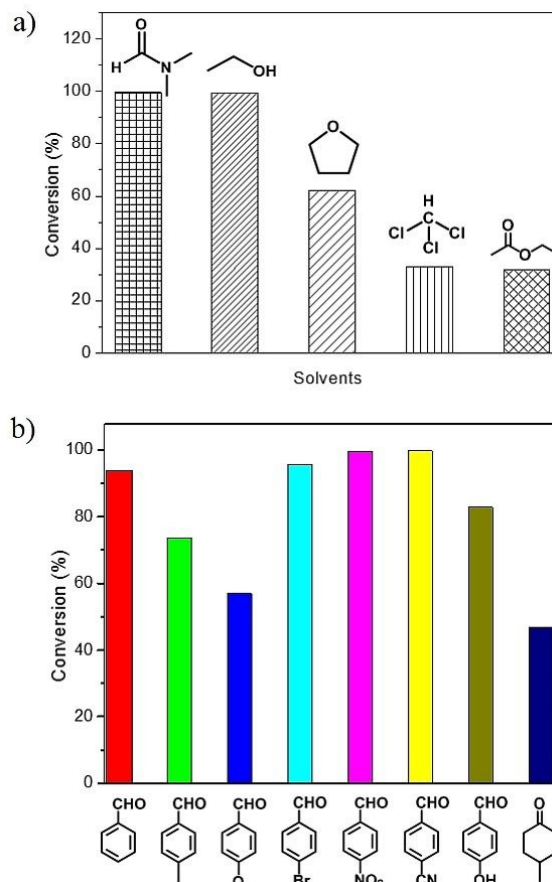

Figure 4. STU-1 catalyzed Knoevenagel condensation reactions in varied solvents (a) and different aldehyde substrates (b).

venagel condensation reaction between benzaldehyde and malononitrile can also be catalyzed by STU-1 without additional solvent. As shown in Figure S2, pure yellow solid product was formed after the clear solution of the reactants being stirred for 15 minutes, which manifests the high efficiency of the catalyst. The conversion is above 99%. This results further suggest that STU-1 is an efficient and green catalyst for Knoevenagel condensation reaction.

Due to the good catalytic performance of STU-1 for the Knoevenagel condensation reaction, we studied the scope of this condensation reaction. As shown in Figure 4b, STU-1 also demonstrated a wide applicability towards different aldehyde substrates with various functional groups. The reaction was performed in THF at 45 °C for 4 h with 3 mol% of STU-1 as catalyst. It is commonly considered that the nucleophilic addition is the rate-determining step in most condensation reactions,[31] and the aldehydes with electron withdrawing group, always displayed a much better catalytic conversion than that contains electron-donating functional groups.[35] The electron withdrawing group could activate the carbonyl group in the aldehyde substrate and promote the nucleophilic attack of active methylene site, which will probably improve the reactivity of the Knoevenagel condensation reaction. The catalytic results in Figure 4b verify this rule in a good manner. The catalytic activity was enhanced by using 4-bromobenzaldehyde, 4-nitrobenzaldehyde and 4-cyanobenzaldehyde as substrates, the conversions can achieve to 95–99%, benefiting from electron withdrawing character of -Br, -NO_2 and -CN groups. When 4-methyl benzaldehyde, 4-methoxy benzaldehyde and 4-hydroxy benzaldehyde act as substrates, a less reactive ability than benzaldehyde is observed, with conversions of 74%, 57% and 83% respectively. The reason is probably ascribed to the electron-donating groups of -CH_3, -OCH_3 and -OH on these substrates. The same situation also happened in the reaction using 4-methyl-cyclohexanone as substrate, with a low conversion of 47% being observed.

Stability/recyclability is an important factor for evaluating the industrial utility of catalyst in heterogeneous catalytic reactions. STU-1 was chosen as a model for assessing the recyclability. The conversion can be increased from 94% to 98% after 3 cycles, and STU-1 could maintain the initial conversion value in the fifth cycle (Figure 5a). To seek the possible explanation for the higher conversion rate after 3 cycles, we performed PXRD experiments for the catalysts. STU-1 can keep its crystalline structure very well during the five catalysis cycles as depicted in Figure 5b.

SEM images were taken for fresh STU-1 and the sample after three cycles (Figures S3a and S3b). It can be clearly observed that after three catalytic cycles, the particle sizes decreased obviously. To be precise, particle sizes of fresh STU-1 and that after three cycles were calculated in the random selected district and the distributions were demonstrated in Figures S3c and S3d. Before catalysis, the most probable particle size of fresh STU-1 was centered at 9–15 μm, while after three cycles, the particle size distribution became narrower and centered at 3 μm (Figure S3d), much smaller than that of fresh STU-1. The much smaller and finer particle sizes of the catalyst increase
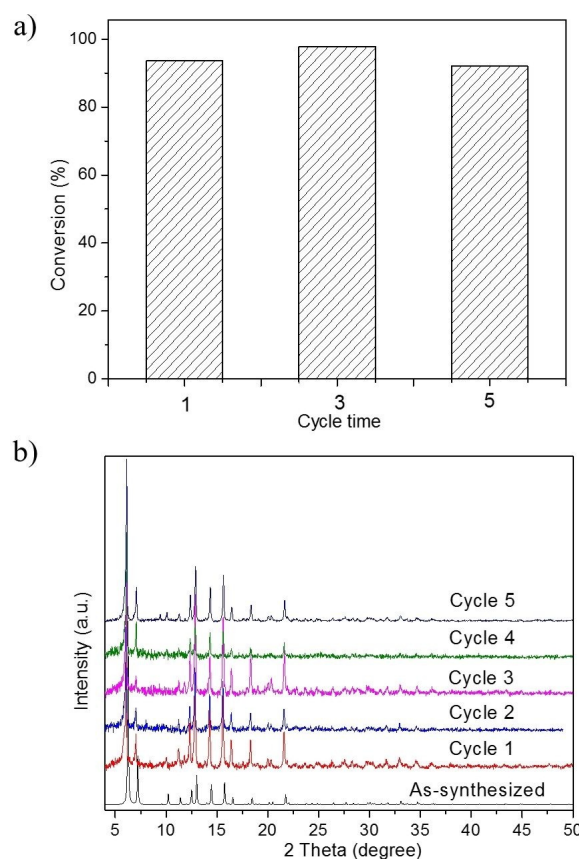
Figure 5. (a) Recyclability of STU-1 in catalyzing the Knoevenagel reaction at 45 °C, (b) PXRD patterns of the STU-1 catalysts after being used for each cycle.

the external surface, thus endows a more reactive activity. The recycled catalyst having a higher reaction conversion than the fresh catalyst (Figure 5a) agreed with the reported studies.[31,36] Not only STU-1 could maintain its stability during the catalysis process, STU-3 and STU-4 also displayed good stability in this Knoevenagel reaction, as shown in Figure S4.

Lewis acid catalytic activity of STU-4 in cyanosilylation reaction

Cyanosilylation reaction is a typical and powerful synthesis route for the C−C bond formation, and the produced cyanohydrins are important intermediates, which can further transform into other industrial compounds like α-amino acids, β-amino alcohols etc.[37] The cyanosilylation reaction was generally catalyzed by Lewis-acid sites.[38,39] This can be used for the evaluation of Lewis-acid catalytic activity of STUs. With unsaturated Ni center as Lewis-acid sites, STU-4 probably can be further applied as catalyst for cyanosilylation reaction (Scheme 2).

The sample of STU-4 was activated to remove the coordinated water molecules on the Ni metal centers before being used, creating an unsaturated metal environment. As shown in Table S1, STU-4 could effectively catalyze this reaction, with a conversion of 99% at 40 °C after a reaction time of 6 h. This value was almost equivalent with that of mesoporous MIL-
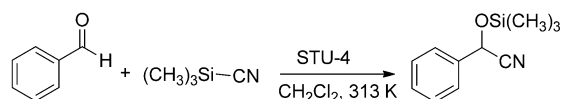
Scheme 2. Catalysis of Cyanosilylation reaction between benzaldehyde and trimethylsilyl cyanide by using STU-4 as catalyst.

101,[38] which could catalyze this reaction with a conversion of 99% in 3 h (Table S1). The reaction activity is also similar to that of STU-2 ($>99\%$,[26] unfortunately not stable in air). In addition, the catalytic activity of STU-4 is also better than CPO-27-Ni, CPO-27-Co and $Cu_3(BTC)_2$ MOFs catalysts.[40,41] These three catalysts had a poor activity (conversions of 27%, 27% and 50%, respectively), even with a long reaction time of 48 h (Table S1). The catalysis efficiency of STU-4 is also comparable to Tb-tca MOF, which was precisely designed to fabricate an acidic-basic coordination interaction in the aim of elevating its catalysis efficiency. A conversion of 98% was observed when Tb-tca was used as a catalyst with a longer reaction time (16 h).[42,43]

Structural stability was an important property of a solid/heterogenous catalyst, we evaluated the stability of STU-4 using PXRD technique. As shown in Figure S5 a, STU-4 structure could be retained after reaction time of 6 h. However, when the catalysis was proceeded further to 48 h, the structure of STU-4 collapsed, as can be identified from the disappeared crystalline peaks of STU-4 in Figure S5 b.

Conclusions

We have successfully applied bifunctional gyroidal STU MOFs as Lewis base and Lewis acid catalysts, showing excellent acitvities in both Knoevenagel condensation and cyanosilylation reactions. Effects of solvents, aldehydes, the molar ratio of aldehydes and active methylene compounds, and metal ionson the conversion have been studied in detail for the Knoevenagel condensation reaction. The STU catalysts display good catalytic activity, stability and recyclability. Among them, STU-4 shows the best catalytic activity. Not limited to the base reaction, STU-4 also exihibits excellent catalytic activity in the cyanosilylation reaction with a conversion of 99%. This work demonstrates that MOFs can be decorated with various active sites in their frameworks for multiple functions. Further studies on employing STU materials as both Lewis base and Lewis acid catalysts for other reactions are worthy to be explored.

Experimental Section

Materials and Instruments

All the starting materials and reagents/solvents were obtained commercially and used without further purification. The ligand 1,2-bis((5H-imidazol-4-yl)methylene)hydrazine (BIm) was synthesized according the literature method.[44] Thermogravimetric analysis (TGA) was carried out on a TGA 2 instrument from 40 to 800 °C with a heating rate of 10 °C min^{-1} in a N_2 atmosphere. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Ultima IV diffractometer (power 40 kV, 40 mA) with $Cu_{K\alpha}$ radiation ($\lambda =$

1.5418 Å) in the 2-theta range from 3 to 50° with a step of 0.02°. Scanning electron microscopy (SEM) images were collected on an EM-30AX+ microscope with the accelerating voltage of electron beam of 20 kV. The catalyst activity was evaluated on GC-MS instrument of Agilent 7890B, column type was HP-5, He as the carrier gas with a velocity of 1 mL min^{-1}, the temperature of injection inlet was 250 °C, AUX-2 was 250 °C, column temperature was 300 °C, ionization temperature was 230 °C, quadrupole temperature was 150 °C.

Synthesis of STUs

STUs were all prepared according to the literature with minor modifications as follows:[24] For the preparation of STU-1, 8.0 mg of BIm was dissolved into the mixed solvent of 3.2 mL DMF and 0.8 mL ethanol, then 12.7 mg of zinc nitrate hexahydrate was added into the above clear solution. The molar ratio of Zn^{2+} ions with BIm ligand was 1:1. Afterwards, the obtained mixture was sealed in a Pyrex glass tube and heated in an oven at 80 °C for 72 hours, then cooled to room temperature at a rate of 5 °C h^{-1}. Light yellow polyhedral crystals were obtained. STU-3 was obtained with the same method of STU-1, except replacing zinc nitrate hexahydrate with copper nitrate trihydrate. The molar ratios of metal ions with Bim for the synthesis of STU-3 was 1:1. Green polyhedral crystals of STU-3 were obtained. The preparation method of STU-4 was a little different with that mentioned above. Bim (66.0 mg) and nickel nitrate hexahydrate (102.1 mg) were dissolved into 33 mL of the mixed solvents of DMF and ethanol (volume ratio of 4:1). The mixture was transferred into a 100 mL autoclave, then 6.6 mL $NH_3·H_2O$ and 3.3 mL water were added dropwise into the above solution separately. Finally the system was sealed and heated in an oven at 100 °C for 72 hours, then cooled to room temperature at a rate of 5 °C h^{-1}. Block like brown crystals were collected.

General Procedure for Knoevenagel condensation reaction: Before catalytic experiment, the samples of STU-1, STU-3, and STU-4 were activated under vacuum at 200 °C for 12 h. The activated STU-1 sample (0.045 mmol, 11.3 mg) was added into a 5 mL vial, then 1.5 mL of THF was added. The mixture was stirred at 45 °C, then benzaldehyde (1.5 mmol, 159.2 mg) and malononitrile (3.0 mmol, 198.2 mg) were added, respectively. The reaction mixture was further sealed and stirred at 45 °C in air atmosphere. After each hour, 50 μL of the reaction liquid was taken and centrifuged. The supernatant was further diluted to 1 mL for detection. The catalytic conversion of the product and its identification was determined by GC-MS and calculated based on the benzaldehyde substrate. Different aldehyde substrates, solvents, temperatures, catalyst amounts and molar ration of two substrates etc. were investigated in a smilar procedure.

The catalytic recyclability of catalyst for STU-1 was studied for five times. After each catalytic run, the catalyst was separated by centrifuging the mixture, and soaked into THF for 1 h. And then it was dried in vacuum at 100 °C for 1 h and used for the next run.

General Procedure for Cyanosilylation reaction: Before the catalytic experiment, STU-4 was desolvated in vacuum at 200 °C for 12 h. 15 mg of the desolvated catalyst STU-4 and 5 mL of CH_2Cl_2 were added into a 10 mL vial. Then benzaldehyde (1.5 mmol, 159.2 mg) and trimethylsilyl cyanide (3 mmol, 297.6 mg) were added into the vial, respectively. The mixture was stirred at 40 °C under N_2 atmosphere for 6 h. After that, 50 μL of the reaction liquid was taken and diluted with CH_2Cl_2 to 1 mL, then centrifuged for 5 min with a speed of 10 000 rpm min^{-1}. The supernatant was analyzed by GC-MS. The reaction conversion was calculated based on the benzaldehyde substrate.

Conflict of interest

The authors declare no conflict of interest.

Keywords: Catalysis · Knoevenagel condensation reaction · Lewis acid · Lewis base · Metal-organic frameworks

[1] E. Knoevenagel, *Angew. Chem.* **1922**, *35*, 29–30.
[2] J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink, F. Kapteijn, *J. Catal.* **2009**, *261*, 75–87.
[3] F. Martínez, G. Orcajo, D. Briones, P. Leo, G. Calleja, *Microporous Mesoporous Mater.* **2017**, *246*, 43–50.
[4] L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136.
[5] Y. Luan, Y. Qi, H. Gao, R. S. Andriamitantsoa, N. Zheng, G. Wang, *J. Mater. Chem. A* **2015**, *3*, 17320–17331.
[6] M. J. Climent, A. Corma, I. Dominguez, S. Iborra, M. J. Sabater, G. Sastre, *J. Catal.* **2007**, *246*, 136–146.
[7] M. B. Ansari, H. Jin, M. N. Parvin, S.-E. Park, *Catal. Today* **2012**, *185*, 211–216.
[8] Y. Kubota, Y. Nishizaki, Y. Sugi, *Chem. Lett.* **2000**, *29*, 998–999.
[9] S. Balalaie, M. Sheikh-Ahmadi, M. Bararjanian, *Catal. Commun.* **2007**, *8*, 1724–1728.
[10] V. S. R. Rajasekhar Pullabhotla, A. Rahman, S. B. Jonnalagadda, *Catal. Commun.* **2009**, *10*, 365–369.
[11] B. M. Reddy, M. K. Patil, K. N. Rao, G. K. Reddy, *J. Mol. Catal. A* **2006**, *258*, 302–307.
[12] N. Jiang, H. Jin, Y.-H. Mo, E. A. Prasetyanto, S.-E. Park, *Microporous Mesoporous Mater.* **2011**, *141*, 16–19.
[13] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.
[14] L. Jiao, Y. Wang, H.-L. Jiang, Q. Xu, *Adv. Mater.* **2018**, *30*, 1703663–1703686.
[15] L. Lu, X.-Y. Li, X.-Q. Liu, Z.-M. Wang, L.-B. Sun, *J. Mater. Chem. A* **2015**, *3*, 6998–7005.
[16] C. Yao, S. Zhou, X. Kang, Y. Zhao, R. Yan, Y. Zhang, L. Wen, *Inorg. Chem.* **2018**, *57*, 11157–11164.
[17] X.-S. Wang, J. Liang, L. Li, Z.-J. Lin, P. P. Bag, S.-Y. Gao, Y.-B. Huang, R. Cao, *Inorg. Chem.* **2016**, *55*, 2641–2649.
[18] J. Liang, R.-P. Chen, X.-Y. Wang, T.-T. Liu, X.-S. Wang, Y.-B. Huang, R. Cao, *Chem. Sci.* **2017**, *8*, 1570–1575.
[19] Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao, *Chem. Soc. Rev.* **2017**, *46*, 126–157.
[20] T.-T. Liu, J. Liang, R. Xu, Y.-B. Huang, R. Cao, *Chem. Commun.* **2019**, *55*, 4063–4066.
[21] P. Valvekens, M. Vandichel, M. Waroquier, V. Van Speybroeck, D. De Vos, *J. Catal.* **2014**, *317*, 1–10.
[22] M. Hartmann, M. Fischer, *Microporous Mesoporous Mater.* **2012**, *164*, 38–43.
[23] Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Ferey, *Angew. Chem. Int. Ed.* **2008**, *47*, 4144–4148; *Angew. Chem.* **2008**, *120*, 4212–4216.
[24] X.-P. Zhou, M. Li, J. Liu, D. Li, *J. Am. Chem. Soc.* **2012**, *134*, 67–70.
[25] Y. Wu, X.-P. Zhou, J.-R. Yang, D. Li, *Chem. Commun.* **2013**, *49*, 3413–3415.
[26] J.-J. Du, X. Zhang, X.-P. Zhou, D. Li, *Inorg. Chem. Front.* **2018**, *5*, 2772–2776.
[27] D. Saliba, M. Ammar, M. Rammal, M. Al-Ghoul, M. Hmadeh, *J. Am. Chem. Soc.* **2018**, *140*, 1812–1823.
[28] L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, *J. Am. Chem. Soc.* **2003**, *125*, 3062–3067.
[29] S. Ernst, M. Hartmann, S. Sauerbeck, T. Bongers, *Appl. Catal. A* **2000**, *200*, 117–123.
[30] P. Valvekens, D. Jonckheere, T. De Baerdemaeker, A. Kubarev, M. Vandichel, K. Hemelsoet, M. Waroquier, V. Van Speybroeck, E. Smolders, D. Depla, *Chem. Sci.* **2014**, *5*, 4517–4524.
[31] U. P. N. Tran, K. K. A. Le, N. T. S. Phan, *ACS Catal.* **2011**, *1*, 120–127.
[32] J. Juan-Alcañiz, E. V. Ramos-Fernandez, U. Lafont, J. Gascon, F. Kapteijn, *J. Catal.* **2010**, *269*, 229–241.
[33] A. Corma, S. Iborra, I. Rodriguez, F. Sanchez, *J. Catal.* **2002**, *211*, 208–215.
[34] I. Rodriguez, G. Sastre, A. Corma, S. Iborra, *J. Catal.* **1999**, *183*, 14–23.
[35] R. Gupta, M. Gupta, S. Paul, R. Gupta, *Bull. Korean Chem. Soc.* **2009**, *30*, 2419–2421.
[36] R. Selvin, H.-L. Hsu, T.-M. Her, *Catal. Commun.* **2008**, *10*, 169–172.
[37] M. North, D. L. Usanov, C. Young, *Chem. Rev.* **2008**, *108*, 5146–5226.
[38] A. Henschel, K. Gedrich, R. Kraehnertb, S. Kaskel, *Chem. Commun.* **2008**, 4192–4194.
[39] S. Neogi, M. K. Sharma, P. K. Bharadwaj, *J. Mol. Catal. A Chem.* **2009**, *299*, 1–4.
[40] H.-F. Yao, Y. Yang, H. Liu, F.-G. Xi, E.-Q. Gao, *J. Mol. Catal A* **2014**, *394*, 57–65.
[41] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* **2004**, *73*, 81–88.
[42] R. F. D'Vries, V. A. de la Peña-O'Shea, N. Snejko, M. Iglesias, E. Gutiérrez-Puebla, M. Á. Monge, *Cryst. Growth Des.* **2012**, *12*, 5535–5545.
[43] O. R. Evans, H. L. Ngo, W. B. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396.
[44] K. Fujita, R. Kawamoto, R. Tsubouchi, Y. Sunatsuki, M. Kojima, S. Iijima, N. Matsumoto, *Chem. Lett.* **2007**, *36*, 1284–1285.