NH₂-Ga-MIL-53 催化剂对 Strecker 反应的底物选择性

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摘要：研究了金属有机骨架化合物 NH₂-Ga-MIL-53 对多种 N-苯基亚胺底物的 Strecker 反应的催化性能，研究结果表明：(1) NH₂-Ga-MIL-53 具有高度催化活性和良好的底物普适性；(2) 亚胺底物上取代基的电子效应是影响催化反应速率的关键因素，在亚胺底物上引入给电子取代基团(如甲氧基和苯基)可以加快反应速率，引入吸电子取代基团(如三氟甲基和硝基)可降低反应速率；(3) 亚胺底物上取代基的位置对于催化反应速率同样具有重要影响，在亚胺底物的邻位引入甲氧基取代基团时，反应速率加快得最明显；(4) 作为非均相催化剂，NH₂-Ga-MIL-53 可循环使用 9 次而不失活且保持骨架结构不变；(5) NH₂-Ga-MIL-53 和 Ga-MIL-53 催化性能的对比结果表明，NH₂-Ga-MIL-53 结构中的氨基可以作为路易斯碱活性中心协同路易斯酸催化中心(Ga³⁺)有效促进 strecker 反应的进行。此外，由 NH₂-Ga-MIL-53、六水合硝酸镓和 2-氨基对苯二甲酸对 Strecker 反应的催化效果的对比可知，NH₂-Ga-MIL-53 的孔结构是提高反应产物专一性的重要因素。

关键词：金属有机骨架配合物；镓；非均相催化；Strecker 反应；底物选择性
中图分类号：O614.37⁺1；O625；O643.3　　文献标识码：A　　文章编号：1001-4861(2020)03-0547-08
DOI：10.11862/CJIC.2020.036

Substrate-Selectivity of Strecker Reaction Based on Amino-Functionalized Ga-MIL-53 Catalyst

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Abstract: This work focuses on Strecker reactions catalyzed by metal-organic framework (MOF) of amino-functionalized Ga-MIL-53 (NH₂-Ga-MIL-53) in regard to substrates of a series of N-Ph aldimines, and the results showed that: (1) NH₂-Ga-MIL-53 exhibited excellect catalytic activity and good univisality among various substrates; (2) the electronic effect of substituents for substrates primarily affects the catalytic reaction rate, and the electron-donating substituted groups (i.e., MeO, Ph) and electron-withdrawing substituted groups (i.e., CF₃, NO₂) show promotion and suppression effects on the reaction, respectively; (3) the substituted position of substituents in respect of substrates secondarily influences the reaction rate, and the ortho-substituted MeO group perform the strongest promotion effects on the reaction; (4) as a heterogeneous catalyst, NH₂-Ga-MIL-53 can be reused for 9 runs without obvious loss of conversion efficiencies and collapse of MOF structure; (5) contrasting the catalytic performances between NH₂-Ga-MIL-53 and Ga-MIL-53, it is indicated that the amino groups of NH₂-Ga-MIL-53 can be served as Lewis base moieties, facilating the reaction according to Lewis acid-base synergistic mechanism. Furthermore, comparing the catalytic effects among NH₂-Ga-MIL-53, Ga(NO₃)₃·6H₂O and 2-aminoterephthalic

acid, it is concluded that the pore structure of NH$_2$-Ga-MIL-53 framework plays a significant role in avoiding the side reactions with respect to Strecker reaction.

Keywords: metal-organic frameworks; gallium; heterogeneous catalysis; Strecker reaction; substrate-selectivity

0　Introduction

Strecker-type reactions, involving nucleophilic addition of cyanide sources to aldimine, have become one of the most versatile and efficacious approaches in the yielding of α-aminonitriles on lab and technical scale[1-5]. To enhance the conversion efficiency of Strecker-type reactions, several heterogeneous catalysts such as metal complexes[6], metal-salen complexes[7-8] and metal oxides[9] have been extensively investigated over the past few years, owing to the advantages of catalysts recycle as well as product separation. For instance, a molybdenum Schiff base complex supported on MNPs (magnetic nanoparticles) has been utilized as an efficient and easily recyclable catalyst for the syntheses of α-aminonitrile derivatives[6]. Most recently, Gao and Yang et al.[9] applied strong Lewis base Ga$_4$B$_2$O$_9$ with GaO connectivity enhanced basicity as well as Lewis acidic sites of five-coordinated Ga^{3+} as an efficient catalyst to facilitate Strecker-type reactions. Now the Strecker reactions have gained extensive research interests during the recent years, becoming the hot topic in the field of catalysis.

Metal organic frameworks (MOFs)[10-15] have attracted widespread attention in the promotion of various organic reactions, especially for Strecker reaction, showing several essential advantages[16-21]. On the one hand, by appropriately selecting Lewis acid centers of metal-containing secondary building units[22-23] and organic linkers with potential Lewis base sites[24-26], MOFs demonstrated impressive attractions to achieve high performances for Lewis acid-base bifunctional activations [27-28]. In 2014, Indium(III)-based MOFs were first reported as recyclable heterogeneous Lewis acid-base bifunctional catalysts for Strecker reactions, while cyanide source of trimethylsilyl cyanide (TMSCN) can be activated by Lewis basic sites of exposed ether groups, which has been confirmed by ^{29}Si NMR [29]. On the other hand, as other heterogeneous catalysts, the heterogeneous nature of MOFs can readily promote catalyst recycling and product separation[27,30-31]. For instance, Monge and Gándara et al. have developed a new highly porous and heterogeneous Lewis acid catalyst of Indium(III)-based MOF to facilitate Strecker-type reactions, which can be recycled for 10 runs without significant loss of yield[32].

To our knowledge, in the case of Strecker reactions, the detailed substrate-selectivity patterns for substrates with complex combination between electron-withdrawing and electron-donating substituents have not been summarized in previous reported papers. Herein, we employed a series of N-Ph aldimines as substrates to study these complicated substrate-selectivity regulars with respect to Strecker reactions. Meanwhile, the present work focuses on the catalytic research of amino-functionalized Ga-MIL-53 (NH$_2$-Ga-MIL-53) material in Strecker reactions after considering the above-mentioned advantages of the catalysts of MOFs. As a result, NH$_2$-Ga-MIL-53 exhibited excellent catalytic performance in Strecker reactions as well as significant catalytic universality for numerous substrates of aldimines. Most importantly, the intricate influences on Strecker reaction with various substrates were firstly discussed in this work. Noteworthy, as a heterogeneous catalyst, NH$_2$-Ga-MIL-53 can be recycled for 9 runs with no obvious loss of conversion efficiencies. Furthermore, the influence of Lewis base amino moieties[33-34] on conversion efficiencies, along with the effect of the structure of NH$_2$-Ga-MIL-53 framework on the catalytic performance, have been explored during the present work.

1　Experimental

1.1　Materials and instrumentation

All solvents and reagents adopted in this work were of reagent grade and utilized with no further purification. X-ray diffraction (XRD) was performed by

Rigaku D/max-2550 diffractometer with copper anode and graphite monochoromator to select Cu $K\alpha_1$ radiation (λ =0.154 18 nm with an operating voltage of 40.0 kV and a beam current of 30.0 mA) at room temperature, and XRD data were collected in a 2θ range of 4°~40° with a scanning rate of 6° · min^{-1}. Thermogravimetry (TGA) was performed with a Perkin-Elmer TGA 7 Instruments equipment under air atmosphere with a heating rate of 10 ℃·min^{-1} (the temperature range was from 16 to 800 ℃). IR spectra were collected on a Nicolet FT-IR 20SXC spectrometer from KBr pellets in a range of 4 000~400 cm^{-1}, while pure KBr peaks were excluded as background, and IR spectra was processed with data turn-up and smoothing. N₂ adsorption-desorption isotherms were recorded on an ASAP 2020 surface area and pore volume automatic analysis instrument. ¹H NMR spectra was collected by a Bruker Avance 400 equipment with a test frequency of 400 MHz.

1.2 Catalyst synthesis

1.2.1 Synthesis of NH₂-Ga-MIL-53

The synthesis of NH₂-Ga-MIL-53 was adapted from that of amino-functionalized Al-MIL-53[35-36]. At first, 1.05 mmol Ga(NO₃)₃·6H₂O was dissolved into 7.5 mL N,N-dimethyl-formamide (DMF), while 1.56 mmol 2-aminoterephthalic acid (ATA) was added into another 7.5 mL DMF. These two DMF solutions were mixed together until both Ga(NO₃)₃·6H₂O and ATA were dissolved completely. Hereafter, the mixture was put into a 23 mL Teflon-lined autoclave, and heated under autogenous pressure at 130 ℃ for 3 days. The gel product was separated by centrifugation, washed with acetone and methanol respectively, and refluxed by methanol overnight. Finally, the product was collected by centrifugation and dried under vacuum oven at 110 ℃ for 24 h, then pale-yellow powder was collected.

1.2.2 Synthesis of Ga-MIL-53

Ga-MIL-53 was synthesized by a similar procedure as NH₂-Ga-MIL-53, except that ATA was replaced by terephthalic acid. Ultimately, white powder was collected after dried under vacuum oven at 110 ℃ for 24 h.

1.3 General procedure for Strecker reactions

In a typical batch experiment, 0.14 mmol aldimine was dissolved into 2.4 mL CDCl₃, followed by 0.04 mmol catalyst (NH₂-Ga-MIL-53, Ga-MIL-53, Ga(NO₃)₃·6H₂O or ATA) and 0.35 mmol TMSCN, respectively. The mixture was continuously stirred in a vial, and the conversion efficiencies were recorded by ¹H NMR spectra at certain discrete time-points (the time to adding TMSCN was set as the initial point).

1.4 Catalyst recycling

After 99% conversion efficiency aldimines was achieved for each Strecker reaction, the mixture was centrifuged and washed with chloroform for 3 cycles to get the purified precipitates of catalyst. The final precipitates were dried under vacuum oven at 110 ℃ for 24 h.

2 Results and discussion

2.1 Characterizations

All synthetic MIL-53 catalysts were characterized by XRD (Fig.S1), N₂ adsorption-desorption analysis (Fig.S2), TGA (Fig.S3) and IR spectra (Fig.S4).

XRD patterns for NH₂-Ga-MIL-53 and Ga-MIL-53 are displayed in Fig.S1. As we known, MIL-53 MOFs displayed very large breathing effect with large pore (lp) form and narrow pore (np) form mutual transformation[37-39]. It is noted that XRD patterns of NH₂-Ga-MIL-53 show np form (CCDC number of Al-MIL-53 with np form: 220477) (Fig.S1a), while XRD pattern of Ga-MIL-53 can be corresponded to opened lp form (CCDC number of Al-MIL-53 with lp form: 220475)[40-41] (Fig.S1b).

Nitrogen adsorption-desorption isotherms at 77 K used for BET (Brunauer-Emmett-Teller) surface area and pore diameter estimations are depicted in Fig.S2 and Table 1. NH₂-Ga-MIL-53 performs a Type Ⅲ isotherm characteristic with the BET surface area and pore diameter of 26 m²·g^{-1} and 0.67 nm, respectively. Ga-MIL-53 exhibited a typical Type Ⅰ isotherm characteristics of microporous materials, while the BET surface area and pore diameter were 1 267 m²·g^{-1} and 0.61 nm, respectively.

Evidence for the successful preparation of NH₂-Ga-MIL-53 was demonstrated by the IR analyses. As shown in Fig.S4a, the peaks at 3 498 and 3 387 cm^{-1}

<div align="center">

Table 1　Parameters of pore collected by N_2 adsorption analysis

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Compound	BET surface area / $(m^2 \cdot g^{-1})$	Langmuir surface area / $(m^2 \cdot g^{-1})$	Pore volume / $(cm^3 \cdot g^{-1})$	Pore diameter / nm
NH_2-Ga-MIL-53	26	36	0.058	6.7
Ga-MIL-53	1 267	1 667	0.644	6.1

were ascribed to the stretching vibration band of N-H in NH_2, and the peak at 774 cm^{-1} was assigned to the bending vibration band of N-H, all results evidently certifying the introducing of amino groups[41].

2.2　Catalytic activity of NH_2-Ga-MIL-53 in Strecker reactions

2.2.1　Catalyst activity and universality with various substrates

Initially, experiments were performed with $CDCl_3$ at room temperature to optimize the reaction conditions for the Strecker reaction using benzaldimines as substrates, while optimized experimental procedure was illustrated in experimental section. Furthermore, with the purpose of avoiding the use of highly toxic cyanide derivatives, environmentally-benign TMSCN was utilized in our work[6,42]. As a result, NH_2-Ga-MIL-53 performed excellent catalytic performance as well as significant universality for various substrates, giving high conversion efficiencies with a few aldimines (Table 2, entries 1~14). For instance, with the substrate of N-Ph benzaldimine, 85% conversion efficiency was achieved within 11.5 h incubation (Table 2, entry 1), compared with only 2% conversion efficiency at 31.5 h for the substrate with control groups (Table 2, entry 19).

<div align="center">

Table 2　Strecker-type reactions for NH_2-Ga-MIL-53 catalyst

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Entry	R	PG	Time / h	Conversion efficiency[a] / %
1	Ph	Ph	11.5	85
			31.5	99
2	Ph	4-MeOPh	11	93
3	2-MeOPh	Ph	11	96
4	3-MeOPh	Ph	11	91
5	4-MeOPh	Ph	11	91
6	4-MeOPh	4-MeOPh	11	93
7	Ph	4-CF_3Ph	31.5	81
8	2-CF_3Ph	Ph	31.5	88
9	3-CF_3Ph	Ph	31.5	96
10	4-CF_3Ph	Ph	31.5	84
11	4-CF_3Ph	4-CF_3Ph	35	29
12	4-CF_3Ph	4-MeOPh	31.5	95
13	4-MeOPh	4-CF_3Ph	32.5	89
14	4-PhPh	Ph	11.5	89
15	4-NO_2Ph	Ph	11.5	2
16[b]	Ph	Ph	23.5	85
17[c]	Ph	Ph	0.5	100[d]
18[e]	Ph	Ph	48.5	41[d]
19[f]	Ph	Ph	31.5	2

[a] Conversion efficiency was confirmed by ^1H NMR; [b] Ga-MIL-53 catalyst was used instead; [c] $Ga(NO_3)_3 \cdot 6H_2O$ catalyst was used instead; [d] Unexpected side reactions procceed largely; [e] ATA catalyst was used instead; [f] No catalyst was added

Hereafter, on the basis of substrates with PGs (PGs=protecting groups) of Ph, the effect of electron-withdrawing and electron-donating substituted groups of aldimines on the reactivity was preliminarily investigated. In the case of 4-substituted aldimines, substrates with electron-withdrawing groups (*i.e.*, CF_3, NO_2) gave much slower reaction rates compared to that of N-Ph benzaldimine (Table 2, entries 1, 10 and 15), and substrates with electron-donating groups (*i.e.*, MeO, Ph) afford higher conversion efficiencies in comparison with that of N-Ph benzaldimine (Table 2, entries 1, 5 and 14). Furthermore, as achieving conversion efficiencies of 99% among substrates of 3-substituted aldimines, the substrate with R group of 3-MeOPh required merely 24.5 h while aldimine with R group of 3-CF_3Ph demanded up to 48.5 h, and aldimine with R group of Ph required 31.5 h under identical conditions (Fig.S5a and Table S1, entries 1, 4 and 9). In conclusion, the electron-withdrawing groups of aldimines significantly retard the Strecker-type reaction rate, while the electron-donating groups of aldimines slightly advance the reactivity of substrates. It can be deduced that the electron-withdrawing substituted groups can weaken the electrophilic Ga coordination with nucleophilic nitrogen atoms of aldimines via lowering the nucleophilic nature of aldimines according to the inductive effect of electron-withdrawing substituents[43], hindering the subsequent reactions for synthesis of α-aminonitriles.

Furthermore, it should be noted that reaction rates of aldimines depend on the position of substituents and decrease in the following order: R group of 2-MeOPh > PG of 4-MeOPh ≈ R group of 3-MeOPh ≈ R group of 4-MeOPh (hereafter; both R groups and PGs are Ph unless specially mentioned) (Fig.S5b and Table 2, entries 2, 3, 4 and 5). In addition, with further increase of the number of MeO substitutions, this reaction rate no longer increased (Fig.S5b and Table 2, entry 6). Apart from MeO substituents, one can see from Fig.S5c that reaction rates of aldimines also depended on the position of CF_3 substituents and decreased in the following order: R group of 3-CF_3Ph > R group of 2-CF_3Ph > R group

of 4-CF_3Ph > PG of 4-CF_3Ph (Table 2, entries 7, 8, 9 and 10). With further increase of the number of CF_3 substitutions, it performs the worst catalytic effect among all the substrates (Fig.S5c and Table 2, entry 11). It can be concluded: (1) the ortho-substituted and PG-substituted aldimines perform the most obvious promotion and suppression effects on the reaction for MeO and CF_3 substituents, respectively; (2) the multiple MeO groups on substrates facilating the reaction is rather limited, while the multiple CF_3 substituents of the substrates obstructing the reaction is illimited.

To investigate the synergy effect between MeO groups and CF_3 groups, two substrates of aldimines were selected with PGs of 4-MeOPh and R group of 4-CF_3Ph as well as PGs of 4-CF_3Ph and R group of 4-MeOPh, respectively. However, both of them showed lower Strecker-type reactivities compared with the aldimine with both R group and PG of Ph (Fig.S5d and Table 2, entries 1, 12 and 13). Herein, we draw the conclusion that CF_3 groups performed stronger electron-withdrawing effect than the electron-donating effect of MeO groups, hence reducing the reactivities of these substrates.

2.2.2 Heterogeneity and reusability of catalyst

The heterogeneity and reusability are important properties in the catalytic reactions, which largely reduce the cost and guarantee the high efficiency of product formation[44-46]. For the leaching test, the removal of NH₂-Ga-MIL-53 from the system by centrifugation at 2 h can completely terminate the reaction (Fig.S6). It can be concluded that no homogeneous catalyst species existed in the reaction solution[47]. Furthermore, the repeated catalytic experiment of NH₂-Ga-MIL-53 was devised. As shown in Fig.1, NH₂-Ga-MIL-53 was easily recovered by centrifugal separation and recycled for 9 runs without significant loss of conversion efficiency at 31.5 h. In addition, this stability of the heterogeneous NH₂-Ga-MIL-53 catalyst was revealed by XRD, and no obvious collapse in the structure of np forms was observed after 9-time recycling (Fig. S1c), implying the reusability and structure stability of NH₂-Ga-MIL-53 as a catalyst.
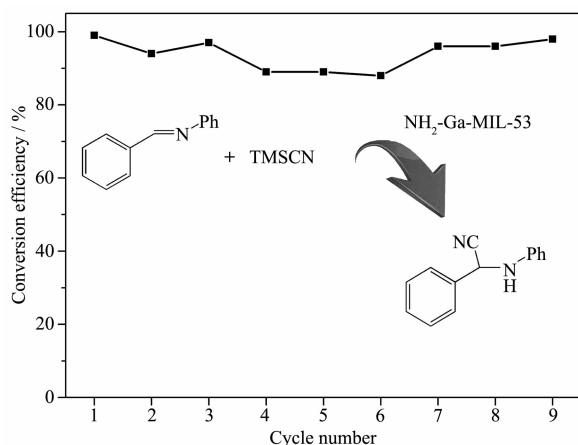
Reaction was allowed to run for 31.5 h and conversion efficiency was confirmed by ^{1}H NMR

Fig.1　Strecker-type reaction with the catalyst of NH$_2$-Ga-MIL-53 up to 9 cycles

2.2.3　Effect of amino groups on the catalyst

To explore the role of Lewis base sites (amino groups) of NH$_2$-Ga-MIL-53 in the Strecker-type reactions, Ga-MIL-53 catalyst was used instead. It is noted that NH$_2$-Ga-MIL-53 with np form showed a much smaller BET surface area compared to Ga-MIL-53 with lp form, blocking the reaction because of the limited contact area. However, NH$_2$-Ga-MIL-53 exhibited a better catalytic performance in Strecker-type reaction than Ga-MIL-53 conversely (Fig.S7). Only 11.5 h was required to achieve 85% conversion efficiency for the NH$_2$-Ga-MIL-53 catalyst (Table 2, entry 1), while the conversion efficiency of substrate reached 85% up to 23.5 h in the presence of Ga-MIL-53 (Table 2, entry 16). Therefore, we get the conclusion that the introducing of the Lewis base sites of amino groups for Ga-MIL-53 can readily improve the catalytic performance effectively on the basis of the Lewis acid sites (trivalent Ga cations). This result could be explained as the classic Lewis acid-base synergistic catalytic mechanism[29,48-49].

2.2.4　Effect of the framework structure of the catalyst

Herein, the influence of the catalyst framework on Strecker reaction was investigated. Firstly, Ga(NO$_3$)$_3$·6H$_2$O was used as the catalyst to promote the reaction instead of NH$_2$-Ga-MIL-53. It is observed that this reaction could be finished within 0.5 h, however, the unexpected side reactions procceed largely (Table

2, entry 17). In comparison, NH$_2$-Ga-MIL-53 gave no side reaction but a longer reaction time to achieve high conversion efficiency (Table 2, entry 1). Hereafter, the possible mechanisms were analyzed. On the one hand, the high catalytic activity of Ga(NO$_3$)$_3$·6H$_2$O is caused by the strong Lewis acid metal center, owing to the induction effect of electron-withdrawing nitrate anions[50-53]. On the other hand, because of the lack of pore structure, Ga(NO$_3$)$_3$·6H$_2$O is unable to immobilize the substrate at the catalytic sites, leading to unexpected side reactions. In conclusion, the pore structure of NH$_2$-Ga-MIL-53 framework is essential in enhancing the reaction selectivity while gaining single product[16,31].

Furthermore, ATA was adopted as catalyst on the Strecker reaction. It affords low conversion efficiency with a much longer reaction time as well as unexpected side products with the catalyst of ATA (Table 2, entry 18). The absence of Lewis acid metal sites for ATA might result in the low conversion efficiency. In addition, this result could further suggest that there is no pore structure for ATA to immobilize the substrate at the reaction sites, leading to poor reaction selectivity and unexpected side reactions[16,31].

3　Conclusions

In summary, the catalytic activity of NH$_2$-Ga-MIL-53 has been assessed in Strecker reaction, which is found to be a highly reactive catalyst with essential catalytic universality for extensive substrates. Furthermore, the substrate-selectivity patterns for various substrates of N-Ph aldimines were concluded: (1) the electronic effect of substituents primarily influences the reaction rate, while the electron-donating substituents (*i.e.*, MeO, Ph) and electron-withdrawing substituents (*i.e.*, CF$_3$, NO$_2$) exhibit promotion and suppression effects for the reaction, respectively; (2) the substituted position with respect to substituents secondarily impacts the reaction rate, while the ortho-substituted MeO performs the strongest promotion effect on the reaction. As a heterogeneous catalyst, it is noteworthy that NH$_2$-Ga-MIL-53 has a significant

structural stability that allows its use in Strecker-type reactions for 9 cycles without obvious loss of activity, being easily recovered after each cycle. Comparing the catalytic effects between NH$_2$-Ga-MIL-53 and Ga-MIL-53, it is illustrated that the amino groups on NH$_2$-Ga-MIL-53 can be served as Lewis base sites, promoting the Strecker reaction via Lewis acid-base synergistic catalytic process. Ultimately, by contrasting the catalytic performances among NH$_2$-Ga-MIL-53, Ga(NO$_3$)$_3$·6H$_2$O and ATA, it is indicated that the pore structure of NH$_2$-Ga-MIL-53 framework plays a major role in improving the reaction selectivity while ensuring the product purity. We expect the present work can provide an idea of developing a catalyst with outstanding reusability, structural stability and remarkable universality and selectivity for different substrates in Strecker reactions to increase the economic effectiveness in industrial application.

Supporting information is available at http://www.wjhxxb.cn

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