

Synthesis of furfurylamine by reductive amination of biomass-based furfural over Raney Ni catalyst

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Abstract. Furfurylamine, a very versatile primary amine, is an important intermediate in organic synthesis, pharmaceutical industry and chemical products. Reductive amination of biomass derived furfural is an effective method for the production of furfurylamine. Here, we investigated the reductive amination of furfural to furfurylamine over commercial Raney Ni using ammonia as ammonia source, the effects of hydrogen pressure, reaction temperature, molar ratio of substrate/ammonia, solvent, and catalyst dosage on the reaction were investigated. The results showed that the conversion of furfural was 100% and the highest selectivity to furfurylamine was 96.3% at the optimized reaction conditions of $n(\text{furfural})/n(\text{ammonia}) = 1/2$, 130 °C, 2.0 MPa H₂ for 3 h in 1,4-dioxane solvent. Compared with the conventional method, this technique enables the preparation of furfurylamine with high selectivity under non-noble metal catalyst, which was characterized by simple operation, low cost and high yield.

Keywords. Furfural, furfurylamine, reductive amination, Raney Ni, condition optimization, synthesis.

Amines play an important role in the production of polymers, dyes, pharmaceuticals, pesticides and bioactive compounds [1], among which primary amines have attracted extensive attention in recent years due to their extensive derivatization [2]. Among many methods for the synthesis of primary amines, reductive amination has become one of the most widely used methods for the preparation of primary amines due to the extensive sources of aldehydes and ketones and their low prices. At present, researchers have reported a variety of homogeneous and heterogeneous catalysts for reductive amination of aryl compounds. Among them, homogeneous catalysts are difficult to be separated and reused, so reductive amination of heterogeneous catalysts is a research hotspot in recent years.

In recent years, it is particularly important to develop and utilize renewable biomass energy to replace fossil resources with the increasing depletion of traditional fossil resources [13]. Among them, furfural prepared from biomass xylose dehydration is an ideal choice for sustainable development of amine chemistry as an important platform compound [14]. At present, there are many reports on the preparation of furfural amine by reductive amination of furfural. Researchers often use noble metal catalysts to improve furfurylamine selectivity. Nishimura et al. [15] used poly (N-vinyl-2-pyrrolidone) stabilized Ru supported hydroxyapatite (Ru-PVP/HAP) to carry out reductive amination of furfural at 100 °C and 0.25MPa H₂, and the yield of furfural amine was 60%. Deng et al. [16] found that Ru/Nb₂O₅ catalyst reduced at 300 °C had good catalytic performance at 70 °C by fine-tuning the surface acidity of Nb₂O₅, and the yield of furfurylamine was 89%. The results showed that the acidic sites played an important role in the activation of furfural, which promoted the formation of furfural amine. Chandra et al. prepared Ru NP catalyst by loading Ru nanoparticles on Ca (NH₂)₂, removing the support after acid treatment, and reacted for 2h at 90 °C and 2MPa H₂ to obtain 99% furfurylamine yield. Chatterjee et al. [18] used Rh/Al₂O₃ as catalyst to react for 2h at 80 °C and 2MPa H₂, and the selectivity of furfural amine was 92%. XIN et al. [19] prepared Pd NPs catalyst, which reduced aminated furfural at room temperature, and the yield of furfural amine was 97%.

Although the above noble metal based catalysts have good activity, the cost of catalysts is high. Therefore, it is of great significance to develop a cheap and easily available non-noble metal based catalyst for preparing furfural amine by reductive amination of furfural. ZHOU et al. [20] used Raney Co for reductive amination of furfural at 120 °C and 1MPa H₂. The yield of furfural amine was 98.9%, but the amount of catalyst used was too high, which was not suitable for industrial production.

In the reduction amination reaction of furfural, NH₃ and ammonia water are mostly used in the selection of ammonia source at present. Ammonia water can more stably control the concentration of ammonia in the system, and it is more and more widely used in the reduction amination. Yuan et al. [24] prepared Ni₆AlOx catalyst by coprecipitation method, and reacted for 5h at 100 °C and 0.4MPa H₂. The yield of furfural amine was 90%. Recently, Manzoli et al used Fe₃O₄@SiO₂-Ni as a catalyst, the yield of furfural amine can reach 100% when it is heated under microwave radiation for 3h at 115 °C and 2.0MPa H₂. However, the preparation process of the catalyst is cumbersome and difficult to produce on a large scale.

In the previous work, our research group found [26] that different metals in the catalyst have different adsorption energies for NH₃ and H₂. The adsorption energy difference of precious metals, such as Pt, Pd, Ru is greater than that of non-precious metals, such as Co and Ni. Under the same reaction conditions, the catalytic effect of non-precious metal catalysts for reductive amination is better. In general, Ni can be used as the preferred metal for research because of its inherent stability, high activity and low cost. As a multi-phase non-noble metal catalyst composed of fine grains of aluminum alloy with porous structure, commercial Raney Ni is commonly used in the hydrogenation reduction reaction of aldehydes, ketones and other compounds containing unsaturated bonds.

Generally, from the perspective of the industrial production of furfural amine, in this paper, commercial Raney Ni is selected as the ammonia source to prepare furfural amine by reductive amination of furfural, and investigates the influence of solvent, time, temperature, hydrogen pressure, and catalyst dosage, etc., to develop a reaction process for highly

efficient conversion of furfural-to-furfural amine under the action of non-precious metal catalysts.

1. Experiment

1.1. Instruments and Reagents

Instrument: multi-kettle series high-pressure reaction device (model: SLM25, manufacturer: Beijing Century Senlang Instrument Co., Ltd.); Gas chromatograph (Model: Agilent 7820A, Manufacturer: Agilent Technology Co., Ltd.); Electronic analytical balance (Model: BS224S, manufacturer: Sartorius AG); Low speed centrifuge (Model: SC2546, Manufacturer: Zhongjia Branch of Keda Innovation Co., Ltd.).

Reagents: ammonia (25%~28%), furfural (AR), 1,4-dioxane (AR), N-methylpyrrolidone (AR), Raney Ni (W-2 type, $\leq 50 \mu\text{m}$), all purchased from Aladdin Reagent Co., Ltd.

1.2. Synthesis of Furfural Amine

1,4-dioxane (10mL), furfural (10mmol), N-methylpyrrolidone (NMP) (200 μL), ammonia water (20mmol) and Raney Ni (0.03g) was added, the kettle was sealed, H_2 was blown in repeatedly for 5 times to replace the air in the kettle, and 2MPa H_2 was injected. The temperature was warmed to 130 $^\circ\text{C}$, stirring and reaction was started. After the reaction, samples were taken, centrifugated, the upper clear liquid was taken and gas chromatography (Agilent 7820A) was used to quantitatively analyze the reaction products. N-methylpyrrolidone was used as the internal standard, hydrogen flame ionization detector, and DB-WAX polar quartz capillary column (30.0m \times 300 $\mu\text{m}\times$ 0.25 μm).

Table 1. Effect of hydrogen pressure on reductive amination of furfural to furfurylamine

Entry	Hydrogen pressure/MPa	Conversion rate/%	Selectivity/%					
			Furfural amine	Tetrahydrofurfurylamine	Furfuryl alcohol	N - (2-furylidene) - 2-furomethylamine	N - (2-furomethyl) - 2-furomethylamine	Polymer
1	0.5	90.5	28.1	0	0.3	67.4	0.1	4.1
2	1	100	31.0	0	0.9	57.8	0.3	10.0
3	1.5	100	51.3	0	0.6	35.4	0.3	12.4
4	2	100	78.6	0	0	15.5	0	5.9
5	2.5	100	52.6	9.2	1.0	32.8	0.5	3.9

Table 2. Effect of reaction temperature on reductive amination of furfural to furfurylamine

Entry	Temperature/ $^\circ\text{C}$	Percent conversion/%	Selectivity/%					
			Furfural amine	Tetrahydrofurfurylamine	Furfuryl alcohol	N - (2-furylidene) - 2-furomethylamine	N - (2-furomethyl) - 2-furomethylamine	Polymer
1	70	95.4	18.9	0	0.6	75.8	0.2	4.5
2	90	100	78.6	0	0	15.5	0	5.9
3	110	100	88.4	0	0.6	7.3	1.2	2.5
4	130	100	96.3	0	1.1	1.3	1.0	0.3
5	150	100	69.1	0	1.6	0	1.8	27.5
6	170	100	57.3	13.2	1.1	7.3	2.7	18.4

2. Results and discussion

2.1. Effect of hydrogen pressure

Table 1 shows the results of exploring the effect of hydrogen pressure on the reductive amination of furfural-to-furfural amine over Raney Ni catalyst at 90 $^\circ\text{C}$. It can be found that at 0.5MPa H_2 , the selectivity of furfurylamine is low, only 28.1%, and the main product is Schiff base by-product (Entry 1). With the increase of hydrogen pressure, the content of by-products of Schiff base decreased, and the selectivity of target product furylamine increased, which reflected that Schiff base could be converted to primary amine through hydrogenolysis step. When the hydrogen pressure is 2MPa, the furfural amine selectivity is the highest, which is 78.6% (Entry 4). Further increasing the hydrogen pressure, the selectivity of furfural amine began to decline, and the content of tetrahydrofurfural amine and furfuryl alcohol, a by-product of carbonyl hydrogenation, increased, indicating that high hydrogen pressure was not conducive to the formation of furfural amine.

2.2. Effect of reaction temperature

The influence of reaction temperature was investigated at 70-170 $^\circ\text{C}$, and the results are shown in Table 2. It can be seen from Table 2 that temperature has a great influence on the selectivity of furfural amine. When the reaction temperature is 70 $^\circ\text{C}$, the product is mainly Schiff base, and the selectivity of furfurylamine is less than 20% (Entry 1). The furfural amine selectivity can be significantly improved by increasing the temperature. At 130 $^\circ\text{C}$, the furfural amine selectivity reaches the maximum (96.3%, Entry 4). Further temperature rise has no positive effect on the selectivity of

furfural amine. On the contrary, the temperature rise led to direct hydrogenation of furfural amine to produce tetrahydrofurfural amine by-product, and polymer appeared in the system. It could be inferred that the reaction temperature below 130 °C was not enough to convert furfural to furfural amine within 3h, but excessive hydrogenation and side reaction of polymerization occurred if the temperature was too high. In addition, the content of Schiff base decreased with the increase of temperature, but there was no obvious secondary amine formation, indicating that Schiff base could be converted to furfural amine. 130 °C was considered as the appropriate reaction temperature based on comprehensive consideration.

2.3. Effect of material ratio [n (furfural)/n (ammonia)]

Table 3 shows the results of exploring the influence of furfural/ammonia (molar ratio) on furfural reductive amination to furfural amine. The 10mmol substrate was kept, and the amount of ammonia was changed to adjust n (furfural)/n (ammonia). In the whole process, furfural could be completely transformed. When the molar ratio of substrate to ammonia is 1/1, the furfural amine selectivity is only 41.4%, and there are a large number of Schiff bases and secondary amine by-products (Entry 1). The selectivity of furfural amine increased with the increase of the amount of ammonia, and reached the highest (96.3%, Entry 3) when n (furfural)/n (ammonia)=1/2. The amount of ammonia was further increased, furfural amine selectivity began to decline, and polymer appeared. It is reported that in the presence of ammonia and hydrogen, Schiff bases could react with ammonia to form secondary amines, and then hydrogenolysis to obtain primary amines [27]. This may be the reason why excessive ammonia can improve the selectivity of primary amine. However, excessive ammonia reduces the selectivity of furfural amine, which may be due to the competitive occupation of NH₃ on the metal active center, which inhibited the hydrogenation performance of the metal catalyst, leading to the formation of by-products.

Table 3. Effect of furfural/ammonia (molar ratio) on reductive amination of furfural to furfurylamine

Entry	Furfural/ammonium hydroxide (mole ratio)	Percent conversion/%	Selectivity/%					Polymer
			Furfural amine	Tetrahydrofurfurylamine	Furfuryl alcohol	N - (2-furylidene) - 2-furomethylamine	N - (2-furomethyl) - 2-furomethylamine	
1	1/1	100	41.4	0	1.4	15.1	23.7	18.4
2	1/1.5	100	90.9	0	1.3	2.1	5.2	0.5
3	1/2	100	96.3	0	1.1	1.3	1.0	0.3
4	1/2.5	100	80.7	0	1.7	1.1	1.5	15.0
5	1/3	100	75.5	0	1.5	1.2	1.2	20.6

Table 4. Effect of solvent on reductive amination of furfural to furfurylamine

Entry	Solvent/mL	Conversion rate/%	Selectivity/%					Polymer
			Furfural amine	Tetrahydrofurfurylamine	Furfuryl alcohol	N - (2-furylidene) - 2-furomethylamine	N - (2-furomethyl) - 2-furomethylamine	
1	MeOH	100	27.8	0	1.5	3.2	2.0	65.5
2	EtOH	100	58.5	0	1.4	0.4	2.3	37.4
3	IPA	100	71.8	0	2.6	0.1	3.1	22.4
4	THF	100	71.6	0	0.9	0.6	1.4	25.5
5	DMSO	100	3.6	0	0	1.4	0.1	94.9
6	1,4-dioxane	100	96.3	0	1.1	1.3	1.0	0.3

2.4. Effects of solvent types

Table 4 shows the results of the effects of three polar solvents methanol, ethanol, isopropanol and three non-polar solvents tetrahydrofuran, dimethyl sulfoxide and 1,4-dioxane on the reduction amination of furfural-to-furfural amine. Among the three polar solvents, the selectivity order of furfurylamine is isopropanol>ethanol>methanol (Entry 1-3); In non-polar solvent, there is almost no furfural amine formation in dimethyl sulfoxide system (Entry 5). In all the reaction processes, there were a small amount of by-products, indicating that the solvent had no significant effect on the by-product generation. The selectivity of furfural amine in 1,4-dioxane was the highest. The yield of furfural amine was 96.3% (Entry 6) at 130 °C for 3h.

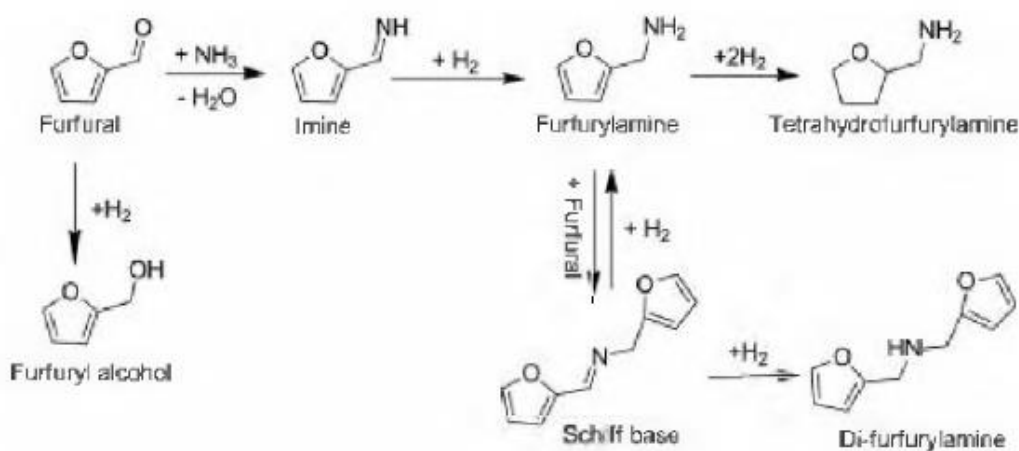
2.5. Effect of reaction time

The reaction kinetics at 130 °C was investigated to further understand the reductive amination reaction of furfural, and the results are shown in Table 5. At the beginning of the reaction, furfural was converted at an extremely fast rate, and the conversion rate was 99.3% at 0.5h. At this time, the selectivity of furfural amine was 35.9%, and the selectivity of Schiff base was 54.9% (Entry 1). This could be attributed to the fact that primary amine is more nucleophilic than ammonia, leading to the immediate reaction between the furfural amine initially formed in the reaction and the remaining furfural to form a Schiff base [27]. The content of Schiff base began to decrease and the content of furfuryl amine increased rapidly with the extension of reaction time. After reaction for 3h, almost all Schiff bases were converted to furfuryl amine, and the selectivity was 96.3% (Entry 4). In the whole process, the content of secondary amine was very low. The results

show that schiff base intermediates are mainly hydrogenated to form furfural amine, followed by hydrogenation of schiff base intermediates to generate secondary amine, which is consistent with the literature [20]. In addition, the selectivity of furfuryl alcohol in the reaction remained basically unchanged, indicating that the hydrogenation of Egly took place in the initial stage of the reaction.

Table 5. Effect of reaction time on reductive amination of furfural to furfurylamine

Entry	Time/h	Conversion rate/%	Selectivity/%					
			Furfural amine	Tetrahydrofurfurylamine	Furfuryl alcohol	N - (2-furylidene) - 2-furomethylamine	N - (2-furomethyl) - 2-furomethylamine	Polymer
1	0.5	99.3	35.9	0	1.6	54.9	1.2	6.4
2	1	99.8	60.8	0	0.9	21.1	1.2	16.0
3	2	100	75.5	0	1.5	6.4	1.8	14.8
4	3	100	96.3	0	1.1	1.3	1.0	0.3
5	4	100	90.4	0	1.3	0.3	2.7	5.3
6	5	100	84.2	0	1.4	0.3	2.9	11.2
7	6	100	74.2	0	1.7	0.5	1.8	21.8



Scheme 1

Table 6. Effect of catalyst dosage on reductive amination of furfural to furfurylamine

Entry	Amount of catalyst/g	Conversion rate/%	Selectivity/%					
			Furfural amine	Tetrahydrofurfurylamine	Furfuryl alcohol	N - (2-furylidene) - 2-furomethylamine	N - (2-furomethyl) - 2-furomethylamine	Polymer
1	0.01	100	53.1	0	0.6	11.4	1.4	33.5
2	0.03	100	96.3	0	1.1	1.3	1.0	0.3
3	0.05	100	80.2	0	1.5	0	2.3	16.0
4	0.07	100	81.9	0	1.7	0	1.7	14.7
5	0.09	100	82.6	0	1.9	0	1.9	13.6
6	0.15	100	61.5	21.6	2.3	0	2.2	12.4
7	0.20	100	52.8	31.9	4.6	0	3.1	7.6
8	0.25	100	30.9	50.5	5.4	0	2.9	10.3

Based on the above results, the reductive amination reaction path of furfural (Scheme 1) is summarized: furfural reacts with ammonia to form imine intermediate in advance, and then hydrogenates to form furfural amine. In this process, because the carbonyl group has higher nucleophilic property than ammonia, the furfural amine generated is easy to react with furfural to generate Schiff base, secondary amine and other by-products. Under high temperature and high pressure, the system generates tetrahydrofurfural amine [10], a by-product of radical hydrogenation reaction. In addition, Schiff base can be converted into furfural amine through hydrogenolysis, and furfural can be directly hydrogenated to produce furfural alcohol at the beginning of the reaction. This result is consistent with the description in the literature.

2.6. Effect of Catalyst Dosage

The amount of catalyst has an important influence on the reaction process, and the results are shown in Table 6. When the dosage of Raney Ni is 0.01 g, the furfural amine selectivity is only 53.1% (Entry 1), accompanied by the formation of a certain proportion of polymer. When the catalyst is increased to 0.03 g, the furfural amine selectivity is significantly increased to 96.3%, and the by-product content reaches the minimum (Entry 2). The amount of catalyst is increased continuously, the selectivity of target product starts to decline, and the content of by-product tetrahydrofurfurylamine increases significantly (Entry 6-8), indicating that excessive amount of catalyst will lead to excessive activity and deep

hydrogenation reaction. Therefore, the optimal amount of Raney Ni is 0.03g, which is 3% of the mass of reaction substrate furfural.

2.7. Catalyst Characterization

W-2 commercial Raney Ni is prepared from Ni Al alloy with Ni/Al ratio of 1/1. After activation, the catalyst consists of Ni content $\geq 90\%$ and Al $\leq 8\%$. Raney Ni was characterized by XRD to further explore the relationship between catalyst and catalytic performance, and the results are shown in Figure 1. The new Raney Ni and the used Raney Ni have three obvious diffraction peaks at the same position, which is $2\theta = 44.4^\circ$, 51.8° , and 76.4° , which belong to (111), (200) and (220) crystal planes (PDF # 01-089-7128) of Ni⁰ respectively, proving that Ni⁰ is the active center of catalytic reaction, which is consistent with the description in the literature [29].

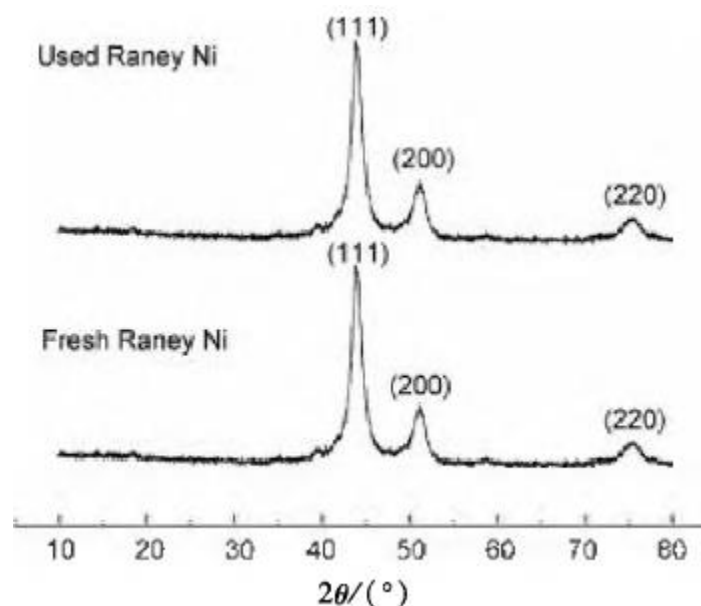


Figure 1. X-ray Diffraction Patterns of Raney Ni

3. Conclusion

Furfural amine was synthesized by reductive amination of furfural with ammonia water as ammonia source and commercial Raney Ni as catalyst. The results showed that in 10 mL 1,4-dioxane, 0.03g Raney Ni, n (furfural)/n (ammonia)=1/2, 130 °C, 2.0 MPa H₂ were reacted for 3 h, the furfural conversion was 100%, and the furfural amine selectivity was 96.3%. The catalyst is cheap and easy to obtain, the amount of catalyst is low, and the yield of target product furfural amine is high, which has broad application prospects.

References

- [1] GOMEZ S, PETERS J A, MASCHMEYER T. The reductive amination of aldehydes and ketones and the hydrogenation of nitriles: Mechanistic aspects and selectivity control [J]. *Advanced Synthesis & Catalysis*, 2002,344:1037 -1057.
- [2] SHIMIZU KI, KON K, ONODERA W, et al. Heterogeneous Ni catalyst for direct synthesis of primary amines from alcohols and ammonia[J]. *ACS Catalysis*, 2012,3(1) :112-117.
- [3] JUNG H S, YUN T, CHO Y, et al. Simple and convenient copper-catalyzed amination of aryl halides to primary arylamines using NH₄ OH [J]. *Tetrahedron*, 2016,72(40) :5988 -5993.
- [4] ADAM R, BHEETER C B, CABRERO J R, et al. Selective hydrogenation of nitriles to primary amines by using a cobalt phosphine catalyst[J]. *ChemSusChem*, 2017,10(5) :842-846.
- [5] DEMIDOVA Y S, SUSLOV E V, SIMAKOVA I L, et al. One-pot monoterpene alcohol amination over Au/ZrO₂ catalyst: Effect of the substrate structure [J]. *Journal of Catalysis*, 2018,360 :127 – 134.
- [6] HAHN G, KUNNAS P, DE JONGE N, et al. General synthesis of primary amines via reductive amination employing a reusable nickel catalyst[J]. *Nature Catalysis*, 2018,2(1) :71 -77.
- [7] BEHR A, WINTZER A, LUBKE C, et al. Synthesis of primary amines from the renewable compound citronellal via biphasic reductive amination [J]. *Journal of Molecular Catalysis A: Chemical*, 2015,404-405:74- 82.
- [8] SENTHAMARAI T, MURUGESAN K, SCHNEIDEWIND J 9 et al. Simple ruthenium-catalyzed reductive amination enables the synthesis of a broad range of primary amines [J]. *Nature Communications*, 2018,9(1) :4123 -4135.
- [9] TAN X, ZENG W, ZHANG X, et al. Development of a novel secondary phosphine oxide-ruthenium (II) catalyst and its application for carbonyl reduction [J]. *Chem Commun (Camb)*, 2018 ,54(5) :535 - 538.
- [10] NAKAMURA Y, KON K, TOUCHY A S, et al. Selective synthesis of primary amines by reductive amination of ketones with ammonia over supported Pt catalysts [J]. *Chem Cat Chem*, 2015,7(6) :921 - 924.
- [11] LIANG G, WANG A, U L, et al. Production of primary amines by reductive amination of biomass-derived aldehydes/ketones[J].

- Angewandte Chemie International Edition, 2017, 56 (11) :3050 -3054.
- [12] XIE C, SONG J L, HUA M L, et al. Ambient-temperature synthesis of primary amines via reductive amination of carbonyl compounds [J]. ACS Catalysis, 2020, 10(14):7763 -7772.
- [13] RAPADO P, FABA L, ORDONEZ S. Influence of delignification and reaction conditions in the aqueous phase transformation of lignocellulosic biomass to platform molecules [J]. Bioresource Technology, 2021, 321:124500 -124511.
- [14] BHOGESWARARAO S, SRINIVAS D. Catalytic conversion of furfural to industrial chemicals over supported Pt and Pd catalysts [J]. Journal of Catalysis, 2015, 327 :65 -77.
- [15] NISHIMURA S, MIZUHORI K, EBITANI K. Reductive amination of furfural toward furfurylamine with aqueous ammonia under hydrogen over Ru-supported catalyst [J]. Research on Chemical Intermediates, 2015, 42(1) :19-30.
- [16] DENG D, KITA Y, KAMATA K, et al. Low-temperature reductive amination of carbonyl compounds over Ru deposited on Nb₂O₅·nH₂O [J]. ACS Sustainable Chemistry & Engineering, 2018, 7(5); 4692 -4698.
- [17] CHANDRA D, INOUE Y, SASASE M, et al. A high performance catalyst of shape-specific ruthenium nanoparticles for production of primary amines by reductive amination of carbonyl compounds [J]. Chemical Science, 2018, 9(27) :5949 -5956.
- [18] CHATTERJEE M, ISHIZAKA T, KAWANAMI H. Reductive amination of furfural to furfurylamine using aqueous ammonia solution and molecular hydrogen: an environmentally friendly approach [J]. Green Chemistry, 2016, 18(2) :487 -496.
- [19] JU X C, SUN S T, ZHANG Q, et al. Efficient and mild reductive amination of carbonyl compounds catalyzed by dual-function palladium nanoparticles [J]. ACS Sustainable Chemistry & Engineering, 2019, 8 (3):1618 -1626.
- [20] ZHOU K, CHEN B X, ZHOU X T, et al. Selective synthesis of furfurylamine by reductive amination of furfural over raney cobalt [J]. Chem Cat Chem, 2019, 11(22) :5562-5569.
- [21] YUAN H, LI J P, SU F, et al. Reductive amination of furanic aldehydes in aqueous solution over versatile Ni₂Al₁₀O_x catalysts [J]. ACS Omega, 2019, 4(2) :2510 -2516.
- [22] LIU X, WANG Y, JIN S, et al. High performance of nitrogen-doped carbon-supported cobalt catalyst for the mild and selective synthesis of primary amines [J]. Arabian Journal of Chemistry, 2020, 13 (4): 4916 -4925.
- [23] YUAN Z L, LIU B, ZHOU P, et al. Preparation of nitrogen-doped carbon supported cobalt catalysts and its application in the reductive amination [J]. Journal of Catalysis, 2019, 370; 347 -356.
- [24] YUAN H K, LI J P, SU F Z, et al. Reductive amination of furanic aldehydes in aqueous solution over versatile Ni₂Al₁₀O_x catalysts [J]. ACS Omega, 2019, 4 (2) :2510-2516.
- [25] MANZOLI M, GAUDINO E C, CRAVOTTO G, et al. Microwave-assisted reductive amination with aqueous ammonia: Sustainable pathway using recyclable magnetic nickel-based nanocatalyst [J]. ACS Sustainable Chemistry & Engineering, 2019, 7(6) :5963- 5974.
- [26] ZHOU K, HUH Y, SHU H M, et al. A comprehensive study on the reductive amination of 5-hydroxymethylfurfural into 2,5-bisaminomethylfuran over raney Ni through DFT calculations [J]. ChemCatChem, 2019, 11(11):2649-2656.
- [27] DONG B, GUO X C, ZHANG B, et al. Heterogeneous Ru-based catalysts for one-pot synthesis of primary amines from aldehydes and ammonia [J]. Catalysts, 2015, 5(4) :2258 -2270.
- [28] KOMANOYA T, KINEMURA T, KITA Y, et al. Electronic effect of ruthenium nanoparticles on efficient reductive amination of carbonyl compounds [J]. Journal of the American Chemical Society, 2017, 139 (33): 11493 -11499.
- [29] HE L, HUANG Y, WANG A, et al. H₂ production by selective decomposition of hydrous hydrazine over Raney Ni catalyst under ambient conditions [J]. AIChE Journal, 2013, 59 (11):4297 -4302.