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isolated vanadium species.³² Ideally, primary diamines of 2,5-

bis(aminomethyl)furan can be obtained from DFF via reductive

amination of the aldehyde group.^{22,33} However, DFF and its

corresponding diimine intermediates were found to be very liable to go condensation irreversibly, resulting in the

formation of oligomer by-products.^{18,23} Up to now, the yield of

2,5-bis(aminomethyl)furan from DFF could not exceed 50%

oximation of DFF with high efficiency.¹⁵ The resultant 2,5-

diformylfuran dioxime can be synthesized from DFF in 90%

isolated yield. This is a potential compound for pivotal N-atom

containing derivatives owing to the versatility of oxime.^{15,34}

The oximation of DFF in combination with the hydrogenation

of DFF-derived 2,5-diformylfuran dioxime might provide an

alternative strategy to synthesize 2,5-bis(aminomethyl)furan.

In this context, a potential catalyst with enhanced selectivity in

the hydrogenation of furyl aldoxime to primary amine is highly

reaction pathways could exist, leading to a complicated

reaction network.³⁴⁻³⁶ To provide high selectivity toward

primary amines, control of the reaction of dioxime as a specific

sequence must be critical. Here, we consider a strategy of

enhancing the pathway of dehydration-hydrogenation of 2,5-

diformylfuran dioxime to improve the selectivity of primary

diamine (Scheme 1). Key to this strategy is the design of a

bifunctional catalyst combining excellent acid properties for

the dehydration of aldoxime to nitrile and active sites for the

NOH

Catalyst

selective hydrogenation of in-situ formed cyano group.

2.5-Diformvlfuran dioxime

In the process of oxime reduction reaction, multiple

Very recently, our group reported a practical strategy for

due to the formation of these by-products.^{22,23}

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2,5-Bis(aminomethyl)furan as a promising monomer was efficiently synthesized in 94.1% yield from biomass-derived 2,5diformylfuran dioxime. The high selectivity is likely to be a result of the controlled reaction pathway over Rh/HZSM-5, which enhanced the sequence of dehydration-hydrogenation of 2,5diformylfuran dioxime owing to the surface acidity on the HZSM-5 support.

Primary diamines are key-monomers for the synthesis of polyamides and polyureas which are increasingly used in automotive, aerospace or building industry, and recently found enormous potentials for many functional applications.¹⁻³ They are classically derived from fossil resources, while harsh reaction conditions or toxic intermediates like cyanides are needed during their production.^{4,5} Biomass as a renewable and ubiquitous resource represents the next generation feedstocks for the chemical industry.⁶⁻¹¹ Owing to the reactive C=O and C-O bonds present in biomass-derived chemicals, N-atoms can be introduced under mild conditions.¹²⁻²⁰ Recently, biomassbased primary diamines were synthesized via reductive amination of aldehydes or hydrogen borrowing amination of alcohols.^{8,21-25}

2,5-Diformylfuran (DFF) is believed to be a potential platform chemical which can now be readily synthesized from 5-hydroxymethylfurfural (HMF) or directly from carbohydrates.²⁶⁻³⁰ For example, our group reported a practical catalyst system consisting of Cu(NO₃)₂/VOSO₄, affording kilogram-scale production of DFF from HMF in our lab.²⁶⁻²⁷ Li et al. demonstrated the efficient synthesis of DFF with 99% yield from fructose over sulfonated magnetically separable MOFderived Fe₃O₄ (111) catalyst.³¹ Wang and coworkers reported the synthesis of DFF in 96% yield from fructose, or in 57% yield from glucose catalyzed by high-silica MOR zeolite-supported

Biomass -----

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desirable.

Scheme 1 Dehydration-hydrogenation of 2,5-diformylfuran dioxime to 2,5-bis(aminomethyl)furan.

2.5-Bis(aminomethyl)furan

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⁺Electronic Supplementary Information (ESI) available.

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In this work, well-dispersed Rh on HZSM-5 (Rh/HZSM-5) is found as an efficient bifunctional catalyst for the reduction reaction of oxime. It catalyzes the dehydration-hydrogenation of 2,5-diformylfuran dioxime quantitatively to 2.5bis(aminomethyl)furan. The activity for dehydration of oxime is increased with increasing the acidity of support. In addition, the acidity of support is beneficial to forming Rh nanoparticles with uniform and small size, which is closely related to the reactivity of nitrile hydrogenation. Thus, an increase in the rate of the desired reaction pathway results in the enhanced selectivity for primary diamine from 2,5-diformylfuran dioxime.

The transformation of 2,5-diformylfuran dioxime (1) was conducted in a 15 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. Our initial investigations were focused on commercial type hydrogenation catalysts, and 2.5bis(aminomethyl)furan (2) was not detected while Raney Ni, Ru/C and Rh/C were used as catalysts (Table 1, entries 1-3). Next, Some Rh catalysts on different supports were synthesized and examined (Table 1, entries 4-9). MCM-41, NaY, and aluminium oxide supported Rh catalysts failed to give satisfactory results (Table 1, entries 4-6). A dark red slurry was obtained after reaction, indicating the formation of oligomers (Fig. S1). Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) characterizations demonstrated that the oligomer consisted of amide and substituted amine groups (Fig. S2-5). Thus the rearrangement reaction of aldoxime as well as the condensation of imine intermediate should be the side reactions which need to be suppressed.^{34,37} Due to its tunable acidity and high stability, ZSM-5 has attracted special interest

Table 1 Catalytic conversion of 1 over different catalysts^a ~ ~ ~

HON	NOH> H₂N´			↓ N O N
1		2	3	4
Entry	Catalyst	Conv. (%)	Yield (%)	
Liitiy			2	3+4
1	Raney Ni	16.5	-	-
2	Ru/C	43.7	-	18.4
3	Rh/C	63.9	-	28.9
4	Rh/MCM-41	>99	-	3.6
5	Rh/NaY	>99	7.9	10.5
6	Rh/γ-Al ₂ O ₃	>99	9.1	4.6
7	Rh/NaZSM-5	>99	13.0	-
8	Rh/HZSM-5	>99	94.1	-
9	Rh/Hβ	96.2	87.2	-
10	Ru/HZSM-5	66.9	-	58.5
11 ^b	Rh/HZSM-5	>99	92.8	-
12 ^c	Rh/HZSM-5	>99	93.2	-
13 ^d	Rh/HZSM-5	>99	90.6	-
14 ^e	Rh/HZSM-5	>99	-	-

^aReaction conditions: 1.0 mmol **1** (154 mg), 100 μL 28% aqueous ammonia, 30 mg catalyst (Rh content: 5 wt%), 7.0 mL MeOH, 2.0 MPa H₂, 130 °C, 2 h. For HZSM-5, the SiO₂/Al₂O₃ ratio is 20. ^bEtOH was used as solvent. ^cTetrahydrofuran was used as solvent. ^d4.0 mmol **1** in EtOH, 400 μ L 28% aqueous ammonia, 4 h. ^eWithout 28% aqueous ammonia added.

primary amine.42 The time course of 2 synthesis over Rh/HZSM-5 was shown in Fig. 1. The volcano curves for both 5-[(hydroxyimino)methyl]-2-furancarbonitrile and 2,5-(3) dicyanofuran (4) indicate that they are the reaction intermediates. Interestingly, 3 and 4 disappeared immediately once the conversion of 1 became complete, indicating the considerable high activity for nitrile hydrogenation. Herein, the Schiff base intermediate products were not observed to accumulate, suggesting that the direct hydrogenolysis of 1 to corresponding imine was not a significant pathway over Rh/HZSM-5.³⁴ The yield of **2** gradually increased to 94.1% after 2 h, and remained intact even prolonging the reaction time to 3 h. The undesired hydrogenation by-products of furan ring were not detected. The above results clearly demonstrate that the reaction pathway of dehydration-hydrogenation was involved in the selective synthesis of 2.

diamine, which can further undergo hydrogenolysis to give the



Fig. 1 Time course of the conversion of 1 to 2 over Rh/HZSM-5 (SiO₂/Al₂O₃ ratio is 20). Reaction conditions: 1.0 mmol 1 (154 mg), 100 µL 28% aqueous ammonia, 30 mg Rh/HZSM-5, 7.0 mL MeOH, 2.0 MPa H₂, 130 °C.

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Fig. 2 Conversion of 1 catalyzed by Rh/HZSM-5 with different SiO_2/Al_2O_3 ratio. Reaction conditions: 1.0 mmol 1 (154 mg), 100 μL 28% aqueous ammonia, 30 mg Rh/HZSM-5, 7.0 mL MeOH, 2.0 MPa H_2, 130 °C, 2 h.

To gain further insight about the outstanding catalytic performance of Rh/HZSM-5, a serious of Rh/HZSM-5 catalysts with varying SiO₂/Al₂O₃ ratios were synthesized and their catalytic performances were explored. As seen from Fig. 2, the yield of **2** decreased along with increasing SiO₂/Al₂O₃ ratio. The variation of the initial SiO₂/Al₂O₃ ratio is usually employed to control the amount of acid sites in zeolite materials. The different catalytic results over Rh/HZSM-5 with varied SiO₂/Al₂O₃ ratios might result from the change of surface acidity on the HZSM-5 support.

Next, the correlation between the catalytic dehydration performance and acid amount of Rh/HZSM-5 with varying SiO_2/Al_2O_3 ratios was investigated. The type and concentration of acid sites on Rh/HZSM-5 was examined via Fouriertransform infrared spectroscopy (FT-IR) of adsorbed pyridine (Fig. 3A). The peak at 1454 \mbox{cm}^{-1} is associated with coordinatively bonded pyridine adsorbed on Lewis acid sites, while the peak at 1546 cm⁻¹ is attributed to protonated pyridine adsorbed on Brönsted acid sites. Emeis demonstrated a direct correlation between the amount of acid sites and integration area of the corresponding peaks.⁴³ It is obvious that the amount of both Lewis and Brönsted acid sites on Rh/HZSM-5 decreased along with increasing the SiO₂/Al₂O₃ ratio. To inspect the effect of acid amount on the production of 3, the dehydration reactivity of 1 under milder conditions were compared with the acid amount of Rh/HZSM-5 calculated through the above method (Fig. 3B). When the SiO_2/Al_2O_3 ratio increased from 20 to 500, a sharp decrease of total acid amount for the Rh/HZSM-5 catalyst was observed. In addition, the mass specific activity for Rh/HZSM-5 decreased from 23.3 mmol \cdot g_{cat}⁻¹·h⁻¹ to 2.1 mmol \cdot g_{cat}⁻¹·h⁻¹ upon increasing the SiO_2/Al_2O_3 ratio from 20 to 500. By contrast, the selectivity for nitrile slightly decreased from 97.5% to 86.5% (Fig. S6). Furthermore, the HZSM-5 support also demonstrated an activity comparable to that of Rh/HZSM-5 (Fig. S6). These results indicated that the changed efficiency of aldoxime dehydration might result from the variation of surface acid amount of catalyst support. Above all, a facile dehydration of 1 can be realized over HZSM-5 supported Rh catalyst without apparent side reaction.





Fig. 3 (A) FT-IR spectrum of adsorbed pyridine on Rh/HZSM-5 with different SiO₂/Al₂O₃ ratio. The data in parenthesis were SiO₂/Al₂O₃ ratios. (B) Mass-specific activity (mmol·g_{cat}⁻¹·h⁻¹) of different Rh/HZSM-5 in **1** dehydration as a function of the SiO₂/Al₂O₃ ratio. Reaction conditions: 1.0 mmol **1** (154 mg), 30 mg Rh/HZSM-5, 7.0 mL MeOH, 2.0 MPa N₂, 90 °C, 30 min. *The same reaction conditions as above except that 100 μ L 28% aqueous ammonia was added.



Fig. 4 TEM images of Rh/HZSM-5 catalysts with different SiO_2/Al_2O_3 ratio.

It is noteworthy that ammonia was added in the synthesis process of **2** from **1**. Ammonia or amines was previously found as catalyst poison in a variety of zeolite or metal catalyzed reactions.⁴⁴⁻⁴⁶ Taking into account this situation, we compared the catalytic results of the dehydration reaction in the presence and absence of aqueous ammonia, respectively. As shown in Fig. 3B, the mass specific activity for Rh/HZSM-5 just slightly decreased upon the addition of aqueous ammonia. This manifested that the dehydration of aldoxime over Rh/HZSM-5 is nearly free from the poison of ammonia.

It has been well recognized that the catalytic hydrogenation performance of metal-supported catalysts is influenced by the microstructure of metal nanoparticles.⁴⁷⁻⁵⁰ The Rh particle sizes and dispersions of Rh/HZSM-5 were characterized by transmission electron microscopy (TEM) (Fig. 4 and S7). It can be clearly seen that the particles of Rh with a small average size were uniformly dispersed on HZSM-5 with the SiO₂/Al₂O₃ ratio of 20. With increasing the SiO₂/Al₂O₃ ratio from 20 to 500, the Rh particles with larger sizes were observed to aggregate. Meanwhile the dispersion of Rh became less uniform. The acidic hydroxyl groups present on the zeolite and metal oxides have been frequently found to represent strong anchoring sites for the Rh and Au during the preparation of supported catalysts, rendering high dispersion and small particle sizes of catalysts.⁵⁰⁻⁵⁴ Likewise, it was inferred that the hydroxyl groups on the surface of HZSM-5 support is beneficial to the dispersion of Rh nanoparticles.

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Fig. 5 TOF of 4 hydrogenation as a function of the average size of Rh partials on Rh/HZSM-5 with different SiO₂/Al₂O₃ ratio. Reaction conditions: 1.0 mmol 4 (118 mg), 100 µL 28% aqueous ammonia, 30 mg Rh/HZSM-5, 7.0 mL MeOH, 2.0 MPa H₂, 90 °C, 30min. The data in parenthesis were SiO₂/Al₂O₃ ratios.



Fig. 6 Cycle experiments of the conversion of 1. Reaction conditions: 1.0 mmol 1 (154 mg), 100 µL 28% aqueous ammonia, 30 mg Rh/HZSM-5 (SiO₂/Al₂O₃ ratio is 20), 7.0 mL MeOH, 2.0 MPa H₂, 130 °C.

The effect of particle sizes of Rh on the activity of nitrile hydrogenation was further analyzed. As seen from Fig. 5, the catalytic hydrogenation activities decreased along with the increase of average particle size of Rh. In comparison, no apparent decrease in selectivity of 2 was observed (Fig. S8). Based on the above results, we can deduce that the efficiency of nitrile hydrogenation to primary amine was promoted over the uniformly dispersed and small Rh nanoparticles.

The recyclability of Rh/HZSM-5 catalyst in the conversion of 1 was evaluated. The catalyst was centrifuged and fully washed with N,N-dimethylformamide after each cycle. After dried at 110 °C under vacuum, the catalyst was directly used for the next run. As shown in Fig. 6, there was no obvious decrease in the conversion of 1 and yield of 2 for the 4 consecutive runs. This illustrated the catalyst was stable under the reaction conditions.

Finally, synthesis of 2 using DFF as starting material was performed through the combination of oximation reaction of DFF and subsequent conversion of 1. As shown in Scheme 2, 94.1% yield of 1 was achieved through oximation of DFF. 1 was further transformed to 2 in 80.3% yield without obvious condensed by-products. These results demonstrate the high

Step E 2 (80.3% yield based on DFF) 1.0 mmol

(94.1% yield based on DFF)

Scheme 2 Synthesis of 2 using DFF as starting material. Reaction conditions: step A, 1.0 mmol DFF (124 mg), 10.0 mmol NH₂OH in 50 wt% aqueous solution, 7.0 mL H₂O, 110 °C, 2 h; step B, 100 μL 28% aqueous ammonia, 30 mg Rh/HZSM-5 (SiO₂/Al₂O₃ ratio is 20), 7.0 mL EtOH, 2.0 MPa H₂, 130 °C, 2 h.

efficiency of the strategy of using 1 as intermediate for the synthesis of 2 from DFF.

Conclusions

In summary, we have demonstrated the high-efficiency synthesis of 2,5-bis(aminomethyl)furan in 94.1% yield through conversion of 2,5-diformylfuran dioxime catalyzed by Rh/HZSM-5. In the process of 2,5-diformylfuran dioxime reaction of transformation. sequence dehvdrationhydrogenation was found to be involved in the selective synthesis of 2,5-bis(aminomethyl)furan. The Rh/HZSM-5 catalyst with high surface acid amount enhanced the step of the selective dehydration of aldoxime. In addition, the supported Rh nanoparticles with uniform dispersion on the HZSM-5 showed premium hydrogenation activity for cyano group and enhanced selectivity for primary diamine without further hydrogenation of furan ring or undesired condensation. Considering the facile synthesis of 2,5-diformylfuran dioxime, this study provides an efficient approach for synthesis of primary diamines from sustainable resources.

Conflicts of interest

There are no conflicts to declare.

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Selective synthesis of biomass-derived 2,5-bis(aminomethyl)furan in 94.1% yield was achieved via enhancing catalytic dehydration-hydrogenation of 2,5-diformylfuran dioxime

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