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A comprehensive study on the reductive amination of 5-hydroxymethylfurfural into 2,5-bisaminomethylfuran over Raney Ni through DFT calculations

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Abstract: Reductive amination of furfuryl alcohol, furfural and 5-hydroxymethylfurfural (5-HMF) were carried out on various metal catalysts. Over Raney Ni catalyst, we obtained the highest furfurylamine yields of 81.8% and 94.0% from furfuryl alcohol in absence and presence of H₂, respectively. While furfural was used as the substrate, 100% yield of furfurylamine could be achieved over Raney Ni under rather moderate conditions. Although 5-HMF was completely converted over all catalysts used, the highest yield of 2,5-bisaminomethylfuran (60.7%) was obtained over Raney Ni at 160 °C in 12 h. The DFT calculations on the adsorption behavior of NH₃ and H₂ on different metal surfaces showed that the difference of the adsorption energy between NH₃ and H₂ on Ni is lower than those of other metals, indicating that less metal active sites on Ni surface is occupied by NH₃, which leaves more active sites for dehydrogenation/hydrogenation reactions and in the end promotes the reductive amination reactions.

Introduction

Amine plays an important role in the bulk and fine chemical industries for the production of polymers, dyes, pharmaceuticals, agrochemicals, surfactants and biologically active compounds.^[1] Generally, primary amines can be synthesized by reductive amination of either corresponding carbonyl compounds or alcohols. However, most of the substrate molecules are derived from traditional fossil resources, which are growing shortage and brought a lot of environmental problems.^[2] The aldehydes/ketones and alcohols derived from biorefinery processes, such as furfural, furfuryl alcohol and 5-hydroxymethylfurfural,^[3] may therefore be alternative as starting materials for the production of primary amines.

At present, the transformation of biomass-derived molecules into valuable primary amines is still in its infancy. However, great

research efforts have been devoted to the production of primary amines from the traditional fossil resource-derived carbonyl and alcohol compounds. In general, the reductive amination of C–OH and C=O compounds with ammonia can be catalyzed by metal complex-based homogeneous catalysts, such as Ru- and Ir-based complex,^[4] solid acid catalysts, such as zeolites, phosphates, and oxides,^[5] and metal hydrogenation catalysts, such as Pt, Ir, Ru, Os, Cu, Co and Ni.^[6] It is widely accepted that metal catalysts activate the C–OH by three consecutive steps:^[7] (1) dehydrogenation of the alcohol to form corresponding carbonyl intermediate over a metal catalyst; (2) condensation of the intermediate with ammonia and followed by elimination of water to form an imine over an acid or base catalyst although it can also occur without a catalyst,^[8] and (3) hydrogenation of the imine to produce the final primary amine catalyzed by the aforementioned metal catalyst. Our recent work as well as other reports^[8–9] suggest that the first step, i.e., dehydrogenation of C–OH to the corresponding C=O is the rate-controlling step. Since the reductive amination of C=O only contains the last two steps, it is expectable to be quite easier than that of C–OH.

In recent years, some effective heterogeneous catalyst systems have been reported for reductive amination of biomass-derived C=O compounds. For example, Nishimura et al.^[10] used poly (N-vinyl-2-pyrrolidone)-capped ruthenium-supported hydroxyapatite (Ru-PVP/HAP) as a catalyst to prepare furfurylamine from reductive amination of furfural, with a 60% yield of furfurylamine in 25 wt% aqueous ammonia under 0.4 MPa of H₂. Chatterjee et al.^[11] employed Rh/Al₂O₃ as the catalyst for the same reaction at 80 °C, 2.0 MPa of H₂ and with a furfural/ammonia molar ratio of 0.03, which obtained a yield of 92% of furfurylamine. Liang et al.^[3a] used Ru/ZrO₂ as the catalyst in the reductive amination of glycolaldehyde. The yield of ethanolamine reached 94% at 75 °C, 3 MPa of H₂, and in the presence of 25 wt% aqueous ammonia. However, for the reductive amination of biomass-derived alcohols, the reactions became much more difficult, and only few homogeneous noble metal complex catalysts showed acceptable selectivities under harsh reaction conditions such as higher temperature or longer reaction time. For example, Imm et al.^[4c] reported the synthesis of furfurylamine from furfuryl alcohol using [Ru₃(CO)₁₂]CataCxiuPCy as the catalyst with a yield of 71% at 170 °C in 20 h. Pinggen et al.^[12] had developed a [Ru₃(CO)₁₂]/A-iPr-PNP complex catalyst for the amination of the biomass-derived isomannide, and obtained the corresponding diamines with a yield of 96.0% at 170 °C in 21 h. For the substrates containing both C–OH and C=O functional groups, for example, 5-hydroxymethylfurfural, the reductive amination process became even more complex. One strategy reported from Komanoya et al.^[13] suggested that 5-HMF was firstly converted into 5-hydroxymethylfurfurylamine (HMFA) over Ru/Nb₂O₅ catalyst and then converted into 2,5-furandimethylamine over

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another homogenous complex of [Ru(CO)ClH(PPh₃)₃]. Wang et al.^[14] first transformed the hydroxymethyl group into carboxamide group with CH₃CN through Ritter reaction under strong acid atmosphere, followed by another two-step reductive amination to transform to amide and aldehyde groups into the final primary amine with a yield of only 45.7%. Obviously, the method is rather tedious and not green as more chemicals should be used to reach the goal. Very recently, Li et al.^[15] have developed an ammoxidation process to synthesize 2,5-furandicarboxamide from HMF over metal-cation-doped crytomelanes, through which –OH (–CHO) was consecutively oxidized into –CHO, –CN and –C(=O)NH₂ groups. This might be an another pathway to obtain the targeted 2,5-bisaminomethylfuran as –CN or –C(=O)NH₂ groups can be very easily reduced to primary amines, provided the tedious alternative oxidation-reduction process is tolerable. As a summary, to develop an efficient, cheap and reusable heterogeneous catalytic system for transformation of –C=O, especially –OH into primary amines is extremely urgent and deserves much concentration. Ni-based catalysts are cheap and efficient, which is employed in the reductive amination reaction diffusely. Shimizu et al.^[7b] applied 2-Octanol as substrate to prepare the 2-Octylamine under the Ni/θ-Al₂O₃ catalysts, obtaining 88% yield. Besides, Cho et al.^[16] synthesized monoisopropylamine from 2-propanol with Ni/η-Al₂O₃ and 59.9% yield was achieved. Le et al.^[17], for the first time, achieved the direct reductive amination of 2,5-diformylfuran to 2,5-bis(aminomethyl)furan catalyzed by Nickel-Raney type catalysts with a yield of 42.6%.

In our previous work, Raney Ni was successfully employed in the switchable reductive amination of furfuryl alcohol to tetrahydrofurfurylamine and furfurylamine, achieving 94.0% and 78.8% yield respectively.^[9a] Very recently, Pinggen et al.^[18] obtained 2,5-bisaminomethylfuran yield of more than 90%, in which an expensive and structure-complicated homogenous Ru-based catalyst was used. Herein, biomass-based alcohols and aldehydes compounds, *i.e.* furfuryl alcohol^[9a], furfural and 5-hydroxymethylfurfural containing C=O and C–OH functional groups, were employed as the substrates for the synthesis of primary amines through reductive amination process. In addition, the adsorption energy of NH₃ and H₂ on different metal surfaces was calculated through Density Functional Theory (DFT) calculations in order to make deeper insights into the effects of metal type on the selectivity of primary amines.




Results and Discussion

Reductive amination of furfuryl alcohol over various metal catalysts

We first conducted the reductive amination of furfuryl alcohol in NH₃ and H₂ atmosphere over the commercial noble metal Pd/AC and base metals of Raney Co and Ni as shown in Table 1. According to the “borrowing hydrogen” mechanism,^[4c,19] hydrogen is not stoichiometrically needed^[20] as it can be “borrowed” from the dehydrogenation of alcohol and be returned for the hydrogenation of the imine into the target amine.

Unfortunately, Pd/AC was almost inactive in absence of H₂ (entry 1), indicating that the dehydrogenation reaction of furfuryl alcohol did not occur. Changing hydrogen pressure to 1 MPa still had no contribution to the formation of amino products but only promoted the saturation of the furan ring with a yield of 11.3% (entry 2). These results are quite unusual since noble metals such as Pd or Pt are always quite active for hydrogenation and dehydrogenation reactions. In fact, when we removed NH₃ from the reaction bulk and decreased the amount of Pd/AC (entry 3), the hydrogenation of furan ring in furfuryl alcohol was 100% saturated. We therefore consider that there have strong interactions between Pd surface and NH₃ molecules that block the adsorption/desorption of H₂ on Pd surface which is necessary for the hydrogenation and dehydrogenation reactions. When Raney Co was used as the catalyst, trace amount of amino product (0.99% yield of tetrahydrofurfurylamine) was obtained (entry 5) although it was also inactive in absence of H₂ (entry 4), indicating dehydrogenation of furfuryl alcohol could occur over

Table 1. Reductive amination of FA with different heterogeneous metal catalysts.

Entry	Cat.	H ₂ (MPa)	Conv. (%)	Yield (Sel.) (%)			
							Others
1	Pd/C	0	0	-	-	-	-
2	Pd/C	1	12.4	-	11.3 (91.1)	-	1.10 (8.9)
3 ^[a]	Pd/C	1	100	-	100	-	-
4	Raney Co	0	0	-	-	-	-
5	Raney Co	1	18.4	-	16.4 (89.1)	0.99 (5.4)	0.99 (5.4)
6	Raney Ni	0	24.0	22.2 (92.5)	1.8 (7.5)	-	-
7	Raney Ni	1	27.5	-	15.5 (56.4)	11.0 (40.0)	0.99 (3.6)
8 ^[b]	Raney Ni	1	13.1	-	12.6 (96.2)	-	0.5 (3.8)
9 ^[c]	Raney Ni	1	55.1	3.4 (6.2)	12.6 (22.9)	34.2 (62.1)	4.9 (8.9)
10 ^[d]	Raney Ni	0	86.6	81.8	1.7	-	3.1
11 ^[e]	Raney Ni	1	98.2	-	1.1	94.0	3.1





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] NH₃ pressure changed to 0 MPa, amount of Pd/AC changed to 0.05 g, and reaction time changed to 4 h. [b] Raney Ni amount changed to 0.05 g. [c] Raney Ni amount changed to 0.5 g. [d] temperature and reaction time changed to 180 °C and 60 h, respectively; [e] temperature and reaction time changed to 180 °C and 48 h, respectively.

Raney Co. In contrast, Raney Ni exhibited remarkably dehydrogenation activity in both absence (22.2% yield of furfuryl amine, entry 6) and presence (11.0% yield of tetrahydrofurfurylamine, entry 7) of hydrogen. These results suggest that Ni is the best metal to harmonize NH₃ and H₂ for the amination and dehydrogenation/hydrogenation reactions. By further optimization of catalyst loading, reaction temperature and time, we finally obtained the highest yield of furfurylamine (81.8%) in absence of H₂, at 180 °C in 60 h, and the highest yield of tetrahydrofurfurylamine (94.0%) in presence of H₂ at 180 °C in 48 h.

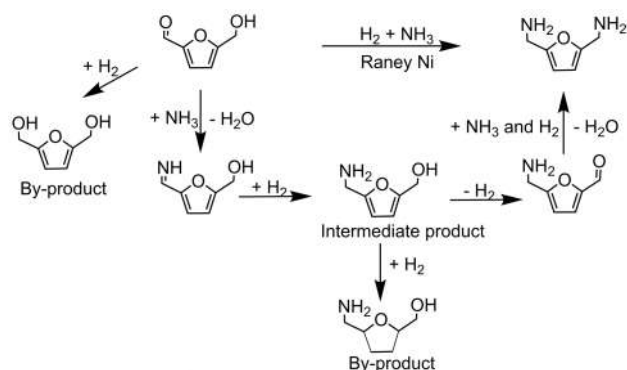
Reductive amination of furfural over Raney Ni catalyst

As aforementioned, the reductive amination of furfural should be much easier than that of furfuryl alcohol. We simply selected Raney Ni for that purpose (Table 2). As expected, we obtained 62.6% yield of furfurylamine under rather moderate conditions: only 0.1 MPa of H₂, 80 °C and 2 h (entry 12). Further increasing H₂ pressure from 0.5 MPa to 1.0 MPa resulted in 100% yield of furfurylamine (entries 13 and 14). However, an even higher H₂ pressure to 2.0 MPa would lead to the over hydrogenation of furfural to furfuryl alcohol and decreased the yield of furfurylamine (entry 15). Bearing in mind our terminal target is the reductive amination of 5-HMF which contains both hydroxyl and carbonyl function groups, we also increased the reaction temperature to 180 °C, the most favorable temperature for reductive amination of furfuryl alcohol in order to harmonize the two reductive amination reactions at a single temperature (entries 16-18). Results showed that a high 99.2% yield of furfurylamine could be achieved at lower H₂ pressure of 0.5 MPa while even higher H₂ pressure in the range of 1.0 to 2.0 MPa led to deep hydrogenation of furan and large amount of tetrahydrofurfurylamine was formed.

Table 2. Reductive amination of furfural into furfurylamine over Raney Ni.

Entry	H ₂ (MPa)	Conv. (%)	Yield (Sel.) (%)				
							Others
12	0.1	100	62.6	-	-	-	37.4
13	0.5	100	100	-	-	-	-
14	1.0	100	100	-	-	-	-
15	2.0	100	80.7	19.3	-	-	-
16 ^[f]	0.5	100	99.2	-	-	-	0.8
17 ^[f]	1.0	100	53.8	-	-	40.7	5.5
18 ^[f]	2.0	100	-	-	5.1	91.0	3.9

Reaction conditions: Furfural, 0.5 g; THF, 15 mL; Raney Ni, 0.25 g; NH₃ pressure, 0.35 MPa; temperature, 80 °C; reaction time, 2 h; stirring speed, 1200 rpm. [f] temperature and reaction time changed to 180 °C and 12 h, respectively.



Scheme 1. The plausible reaction pathway for reductive amination of 5-HMF into BAMF

Reductive amination of 5-HMF over different heterogeneous metal catalysts

Basically, 5-HMF can be viewed as the summation of furfuryl alcohol and furfural in the reductive amination reaction as it contains two reactive function groups from the latter two compounds. As shown in Table 3, we simply checked the effect of reaction temperature on the reductive amination of 5-HMF under the reaction conditions similar to those most favorable for reductive amination of furfuryl alcohol, a highest yield of 2,5-bisaminomethylfuran (2,5-BAMF) (60.7%) was achieved over Raney Ni in 12 h (entry 19). Compared with that of furfuryl alcohol, the reductive amination of 5-HMF seems easier as it needs lower temperature (160 °C vs. 180 °C in entry 11) and shorter reaction time (12 h vs. 48 h in entry 11) to reach the highest yield although the yield to amination product is lower due to the more complex structure of 5-HMF. We contribute it to the p-π conjugation effect between the furan ring and the C=O in 5-HMF which benefits to the removal of hydrogen from the hydroxymethyl group. However, 5-HMF is more likely to polymerize due to the existence of the C=O, which is also a key factor of the unsatisfactory selectivity^[17]. Other catalysts, especially the noble catalysts such as Pd/AC, Pt/AC and Ru/AC showed very poor amination (or dehydrogenation) activity which is similar to reductive amination of furfuryl alcohol, also implying that the stronger adsorption of NH₃ than H₂ on the noble metal's surface may decrease the reductive amination activity. By considering the sequence of amination, hydrogenation and dehydrogenation, and the by-products we have detected, we proposed a plausible reaction pathway for the reductive amination of 5-HMF (Scheme 1). In the process, 5-HMF undergoes the imidization of C=O into C=NH, hydrogenation of C=NH into C-NH₂, dehydrogenation of C-OH into C=O, and the repeating reductive amination of the formed C=O into target BAMF. Besides, two by-products, i.e., 5-hydroxymethyltetrahydrofuranamine and 2,5-furandimethanol are generated by the over-hydrogenation of furan ring and -C=O, respectively.

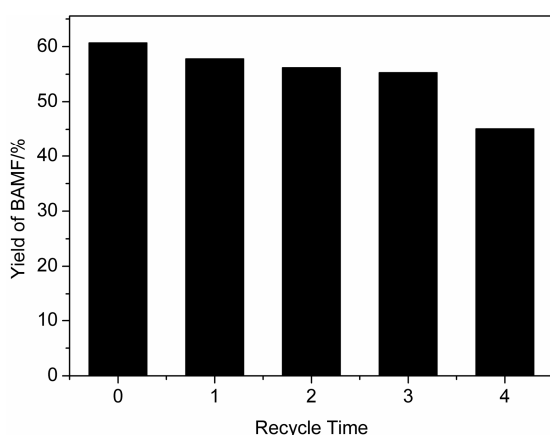


Figure 1. Recycle experiments of Raney Ni catalyst for 5-HMF into BAMF. Reaction conditions: 5-HMF, 0.5 g; THF, 15 mL; catalyst, 0.25 g; NH₃ pressure, 0.35 MPa; H₂ pressure, 1.0 MPa; temperature, 160 °C; reaction time, 12 h; stirring speed, 1000 rpm.

Table 3. Amination of 5-HMF into BAMF over different heterogeneous metal catalysts.

Entry	Cat.	Conv. (%)	Yield (Sel.) (%)				
							Others
19	Raney Ni	100	60.7	8.0	2.3	2.1	26.9
20	Raney Co	100	14.8	25.4	-	-	59.8
21	Pd/C	100	1.5	85.4	-	-	13.1
22	Pt/C	100	0.8	85.1	-	-	14.1
23	Ru/C	100	0.6	83.5	-	-	15.9

Reaction condition: 5-HMF, 0.5 g; THF, 15 ml; catalyst, 0.25 g; NH₃ pressure, 0.35 MPa; H₂ pressure, 1.0 MPa; temperature, 160 °C; stirring speed, 1000 rpm; reaction time, 12 h.

For concise, only the recyclability of Raney Ni for reductive amination of 5-HMF was investigated. As shown in Figure 1., the yield of BAMF shows slight decrease after the first three recycling and declines remarkably at the fourth time. The instability of the catalyst may be ascribed to the generation of Ni₃N during repeated use of our catalyst, which has already been disclosed by our previous study.^[9a]

DFT calculations

In view of the activity difference of different heterogeneous metal hydrogenation/dehydrogenation catalysts in reductive amination reactions of alcohol and furfural, we have carried out DFT calculations on the adsorption behavior of NH₃ and H atoms on different metal surfaces.

Adsorption of hydrogen atom on metal surfaces

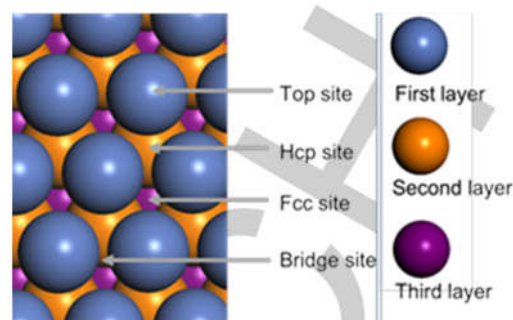


Figure 2. High symmetry adsorption sites on metal (111) surface

There are a variety of stable adsorption sites on metal surfaces, i.e., top, bridge, hollow, fcc and hcp (Figure 2.). It is generally believed that the most stable site for hydrogen atom adsorption is fcc site. According to the reports^[21] and our XRD data, the most stable and predominant surfaces of fcc and hcp cells of metal atoms were (111) and (0001), respectively. We therefore first determine the most stable adsorption sites for hydrogen atoms by calculating the adsorption energy of hydrogen atoms at different adsorption sites on the Ni (111).

Table 4. Adsorption energies and structural data for H atom adsorbed on different site of Ni (111)

H adsorption site	$d_{\text{H-Ni}}$ (nm)	Adsorption energy (eV)
fcc site	0.1705	0.6182
hcp site	0.1714	0.6027

As shown in Table 4, the maximum adsorption energy of hydrogen atom adsorbed on the fcc site of Ni (111) plane is 0.6182 eV, indicating that the hydrogen atom is more stably adsorbed on the fcc site than on the hcp site with a adsorption energy of 0.6027 eV, which is consistent with the reported results in the literature.^[21a] We therefore chose the fcc sites of the rest metal atom surfaces for adsorption of the hydrogen atom. The (111) surfaces of Rh, Pt, Pd, Co and Ni and (0001) surface of Ru were investigated. As shown in Table 5, the

Table 5. Adsorption energies and structural data for H atom adsorbed on different site of Ni (111)

Metal	Ru (0001)	Co (111)	Ni (111)	Rh (111)	Pd (111)	Pt (111)
Adsorption energy (eV)	0.6940	0.6336	0.6182	0.5468	0.4876	0.4070

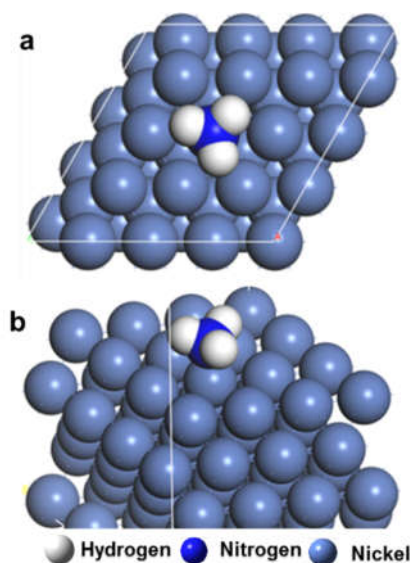


Figure 3. Stable geometric configurations of NH_3 molecule adsorbed on metal surface (a top view, b side view)

adsorption energies of hydrogen atoms adsorbed on different metal surfaces are in the order of $\text{Ru} > \text{Ni} > \text{Rh} > \text{Pd} > \text{Pt}$, which is in agreement with the calculations from Watson et al.^[21a] who obtained the adsorption energies in the order of $\text{Ni} > \text{Pd} > \text{Pt}$, and almost in agreement with the calculations from Ferrin et al.^[21b] except of the order of Rh and Pd. The variation may result from the different selection of density functions in the calculations.

Adsorption of ammonia molecules on metal surfaces

For NH_3 , we also first searched its most stable adsorption sites on the metal surface. Results showed wherever we initiate NH_3 at the bridge, fcc or hcp site of Ni (111) surface, NH_3 will move to the top site of the metal surface during the structure optimization process. As shown in Figure 3., in the final state, the N atom of NH_3 is connected to a metal atom, and the hydrogen atoms in the ammonia molecule are pointed away from the metal surface. This confirmed that the top position is the most stable site for adsorption of NH_3 , which is consistent with the report^[22] and the top site is therefore chosen for calculation of the adsorption energies of NH_3 on the surfaces of other metals. As shown in Table 6, the adsorption energies are in the descending order of $\text{Rh} > \text{Pt} > \text{Ru} > \text{Co} > \text{Pd} > \text{Ni}$.

As aforementioned, the reductive amination of C–OH contains dehydrogenation of the alcohol, imidization of the C=O, and hydrogenation of the imine. Basically, NH_3 is indispensable for the second step of imidization. However, it brings side effects on both the dehydrogenation and the hydrogenation steps due to its stronger interactions than H_2 on the metal surface which decreases the active sites for hydrogen adsorption and dissociation. If the adsorption energy of NH_3 on the metal surface is intensive enough, the metal might lose sites for adsorption of H_2 and therefore deactivate for the dehydrogenation reaction. This should be the reason that Pd/AC and Raney Co are almost inactive for the reductive amination of

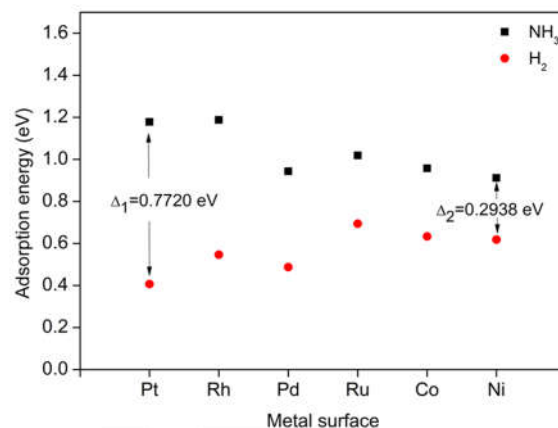


Figure 4. Reported adsorption energy of H_2 and NH_3 on different facets of the metal active sites evaluated on the basis of DFT calculations

Table 6. Adsorption energies for NH_3 molecule adsorbed on different metal surface.

Metal	Ru (0001)	Co (111)	Ni (111)	Rh (111)	Pd (111)	Pt (111)
Adsorption energy (eV)	1.019	0.9578	0.9120	1.188	0.9436	1.179

C–OH, as proved by Figure. 4 in which larger adsorption energy differences for NH_3 and H_2 exist in these two metals. Similar inactivation occurred in other noble metals such as Pt, Rh and Ru in our previous studies^[9a], as they also revealed larger adsorption energy differences between NH_3 and H_2 (Figure 4.). Among all the calculated metals, Ni revealed the lowest adsorption energy differences of 0.2938 eV, which means that excessive adsorption of NH_3 can be avoided and the competitive adsorption of NH_3 to H_2 is reduced. That is to say, Ni could provide the largest portion of active sites for adsorption/desorption of H_2 . As a consequence, furfuryl alcohol and 5-HMF could be dehydrogenated effectively on Ni surface and achieved satisfactory yields of the corresponding amino products.

Decreasing partial pressure of NH_3 seems a feasible strategy to reduce the impact of NH_3 on the adsorption/desorption of H_2 . However, it will inevitably bring side effects of various unwanted by-products such as secondary and tertiary amines being generated.^[23] This is the reason that we and other research groups always used 0.35 MPa of NH_3 , the highest pressure of NH_3 that a gas cylinder can provide. As reported,^[7b] due to the co-existence of acidic and basic sites, $\gamma\text{-Al}_2\text{O}_3$ was optimized as the best support for reductive amination of alcohols, which was also demonstrated by our experimental results. The mechanism is not clear so far. It is therefore possibly interpreted that the basic sites might inhibit the approaching of NH_3 on the metal surface and keep sufficient active sites for dehydrogenation further, while the acid sites contribute to the H atom transfer, which is also in favor of dehydrogenation reaction, the rate-controlling step in the reductive amination of alcohols. Moreover,

our experiments showed that lower partial pressure of NH_3 has greatly prolonged the reaction time for reductive amination of 5-HMF (data not shown), indicating that the aforementioned three steps for reductive amination of C–OH does not simply occurred in sequence, i.e. at least the followed imidization step that forms an imine as a hydrogen acceptor may affect the first dehydrogenation step. This has already been proved in our previous report that dehydrogenation of furfuryl alcohol did not occur in presence of H_2 only if a hydrogen acceptor such as cyclohexene was introduced^[9a].

Adjusting partial pressure of H_2 is also a key factor for improving the reductive amination of C–OH compound. Although H_2 is not necessary for the reaction due to the “borrowing hydrogen” mechanism,^[4c,19] data from Table 1 has shown that the reaction rate for reductive amination of furfuryl alcohol in absence of H_2 is much lower than that in presence of H_2 . This suggests that the exogenous H_2 is beneficial to the dehydrogenation of alcohol, most probably because it can compete with NH_3 on the active sites. Based on our understanding, gaseous H_2 molecule competes with gaseous ammonia in adsorbing on the active sites of Ni surface. The active sites occupied by H atom are determined not only by the dynamic equilibrium between gaseous H_2 and surface H atom, but also by the competitive adsorption equilibrium between surface H_2 and NH_3 . A suitable amount of exogenous hydrogen may be beneficial to the reductive amination of 5-HMF. On one hand, if the exogenous H_2 is too little, the active sites occupied by H_2 will be insufficient to exhibit satisfactory catalytic activity for dehydrogenation, which is the rate-controlling step in the reductive amination reaction of 5-HMF. On the other hand, very high amount of exogenous H_2 would strongly inhibit the dehydrogenation of the –OH, over-hydrogenate the furan ring and C=O and is also unfavorable for the reductive amination of either furfuryl alcohol or 5-HMF.

Conclusions

The reductive animation of furfuryl alcohol, furfural and 5-hydroxymethylfurfural was studied over Raney Ni, Raney Co and Pd/C, Ru/C and Pt/C catalysts. Among them, Raney Ni was proved to be the most favorable catalyst for that purpose. For furfuryl alcohol, the highest tetrahydrofurfurylamine yields of 94% and 81.8% were achieved in presence and absence of H_2 , respectively. For furfural, 100% yield of furfurylamine can be achieved in 2 hours under the condition of 0.35 MPa of NH_3 , 1.0 MPa of H_2 and 80 °C. 5-HMF can produce a 60.7% yield of 2,5-Furandimethylamine in 12 hours under the condition of 0.35 MPa of NH_3 , 1.0 MPa of H_2 , and 160 °C. The DFT calculation shows that Ni reveals the smallest absorption energy difference between NH_3 and H_2 . As a consequence, during the competitive adsorption on the Ni surface, less metal active sites are occupied by NH_3 , which in turn leaves more active sites for the dehydrogenation of the alcohols and hydrogenation of imines and in the end improve the efficiency of reactive amination reactions.

Experimental Section

Materials

Furfuryl alcohol, furfural and 5-hydroxymethylfurfural 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 higher than 99.99%. The commercially available metal catalysts were purchased from the Baoji Ruike Pharmaceutical Chemical Co. Ltd. Other chemicals were analytical reagents and purchased from Sinopharm Reagent Co. Ltd..

Typical procedures of catalytic reactions

Typically, 15 mL of THF (solvent), 0.5 g of substrate (furfuryl alcohol, furfural or 5-hydroxymethyl furfural) and 0.25 g of catalyst were introduced into a 25-mL stainless steel autoclave. After sealing and purging by N_2 (5 times), 0.35 MPa of ammonia was introduced into the reaction vessel and was equilibrated at room temperature (ca 25 °C) with continuous stirring at 1200 rpm. Then, 1.0 MPa of hydrogen was added. Afterwards, the reactor was heated to 180 °C and maintained for 24 h.

After reaction, the autoclave was cooled down to room temperature and sampled for GC analysis using an Agilent 7890 gas chromatograph equipped with an HP-5 capillary column (30.0 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 to 250 °C at a rate of 10 °C $\cdot\text{min}^{-1}$. Both the injector temperature and the detector temperature were set at 260 °C. n-Dodecane was used as an internal standard for quantification of the components.

Structure of the reactants 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.

Calculation method

The adsorption energies of NH_3 and H on metal surfaces have been studied to screen the best catalyst for the amination of C–OH and C=O containing compounds. All the calculations were carried out using the DMol3 program package in Materials Studio.^[24] The core treatment was set to DFT semi-core pseudopotentials (DSPP). The exchange-correlation functional of generalized gradient approximation (GGA) which can give better results of the adsorption energy^[25] was based on the PBE functional form proposed by Perdew and Burke^[26] where the spin-polarization was always allowed. A double numerical plus polarization (DNP)^[27] basis set was employed to describe the valence orbitals of all the atoms. Brillouin-zone integrations were performed using $2 \times 2 \times 1$ k-points grid which was generated automatically by the Monkhorst-Pack method^[28]. A Fermi smearing of 0.005 Ha was used to improve the calculation performance. The tolerances of energy, gradient, and displacement convergence were 1×10^{-5} Ha, 2×10^{-3} Ha/Å and 5×10^{-3} Å (1 Ha=27.2114 eV, to be in accordance to the other reports,^[29] we did not convert them to the international units), respectively.

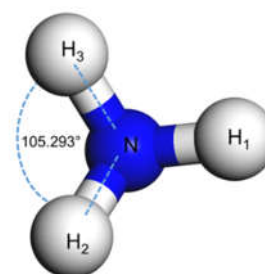


Figure 5. The structure of ammonia molecule

The adsorption energy of the ammonia is calculated by the following equation:

$$\Delta E = -(E_{\text{total}} - E_{\text{metal}(111)} - E_{\text{NH}_3}) \quad (1)$$

The adsorption energy of the hydrogen is calculated by the following equation:

$$\Delta E = -(E_{\text{total}} - E_{\text{metal}(111)} - 0.5E_{\text{H}_2}) \quad (2)$$

E_{total} is the energy of the ammonia or hydrogen on the surface, $E_{\text{metal}(111)}$ is the energy of the bare metal without adsorption of hydrogen or ammonia, E_{NH_3} and E_{H_2} are the energy of ammonia and hydrogen in gaseous state, respectively.

Models

DFT calculations were carried out on Rh, Ru, Pt, Pd, Co and Ni metal surfaces. A hcp (0001) surface was applied to model the flat surface of Ru, while for other metals, fcc (111) surface was applied because these structures are mostly exposed and therefore are the most representative surfaces.^[21] For all the calculations, a 2×2 supercell model including five atomic layers were employed. A 15 Å vacuum layer between the slabs was used to prevent spurious interactions generated by periodic boundary conditions. The three bottom metal layers were fixed and the top two layers were allowed to relax.

The lattice parameter of the optimized cell of Pt, Pd, and Ni were 0.3924 nm, 0.3891 nm and 0.3524 nm, respectively, which agree well with the experimental values of 0.3923 nm, 0.3890 nm and 0.3524 nm, respectively.^[30] The free ammonia and hydrogen molecule were optimized using the same methods. The equilibrium bond lengths of N-H and H-H were 0.1022 nm and 0.0741 nm respectively, while the bonding angle of H-N-H is 105.3° (Figure 5.) which were close to the experimental value (0.1012 nm, 0.0741 nm, 106.7°).^[30] These results indicate that our model is applicable and reliable.

Acknowledgements

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Keywords: Biomass • Furfuryl alcohol • 5-Hydroxymethylfurfural • Raney Ni • Reductive amination

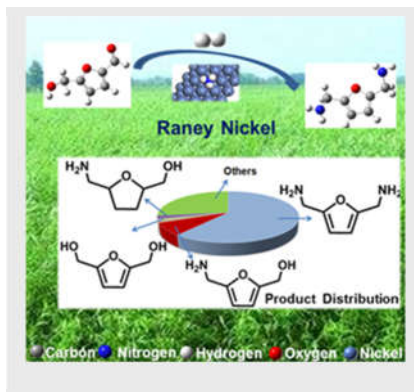
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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

High value-added 2,5-bisaminomethylfuran was one-pot synthesized from 5-HMF over Raney Ni with a yield of 60.7%. DFT calculations were conducted to support our speculation that Ni can harmonize NH_3 and H_2 on its surface most suitably for the reductive amination reactions.



Kuo Zhou, Haiyan Liu, Huimin Shu, Shuwen Xiao, Dechao Guo, Yingxin Liu, and Xiaonian Li, Zuojun Wei*

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A comprehensive study on the reductive amination of 5-hydroxymethylfurfural into 2,5-bisaminomethylfuran over Raney Ni through DFT calculations