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Switchable synthesis of furfurylamine and tetrahydrofurfurylamine from furfuryl alcohol over Raney Nickel

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Raney Ni proved to be an effective heterogeneous catalyst for switchable reductive amination of furfuryl alcohol to tetrahydrofurfurylamine and furfurylamine with NH₃ by simply adding or not adding 1.0 MPa of H_2 into the reaction bulk. After further optimization of the reaction conditions, we finally obtained 94.0% yield of tetrahydrofurfurylamine and 78.8% yield of furfurylamine with high selectivity. By extensively studying the catalytic pathways and mechanism of catalyst deactivation with XRD and XPS characterization, we have confirmed that excess amount of H_2 in the reaction bulk leads to the deep hydrogenation of furan ring while insufficient amount of H_2 leads to the formation of Ni₃N and the deactivation of catalyst.

Introduction

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Amine plays an important role in the bulk and fine chemical industries for production of polymers, dyes, pharmaceuticals, agrochemicals, surfactants and biologically active compounds. Generally, primary amines can be synthesized by reductive amination of either corresponding carbonyl compounds or alcohols. Comparing with the former, amination of alcohols takes advantage of using inexpensive starting material and exhibiting higher atom efficiency, and deserves increasing attention^{1, 2}.

The reductive amination of hydroxyl compound with ammonia can be catalyzed by metal complex-based homogeneous catalysts, such as Ru- and Ir-based complex³⁻⁶, solid acid catalysts, such as zeolites, phosphates, and oxides^{7.8}, and metal hydrogenation catalysts, such as Pt, Ir, Ru, Os, Cu, Co and Ni^{2, 9-13}. It is widely accepted that metal catalysts activate the alcohols by three consecutive steps (Scheme 1)¹⁴⁻¹⁶: (1) dehydrogenation of the alcohol to form corresponding carbonyl intermediate; (2) Condensation of water to form an imine, and (3) hydrogenation of the imine to produce the final primary amine. For steps (1) and (3) a metal catalyst is

required, while for step (2), an acid or base catalyst is preferred, although it can also occur without a catalyst¹⁷. This reaction process is generally carried out under a mixture of ammonia and hydrogen. However, hydrogen is not stoichiometrically consumed¹ due to the existence of a so-called "borrowing hydrogen" or "hydrogen auto-transfer" mechanism^{5, 18}, from which it is suggested that the "borrowed" hydrogen from the dehydrogenation of alcohol is returned by reducing the imine into the target amine. As a consequence, hydrogen is theoretically unnecessary for conducting the amination of alcohol, although it is claimed that excess hydrogen is indispensable to prevent the catalyst from irreversible deactivation caused by the formation of nickel nitride¹⁹⁻²² and coking^{23, 24}.

Furfurylamine and tetrahydrofurfurylamine are important intermediates in the manufacture of pharmaceuticals, fibers and perfumes²⁵⁻²⁹. Similar to most primary amines, furfurylamine can be synthesized through reductive amination of its corresponding aldehyde, furfural, over metal catalysts^{25, 26}, while tetrahydrofurfurylamine can be produced by deep hydrogenation of furfurylamine or 2-furancarbonitrile^{30, 31}.



Scheme 1 General pathway for reductive amination of alcohols

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Table 1 Reductive amination of FA with different neterogeneous metal catalys
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Entry	catalyst	H ₂ (MPa)	NH ₃ (MPa)	Conversion (%)	Yield (Selectivity) (%)			
					NH ₂	O OH	O NH2	Other by- products
1	Pd/C	-	0.35	0	-	-	-	-
2	Pt/C	-	0.35	0	-	-	-	-
3	Ru/C	-	0.35	0	-	-	-	-
4	Rh/C	-	0.35	0	-	-	-	-
5	Raney Co	-	0.35	0	-	-	-	-
6	Raney Ni	-	0.35	24.0	22.2(92.5)	1.8(7.5)		
7	Pd/C	1	0.35	12.4	-	11.3(91.1)		1.10(8.9)
8	Pt/C	1	0.35	16.9	-	12.2(72.2)		4.70(27.8)
9	Ru/C	1	0.35	24.2	-	20.1(83.1)		4.09(16.9)
10	Rh/C	1	0.35	16.3	-	16.2(99.4)		0.2(0.6)
11	Raney Co	1	0.35	18.4	-	16.4(89.1)	0.99(5.4)	0.99(5.4)
12	Raney Ni	1	0.35	27.5	-	15.5(56.4)	11.0(40.0)	0.99(3.6)
13 ^a	Pd/C	1	-	100	-	100		

Reaction conditions: FA, 0.5 g; THF, 15 ml; catalyst, 0.25 g; NH₃ pressure, 0.35 MPa; temperature, 160 °C; reaction time, 24 h; stirring speed, 1200 rpm. ^a catalyst 0.05 g, 160 °C, 4 h, in absence of NH₃.

Alternatively, they can also be synthesized through amination of furfuryl alcohol and followed by the saturation of the furan ring (for tetrahydrofurfurylamine synthesis). To the best of our knowledge, no other catalyst except for homogeneous catalysts such as a Ru-acridine complex³ and a triruthenium dodecacarbonyl complex⁵ have been reported for such reaction so far. The development of heterogeneous catalysts with base metals taking advantage of easier separation and lower cost for the reductive amination of furfural to obtain furfurylamine and tetrahydrofurfurylamine is therefore urgent and falls in our interest. In this study, based on our previous work on hydroamination of isophorone nitrile to isophorone diamine³², we herein aimed at the reductive amination of furfuryl alcohol as a model reaction to achieve high selectivity to furfurylamine and tetrahydrofurfurylamine.

Results and discussion

The reductive amination of furfuryl alcohol was conducted in absence of hydrogen over the commercially available Pt/C, Pd/C, Ru/C, Rh/C, Raney Co and Raney Ni. As shown in Table 1, all the tested catalysts were totally inactive except for Raney Ni (entries 1-6), over which the main product was furfurylamine (92.5% in selectivity, entry 6), although the conversion was low (24.0%, entry 6). After introducing 1 MPa of hydrogen, as expected, the furan ring was saturated over each tested catalyst and formed a considerable amount of tetrahydrofurfuryl alcohol due to deep hydrogenation (entries 7-12). Only tetrahydrofurfurylamine of the amination product was found over Raney Co and Raney Ni, with the yields of 0.99% and 11.0%, respectively.

It is well known that the metal catalysts we have used are active in hydrogenation reactions. Taking Pd/C as an example, deep hydrogenation product of furfuryl alcohol can 100% convert to tetrahydrofurfuryl alcohol in the presence of pure H_2 within 4 h over much less catalyst dosage (10 wt% in respect to

substrate, entry 13). Comparatively, in the similar reductive amination process, such hydrogenation activity of the metals was greatly inhibited, as one can see that the conversion of furfural alcohol over Pd/C was only 12.4% (entry 7). In a typical hydrogenation/dehydrogenation process, H atom is first decomposed from either H-H bond or C-H bond and adsorbed onto a metal active sites for the following reactions^{33, 34}. The deactivation of metals for hydrogenation/dehydrogenation in the reductive amination process can therefore be ascribed to the competitive occupation of NH₃ on the metal active sites. Fig. 1 summarized our calculated and the reported adsorption energy of H₂ and NH₃ on different facets of the metal active cites evaluated on the basis of the first principle calculations. The differences of the averaged adsorption energy for noble metals are higher than those of Co and Ni, indicating that more metal active sites would be occupied by NH₃. This might be the main reason that noble metals are less active in reductive amination, which is also in agreement with our previous study^{32, 35}.

Given that H_2 and NH_3 may compete to adsorb on the same metal active sites, variation of the ratio of H_2 and NH_3 may impact greatly on the reductive amination process. As shown in





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	H ₂ (MPa)	Conversion (%)	Yield (Selectivity) (%)					
Entry						Other by-products		
			NH ₂	O OH		NH ₂ OH	ОН	unidentified compounds
1	2.0	69.3	-	21.3(30.7)	7.5(10.8)	2.8(4.0)	31.8(45.9)	5.9(8.5)
2	1.0	27.5	-	15.5(56.4)	11.0(40.0)	-	-	1.0(3.6)
3	0.5	27.8	8.3(29.9)	12.0(43.2)	7.5(27.0)	-	-	
4	0	24.0	22.2(92.5)	1.8(7.5)	-	-	-	

 Table 2 Effect of hydrogen pressure on amination of furfuryl alcohol

Reaction conditions: FA, 0.5 g; THF, 15 ml; Raney Ni, 0.25 g; NH₃ pressure, 0.35 MPa; temperature, 160 °C; reaction time, 24 h; stirring speed, 1200 rpm.

Table 2, when Raney Ni was employed, we adjust the ratio of H₂ and NH₃ by changing the partial pressure of H₂ while the partial pressure of NH₃ was fixed at 0.35 MPa, a maximum pressure the NH₃ cylinder can provide. The reason we and other publications^{17, 19, 70} used the largest amount of NH₃ is mainly to suppress the formation of secondary amines and tertiary amine. It can be seen that the conversion of furfuryl alcohol was the highest of 69.3% at 2.0 MPa of H₂. However, except for tetrahydrofurfuryl alcohol and tetrahydrofurfurylamine, a large amount of ring-opening products such as, 2-amino-1-pentanol and 1, 2-pentanediol were formed, indicating that high H₂ pressure resulted in over-hydrogenation. As a result, the selectivity of tetrahydrofurfurylamine was only 10.8%. When the partial pressure of H₂ dropped from 2.0 MPa to 1.0 MPa, the conversion decreased remarkably from around 69.3% to 27.5% , while the selectivity of amine (mainly tetrahydrofurfurylamine) increased to 40% and no ring-opening products were observed. When the partial pressure of H₂ dropped to 0.5 MPa, the conversion of furfuryl alcohol almost unchanged, but a new product, furfurylamine, with a selectivity of 29.9% appeared and the selectivity of total amines increased to 56.9% at the same time. In absence of hydrogen, the selectivity of furfurylamine is the highest (92.5%), although the conversion of furfuryl alcohol was only 24.0%. Meanwhile, it is noteworthy that 1.8% yield of tetrahydrofurfuryl alcohol was obtained even no H₂ was introduced, which is also evidence of the existence of dehydrogenation step in the reductive amination process. These results show that the switchable synthesis of tetrahydrofurfurylamine and furfurylamine from furfural alcohol is feasible by conducting the reductive amination of furfuryl alcohol over Raney Ni at 1.0 MPa and 0 MPa of H₂, respectively.

The optimization on amination temperature was tested in the range of 160 °C to 200 °C for both synthesis of tetrahydrofurfurylamine (in presence of 1 MPa of H₂) and furfurylamine (in absence of H₂), as shown in Fig. 2(a) and 2(b), which exhibited similar trends of the product spectra. For example, both target products, i.e., tetrahydrofurfurylamine and furfurylamine, reached the highest yields at 180 °C, which were 46.2 % and 47.7 %, respectively; a lower temperature at 160 °C both resulted in a low furfuryl alcohol conversion while a higher temperature at 200 °C both led to a noticeable increase of unidentified by-products. Only one difference that might be noticed is that the transformation of furfuryl alcohol in absence of H₂ (Fig. 2(b)) stopped increasing when the temperature was higher than 180 °C, while it kept increasing in the case of 1.0 MPa of H_2 (Figure 2(a)). This might be ascribed to the lower thermostability of Raney Ni in pure NH₃ atmosphere.

The reaction kinetics at 180 °C in presence of 1.0 MPa and 0 MPa of H_2 was further conducted in order to optimize the reaction time. As seen from Fig. 3(a), the yield of tetrahydrofurfurylamine kept increasing linearly and reached maximum (94.0%) at 48 h with selectivity of 95.7%. Further extension of reaction time resulted in other unwanted by-products and a decline of tetrahydrofurfurylamine selectivity. While for furfurylamine synthesis (Fig. 3(b)), the transformation rate relatively slowed down during the late of the reaction and only 78.8% of yield was obtained. Further extending the reaction time may obtain higher yield of furfurylamine. However, the reaction rate becomes rather slow,



Fig. 2 Effects on temperature on reductive amination of furfuryl alcohol for synthesis of (a) tetrahydrofurfurylamine in 1.0 MPa of H_2 and (b) furfurylamine in absence of H_2 . Reaction conditions: partial pressure of NH_3 , 0.35 MPa; FA, 0.5 g; THF, 15 ml; Raney Ni, 0.25 g; reaction time, 24 h; stirring speed, 1200 rpm.

Abbreviation: FAM, furfurylamine; THFA, tetrahydrofurfuryl alcohol; THFAM, tetrahydrofurfurylamine

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Fig. 3 Reaction kinetics of reductive amination of furfuryl alcohol for synthesis of (a) tetrahydrofurfurylamine in 1.0 MPa of H_2 and (b) furfurylamine in absence of H_2 . Reaction conditions: partial pressure of NH_3 , 0.35 MPa; FA, 0.5 g; THF, 15 ml; Raney Ni, 0.25 g; reaction temperature, 180 °C; stirring speed, 1200 rpm.

indicating that the activity of Raney Ni may be getting poorer along the reaction time without protection under H₂. Based on the aforementioned amination mechanism in scheme 1, the reductive amination of furfuryl alcohol undergoes dehydrogenation to furfural, imidization to imine, and finally hydrogenation to furfurylamine. In order to determine which one is the rate-limiting step, the reductive amination of furfural was also conducted, which showed that furfural could be completely converted even at the milder condition of 0.1 MPa H₂ and 80 °C in 2 h (entry 1 in Table S2), with a furfurylamine yield of 62.6%. In contrast, much harsher experimental conditions (180 °C and 30 h) were needed to reach the similar vield of furfurylamine if furfurylalcohol was used as the substrate (Figure 3(b)). The corresponding initial rate could be approximately evaluated as 17.4×10⁻² mol·L⁻¹·h⁻¹ and 1.4×10⁻² mol·L⁻¹·h⁻¹, respectively. This indicates that reaction rates from furfuryl alcohol to furfurylamine is more than ten times lower than that from furfural to furfurylamine, without regarding the much harsher reaction conditions the former has been used. In another word, dehydrogenation of furfuryl alcohol is the slowest reaction step that controls the whole reductive amination process, which is also in agreement with other publications17, 24.

When amination of furfuryl alcohol was conducted under 1.0 MPa of H_2 , two intermediates, i.e., tetrahydrofurfuryl alcohol and furfurylamine were observed to peak at 6 h and 36 h,



respectively. This demonstrates that another synthesis path started by saturation of furan ring was switched on to finally reach tetrahydrofurfurylamine. Since tetrafurfuryl alcohol accumulated during the amination process, it is reasonable to consider that the dehydrogenation of tetrafurfuryl alcohol is also the rate limiting step in the "furan-ring saturation path". Furfurylamine cannot be the terminal product in the presence of H_2 , as it will be saturated with H_2 and gradually forms tetrahydrofurfurylamine after 36 h of reaction. The possible overall reaction pathway for amination of furfuryl alcohol is therefore rationalized in Scheme 2.

It should be noted that the dehydrogenation intermediates furfural and tetrafurfural were not detectable in either H₂ presence or absence case. This is mainly because that the two intermediates are quite reactive to condense with NH₃ and then be hydrogenated to the corresponding amines, which was also reported elsewhere.^{17, 71} However, when we replaced NH₃ with cyclohexene as the H₂ acceptor (here NH₃ forms imine with aldehyde as the H₂ acceptor) in the dehydrogenation of furfuryl alcohol, the intermediate furfural with yield of 7.6% was clearly observed (entry 2 in Table S3). In contrast, if neither NH₃ nor any other H₂ acceptor was added, furfuryl alcohol remain unchanged during the reaction and no furfural was detected (entry 3 in Table S3). From the above experiments, we concluded that the aldehyde intermediates may be detected if suitable H₂ acceptor was selected, and the "borrowing H₂" pathway will not occur if no any H₂ acceptor exists.

The reusability of Raney Ni was investigated for both synthesis of furfurylamine and tetrahydrofurfurylamine. After reaction, the catalyst was centrifugated, washed with THF, and returned to the reactor for reuse at the previous reaction conditions. As shown in Table 3, Raney Ni can maintain its activity for synthesis of tetrahydrofurfurylamine synthesis at 1.0 MPa of H₂, which could be reused at least five times without obvious deactivation. However, for synthesis of furfurylamine in absence of H₂, the conversion of furfuryl alcohol dropped sharply from 78.5% at the first run to 53.4% at the second run, showing the poor reusability of Raney Ni. We observed this reused Raney Ni lost magnetism while the Raney Ni reused in presence of H₂ did not (Figure S2). The followed XRD (Figure S3) and XPS (Figure S4) characterization also showed that a new crystalline phase of Ni₃N was formed in the first-reused Raney Ni catalyst for furfurylamine synthesis, which is in agreement with the prevous reports¹⁹⁻²².

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Table 3 Reusability test of Raney Ni for reductive amination of furfuryl alcohol

Entry	Times	H ₂ (MPa)	NH ₃ (MPa)	Conversion (%)	Yield (%)				
					NH ₂	O OH	O NH2	Other by- products	
1	1	1	0.35	66.2	8.8	7.3	45.1	5.0	
2	2	1	0.35	67.6	10.0	7.6	46.7	3.3	
3	3	1	0.35	64.5	10.1	4.8	43.6	6.0	
4	4	1	0.35	64.4	9.7	7.6	43.5	3.6	
5	5	1	0.35	63.9	9.2	8.0	44.1	2.6	
6	1 ^a	-	0.35	78.5	76.5	1.0	-	1.0	
7	2 ^a	-	0.35	53.4	52.7	-	-	0.7	
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Reaction conditions: FA, 0.5 g; THF, 15 ml; Raney Ni, 0.25 g; reaction temperature, 180 °C; reaction time, 24 h; stirring speed, 1200 rpm. Reaction time 48 h

Conclusions

In conclusion, Raney Ni proved to be an effective heterogeneous catalyst for switchable reductive amination of furfuryl alcohol to tetrahydrofurfurylamine and furfurylamine with NH₃ by simply adding or not adding 1.0 MPa of H₂ into the reaction bulk. Its unique performance in reductive amination can be attributed to the proper adsorption ability of NH₃, H₂ and furfuryl alcohol. After optimization, we finally obtained 94.0% yield of tetrahydrofurfurylamine and 78.8% yield of furfurylamine with high selectivity. For synthesis of tetrahydrofurfurylamine in presence of 1 MPa of H₂, Raney Ni catalyzed not only the amination of hydroxyl but also the hydrogenation of the furan ring, and it can be reused at least five times without obvious deactivation. While for furfurylamine synthesis in absence of H₂, Raney Ni catalyzed amination of furfuryl alcohol via the "borrowing hydrogen" mechanism. The activity of Raney Ni dropped sharply. XRD and XPS characterization shows that the formation of a new Ni₃N contributes to the deactivation.

Experimental

Chemicals

Furfuryl alcohol and Raney Ni catalyst were purchased from Aladdin Industrial Co. Ltd, and used as received. Ammonia, hydrogen and nitrogen gases were provided by Hangzhou Jingong Special Gas Co. Ltd, with purity larger than 99.99%. Other chemicals were analytical reagents and purchased from Sino-pharm Reagent Co. Ltd.

Typical procedures of catalytic reactions

Typically, 15 mL of THF (solvent), 0.5 g furfuryl alcohol, and 0.25 g Raney nickel were introduced into a 25 mL stainless steel autoclave. After sealed and purged by N_2 (5 times), ammonia was introduced up to 0.35 MPa with continuous stirring at 1200 rpm. Then, 1.0 MPa of hydrogen was introduced after filling the autoclave with ammonia. Afterward, the reactor was heated to 180 °C and retained for 24 h.

Analytical method

After reaction, the autoclave was cooled down to room temperature and sampled for GC analysis by using an Agilent 7890 gas chromatograph equipped with an HP-5 capillary column ($30.0 \text{ m} \times$

0.32 mm \times 0.25 µm) and a flame ionization detector (FID). The initial column temperature was 80 °C and held for 10 minutes. Then the temperature was ramped at 10 °C/min until it reached 250 °C. Both the injector temperature and the detector temperature were set at 260 °C.

Structure of the reaction components were further identified by GC/MS with an Agilent 6890 gas chromatography system coupled to a mass spectrometer equipped with an Agilent 5973 quadrupole mass analyzer.

The conversions and yields were simply calculated by peak areas of the substrate, target product and the known by-products, which was validated by the carbon balance analysis (carbon recovery>94.8%, see the Supplementary Information) using *n*-dodecane as an internal standard. The typical GC image with by-products and MS spectrums for the known substances were shown in Figure S1.

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Switchable reductive amination of furfuryl alcohol to tetrahydrofurfurylamine and furfurylamine was realized by adding/not adding H₂ over Raney Ni catalyst