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Direct catalytic conversion of furfural to furan-derived amines in the presence of Ru based catalyst

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Abstract: The production of amine intermediates from biomass is capturing increasing attention. Herein we report simple and efficient preparation of 1 furan-derived amines (for instance 1-(furan-2-yl)-4-methylpentan-2-amine) with high yield (up to 95%) from (*E*)-1-(furan-2-yl)-5-methylhex-1-en-3-one. The catalyst used was Ru/C and it was recyclable up to 4th cycle. To further realize cost-efficiency, one-reactor tandem concept was attempted. To this aim direct reaction from furfural was investigated. A high yield (74%) towards 1-(furan-2-yl)-4-methylpentan-2-amine could be achieved starting directly from furfural in the presence of methylisobutyl ketone, NH₃, H₂ and Ru/C catalyst.

Lignocellulosic biomass is the most abundant, and inexpensive source of nonedible biomass that can be used for the synthesis of fuels and chemicals.¹ Using chemo- or biocatalytic processes, a variety of oxygenates can be prepared from lignocellulose based on ethanol, diols, hexitols, furfural, aldehydes/ketones and organic acids among many others.² However, the development of efficient catalytic reactions for the transformation of biomass into valuable nitrogen-containing chemicals is still challenging and starts to be an important goal of research programs.³ In particular, the development of simple and easily accessible catalytic systems to produce amines is an urgent need.⁴ Amines represent a privileged class of compounds with broad interest in chemical industry due to their nucleophilic properties, conferring them high reactivity.⁵⁻⁷ In particular, primary amines constitute valuable fine and bulk chemicals, which serve as versatile feedstocks and key intermediates for the synthesis of advanced chemicals, life science molecules and polymers.^{5,8-10} For example, furfurylamines from biomass-derived furfural can be used in diverse applications, including the preparation of polymers, biologically active compounds and as intermediates for the synthesis of pharmaceuticals such as antiseptic agents, antihypertensives and diuretics.^{11,12}

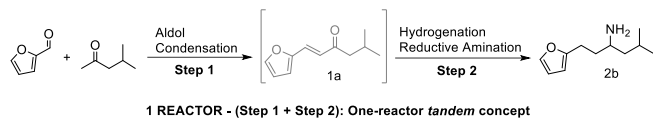
Reductive amination of aldehydes or ketones for preparing primary amines is carried out at industrial level using

heterogeneous catalysts based on supported Cu,¹³ Ni,¹⁴ Pt,¹⁵ Ru,¹⁰ Rh,¹⁶ Pd,¹⁷ due to their easy separation and recyclability, and lack of use of toxic reagents and/or stoichiometric reductants.¹⁸ In particular, reductive amination using NH₃ and H₂ has been explored in the field of Organic Chemistry, giving access to a variety of amines.^{4e,8,15,19} However, reductive amination reactions can suffer from overalkylation and the reduction of the aldehydes/ketones to alcohols, decreasing the selectivity to primary amines.^{8-10,15,20,21} Hence, from an atom-economical and environmental standpoint, there is a need to develop selective and efficient catalysts for producing biobased primary amines, which is the prime task of this investigation.

Furfural, is a cheap furanic derivative (1.0-1.2 €/kg) available in large scale from carbohydrates (>200 kT/year), making it an attractive raw material for the production of biobased chemicals.²² Recently, selective synthesis of biobased amines from furfural has attracted increasing attention.^{9,12,23,24} Here we report the preparation of a furan-derived primary amine [1-(furan-2-yl)-4-methylpentan-2-amine, **2a**] with high selectivity, starting first from the bioderived [(*E*)-1-(furan-2-yl)-5-methylhex-1-en-3-one, **1a**] issued from the aldol condensation reaction of furfural with methyl isobutyl ketone (MIBK), using NH₃ as nitrogen source, H₂ as reducing agent and 5%Ru/C as catalyst. This molecule will find applications such as building-block for polymers, surfactants and solvents. The nature of the ketone used was also investigated. However, a special attention was given to the utilization of MIBK based on its used in the synthesis of furfural from xylose or xylan as an extraction agent. MIBK could be in that case an extraction agent and a reagent. Keeping in mind that the synthesis of furanic amine could be performed in the future from furfural obtained from hemicellulose, we further engineered a one-reactor tandem process by combining the basic Amberlyst-26 (catalyst 1) with 5%Ru/C (catalyst 2) to access the functionalized amine **2a** starting directly from furfural (Scheme 1). This process encompasses two reactions, namely the aldol condensation of furfural with MIBK, and the reductive amination of the furanic

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ketone intermediate with NH_3 and H_2 . This two steps process was also applied to other ketones (2-pentanone and 2-heptanone).



Scheme 1 Reaction pathway for the synthesis of 1-(furan-2-yl)-4-methylpentan-2-amine (**2a**) from furfural.

Different types of carbonyl-conjugated vinylfurans can be selectively synthesized from furfural and ketones over solid basic catalysts.²⁵⁻²⁷ Initially, (*E*)-1-(furan-2-yl)-5-methylhex-1-en-3-one (**1a**) was selected as model reagent. In 2015, $\text{Ru}/\text{Al}_2\text{O}_3$ was reported as an active and selective catalyst for the reductive amination of aldehydes/ketones with NH_3 and H_2 to primary amines.²⁸ Up to 97% yield of 2-nonylamine was achieved in the reductive amination of 2-nonanone after 10 h, whereas 75% yield of furfurylamine was obtained starting from furfural after 2 h reaction. Based on these results, four Ru based catalysts were investigated. Ru/CeO_2 and $\text{Ru}/\text{H-BEA}$ (5 wt% Ru) were prepared by incipient wetness impregnation using a precursor solution of aqueous RuCl_3 , while Ru/C and $\text{Ru}/\text{Al}_2\text{O}_3$ (5 wt% Ru) were obtained commercially. All the catalysts were pretreated under a H_2/Ar flow at 200 °C before use. This temperature was chosen according to the reduction (H_2 -TPR) profiles of the different catalysts, showing in all cases a main band in the range 60-120 °C (Fig. S1). The Ru dispersion was determined by CO pulse chemisorption (Fig. S2). Ru/C exhibited the highest Ru dispersion (45%), followed by Ru/CeO_2 (40%) (Table 1). Besides, $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Ru}/\text{H-BEA}$ show a Ru dispersion of 16% and 18%, respectively. The average size of Ru nano-particles was in the range 1.7-2.0 nm measured by HR-TEM (Fig. S3 and S4).

Table 1. Metal dispersion and average size of Ru nanoparticles on the different catalysts used in this study

| Catalyst | Ru/C | $\text{Ru}/\text{Al}_2\text{O}_3$ | $\text{Ru}/\text{H-BEA}$ | Ru/CeO_2 |
|-----------------------------------|----------------------|-----------------------------------|--------------------------|--------------------------|
| Ru dispersion (%) ^[a] | 45 | 16 | 18 | 40 |
| Particle size (nm) ^[b] | 1.7 | 2.0 | 2.0 | 2.0 |

[a] Ru dispersion measured by CO-pulse chemisorption using a CO/Ru stoichiometry of 1. [b] average Ru particle size (nm) measured by TEM analysis.

The reductive amination of **1a** was carried out in ethanol at 15 bar H_2 and NH_3 (0.3 g, $\text{NH}_3/1a = 10/1$) over the different catalysts at 100 °C for 14 h (Table 2). In all these experiments, the conversion of **1a** was above 99% after 20 min of reaction. When $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst was used (10 wt% with respect to **1a**), 78% and 12% yield of the furanic primary amine **2b** and ketone **2a** were obtained, respectively, with 90% carbon balance (entry 1, Fig. S5). $\text{Ru}/\text{H-BEA}$ exhibited a slightly lower performance with 67% and 20% yield of **2b** and **2a**, respectively, and 87% carbon balance (entry 2). In the case of Ru/CeO_2 , **2b** and **2a** were formed with 53% and 20% yield, respectively, as well as 8% yield of the THF-derived ketone (entry 3), but the carbon balance was lower (81%). Finally, Ru/C afforded the highest **2b** yield (95%, entry 4) with 96% carbon balance. On the guidance of the present results combined with the similar Ru dispersion and average particle size on the different catalysts, the support appears to play an important role on

generating the furanic amine **2b** with the selectivity evolving in the sense $\text{C} > \text{Al}_2\text{O}_3 > \text{H-BEA} > \text{CeO}_2$.

Table 2. Catalyst screening for reductive amination of **1a**^[a]

| Entry | Catalyst ^[b] | T / °C | Yield / % | | Carbon balance / % |
|-------|-----------------------------------|--------|-----------|-----------|--------------------|
| | | | 2a | 2b | |
| 1 | $\text{Ru}/\text{Al}_2\text{O}_3$ | 100 | 12 | 78 | 90 |
| 2 | $\text{Ru}/\text{H-BEA}$ | 100 | 20 | 67 | 87 |
| 3 | Ru/CeO_2 | 100 | 20 | 53 | 81 |
| 4 | Ru/C | 100 | 1 | 95 | 96 |
| 5c | Ru/C | 100 | 10 | 85 | 95 |
| 6d | Ru/C | 100 | 35 | 40 | 75 |
| 7 | Ru/C | 60 | 20 | 75 | 95 |

[a] Reaction conditions: **1a** (0.3 g), EtOH (1 g), NH_3 (0.3 g), H_2 (15 bar), catalyst (30 mg), 100 °C, 14 h; [b] The metal loading was 5 wt%. The conversion was >99% for all catalysts; [c] Catalyst (15 mg); [d] Catalyst (5 mg).

The acid properties of the different catalysts were characterized by NH_3 -TPD (Figure 1). H-BEA exhibited the strongest acid properties, as inferred by the large band appearing at a temperature higher than 400 °C, potentially causing the degradation of the furan ring in the presence of water and in turn a carbon balance decrease. $\text{Ru}/\text{Al}_2\text{O}_3$ showed a lower acid strength, while the acidity of Ru/CeO_2 and Ru/C was even lower. In the case of Ru/C , an increasing trend of the signal was observed above 400 °C, which can be attributed to partial decomposition of the carbon support. Based on all these characterizations, and according to the literature⁹, Ru on oxides with base sites, which act as electron-donating surfaces, can prevent reduction and reductive amination which is the case of Ru supported over CeO_2 . It was reported that an appropriate acidity can enhance the activation of carbonyl groups. In the case of CeO_2 -based catalyst, basic sites have negative effect and a repulsion may take place between the electron-rich substrate (**1a** or **2a** unsaturated carbonyl compound) and the surface of CeO_2 , which leads to weaker adsorption and thus the decrease of the amine product selectivity.¹⁰ The support should be not a strong acid one and Ru should be well dispersed on the support to favour the reductive amination of the ketone **1a**.

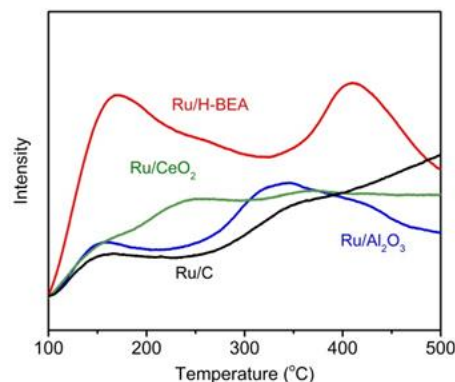


Figure 1. NH_3 -TPD profiles of different catalysts: $\text{Ru}/\text{H-BEA}$, Ru/CeO_2 , $\text{Ru}/\text{Al}_2\text{O}_3$ and Ru/C .

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The Ru/C catalyst loading was then decreased 10 wt% to 5 wt% (entry 5). A decrease of the **2b** yield (from 96% to 85%) was observed along with an increase of the **2a** yield from 1 to 10%. A further decrease to 2.5 wt% (entry 6) resulted in 40% yield of **2b** along with 35% yield of **2a** with 75% carbon balance. These results point out that **2a** is a reaction intermediate and that depending on the catalyst loading, this can be converted into amine or not. Moreover, by increasing the reaction time, **2a** could be converted into **2b**, but a longer reaction time led to product degradation and to a decrease of the carbon balance. A decrease of the temperature from 100 °C to 60 °C resulted in only 20% and 75% yield of **2a** and **2b**, respectively, after 14h reaction (entry 7).

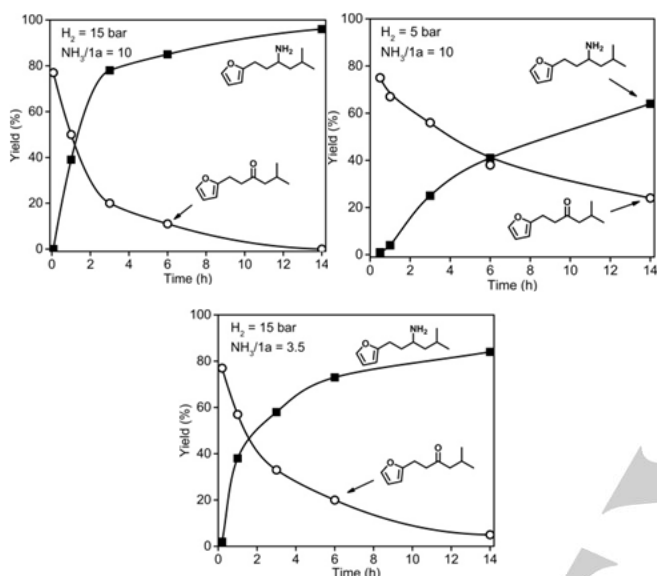


Figure 2. Kinetic profiles of the reductive amination of **1a** over Ru/C; (a) catalyst (30 mg), **1a** (0.3 g), EtOH (1 g), $\text{NH}_3/\mathbf{1a} = 10/1$, H_2 (15 bar), 100 °C, 14 h; (b) catalyst (30 mg), **1a** (0.3 g), EtOH (1 g), $\text{NH}_3/\mathbf{1a} = 10/1$, H_2 (5 bar), 100 °C, 14 h; (c) catalyst (30 mg), **1a** (0.3 g), EtOH (1 g), $\text{NH}_3/\mathbf{1a} = 3.5/1$, H_2 (15 bar), 100 °C, 14 h.

It was thus interesting to evaluate the kinetic profile of the reductive amination of **1a** in the presence of Ru/C (Figure 2) under 15 bar H_2 and using a $\text{NH}_3/\mathbf{1a}$ molar ratio of 10 : 1. During the first 5 min, **1a** was rapidly converted into **2a** with a yield of 77% and 9% yield of the furanic imine, but only trace amounts of **2b**. The **2b** yield increased gradually to 95% after 14 h at the expense of **2a**. It appears from these results that, **1a** is first converted into **2a**. In the presence of NH_3 , the furanic imine was generated, which was further hydrogenated to **2b** (Scheme 2). Deep hydrogenated THF-derived ketone, amine and alcohol were detected only in trace amounts.



Scheme 2. Reaction pathway for the catalytic conversion of **1a** into the furanic amine **2b** over Ru/C.

The effect of the H_2 pressure and $\text{NH}_3/\mathbf{1a}$ molar ratio was further investigated in the presence of Ru/C. A decrease of the H_2 pressure from 15 bar to 5 bar strongly influenced the initial formation rate of **2b** (0.657 mmol h⁻¹ vs. 0.067 mmol h⁻¹ after 1 h), while the **2b** yield decreased from 96% to 64% within the same reaction time. The maximum **2a** yield was higher (24% vs 1%)

after 14 h reaction, while the carbon balance decreased from 96% to 88%. A certain amount of H_2 is required to fully convert **2a** into **2b**. In parallel, a decrease of the $\text{NH}_3/\mathbf{1a}$ molar ratio from 10/1 to 3.5/1 resulted in a decline of the formation rate of **2b** from 0.438 mmol h⁻¹ to 0.326 mmol h⁻¹, leading to slight decrease of the yield of **2b** from 95 to 84%. A certain amount of NH_3 is required to carry out the reductive amination of **2a** to **2b**. However, this can be decreased while keeping an interesting yield of **2b**, which it is not the case for the H_2 pressure. Based on the reaction kinetics study, 15 bar H_2 is required to achieve high yield of the furanic primary amine **2b**.

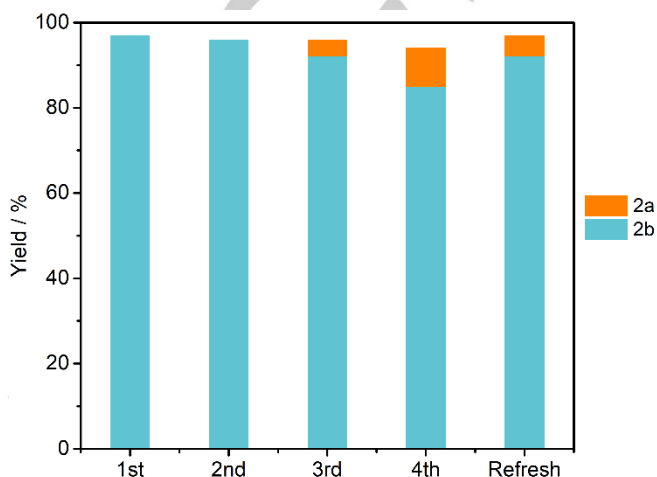


Figure 3. Catalytic performance of Ru/C in consecutive runs in the reductive amination of **1a**. Reaction conditions: Ru/C (100 mg), **1a** (1 g), EtOH (3 g), NH_3 (1 g), H_2 (15 bar), 100 °C, 14 h.

The recyclability of Ru/C was further investigated (Figure 3). After each run, the catalyst was separated by centrifugation and was reused without any treatment. The yield of desired furanic amine remained constant after the 1st and 2nd runs, whereas a slight decrease of the amine yield by ca. 5% and 12% was obtained after the 3rd and 4th runs, with 4% and 9% yield of the furanic ketone, respectively. However, the carbon mass balance always kept around 95%. In order to evaluate the reasons of this slight decrease, ICP analysis of the liquid phase were performed after each run and showed only slight metal leaching (Table 3).

Table 3. ICP analysis of the liquid phase after each run. Amount of Ru calculated in the solution

| | 1 st Cycle | 2 nd Cycle | 3 rd Cycle | 4 th Cycle |
|----------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Metal Ru (ppm) | 14 | 43 | 53 | 44 |



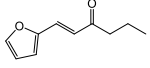
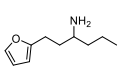
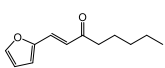
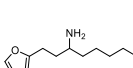
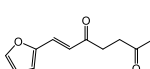
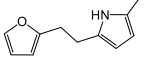
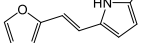
To assess if the leached species have catalytic activity, a reaction was performed and Ru/C was recovered by hot filtration. In this experiment, the catalyst was removed from the reaction mixture after 1 h reaction at 100 °C. Then, the reaction was pursued with the filtrate for another 6 h and 13 h at 100 °C. No further formation of the furanic amine **2b** was observed showing that even if there is a leaching of Ru, the leached species were not active during the reaction and Ru/C behaved as a truly heterogeneous catalyst (Fig. S6). Further characterizations of the catalysts were performed. TEM analysis of the fresh and four-times-used Ru/C catalyst evidenced almost no difference in the average of Ru

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particle size (Fig. S3). However, the Ru dispersion of the recycled Ru/C decreased from 45% to 8%, suggesting a sintering of Ru particles (Fig. S2). The used catalyst was washed with ethanol, dried at 80 °C under vacuum for overnight, and reduced again under a H₂/Ar flow. The refreshed catalyst was reused using the same experimental conditions.

We were pleased to see that the yield of product **2b** increased to 92%. This result confirms that the integrity of the catalyst was kept during the reaction and that it could be reused after some treatment due to the absorption of side products on its surface. TGA analysis of fresh catalyst and recovered catalyst after washing with ethanol and drying confirms this result. Similar weight loss were observed between the fresh Ru/C and the washed with ethanol and dried catalyst (Fig. S8, S9).

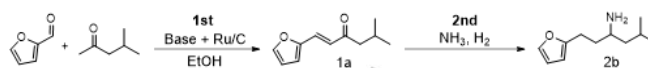
Table 4 Production of bio-based amines over Ru/C catalyst

| Entry | Substrate | Product | Yield / % |
|-------|---|---|-----------|
| 1 |  |  | 78 |
| 2 |  |  3b | 93 |
| 3 |  |  4b | 94 |
| 4 |  |  | 65 |
| | |  | 28 |

Reaction conditions: Ru/C (30 mg), EtOH (1 g), NH₃ (0.3 g), H₂ (15 bar), 100 °C; Acetophenone (0.3 g), 1.5 h; furanic ketone (0.3 g), entries 1-3: reaction time of 6 h and entries 4- 5 reaction time 14h.

To evaluate the generality of Ru/C, we extended the scope for aldol condensation reaction, other ketones were investigated (2-pentanone, 2-heptanone, benzaldehyde, 2,5-hexanedione) and the yield obtained were respectively 93, 94, 78 and 84% of the aldol compound. For reductive amination the scope was also investigated (Table 4) and the corresponding amines were obtained with high yield. In the case of benzaldehyde, the by-product formed was bis(1-phenylethyl)amine. In the presence of hexanedione, a cyclization occurs to produce pyrrole as was reported by Johannes G. de Vries *et al.*²⁹ with the formation of 2-(2-(furan-2-yl)vinyl)-5-methyl-1H-pyrrole(28%) and 2-(2-(furan-2-yl)ethyl)-5-methyl-1H-pyrrole (65%). These results confirm that Ru/C enables a selective synthesis of bio-based primary amines and with the possibility to produce pyrrole.

To access bio-based amines in a suitable way, the catalytic system was extended to a process starting from furfural and directly combining first an aldol condensation reaction with sequential reductive amination in a single reactor (Scheme 3).



Scheme 3 One-reactor synthetic strategy for the synthesis of furan-derived amines starting from furfural.

First, MIBK was used as a ketone and to prevent the amination of MIBK, the optimization of the aldol condensation reaction between furfural and MIBK (equimolar ratio) over A26 was investigated. A yield up to 91% of **1a** was achieved at 100 °C after 4 h reaction with the 98% furfural conversion (Fig. S7). A mechanical mixture of A26 and Ru/C was further added to the reactor and a promising 90% yield of **1a** was achieved at 100 °C for 4 h in ethanol with an equimolar furfural/MIBK mixture. After 4 h for promoting the aldol condensation of furfural with MIBK, NH₃ (0.3 g) and H₂ (15 bar) were added to the reactor. A **2b** yield up to 71% was achieved after 20 h reaction (Figure 4). To increase the **2b** yield, the reaction time and the H₂ pressure were further optimized (Table 5). When the reaction time was prolonged to 24 h (entry 3), or the H₂ pressure was increased to 30 bar (entry 4), the **2b** yield reached a similar value (74%) with the concomitant formation of **2a**. Compared with the maximum theoretical yield (91%), the decrease in the yield for the one-reactor process might be attributed to the degradation of furfural or intermediates during both reactions. However, a high **2b** yield could be obtained from furfural.

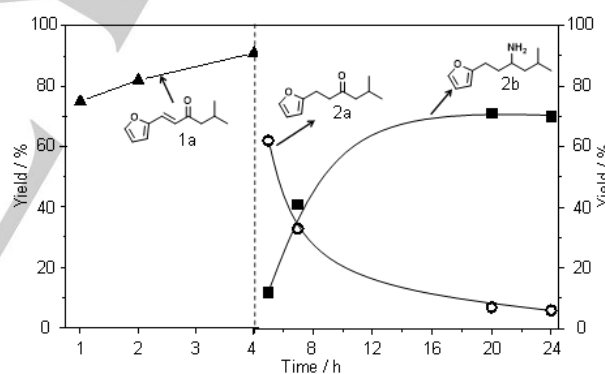


Figure 4. Kinetics of the one-reactor process using a mechanical mixture of A26 and Ru/C. Reaction conditions: furfural (162 mg, 1.69 mmol), MIBK (169 mg, 1.69 mmol), ethanol (1 g), A26 (64.8 mg), Ru/C (30 mg), 100 °C. First step: 4 h. Second step: NH₃ (0.3 g), H₂ (15 bar), variable time.

Secondly, it was interesting to evaluate the scope of the ketone used in the combination of an aldol condensation reaction with sequential reductive amination in a single reactor. 2-pentanone and 2-heptanone were investigated to perform aldol condensation and reductive amination reactions in a two steps one single reactor (Table 5, entries 6, 7). The aldol condensation reaction was 1h30 for these two ketones. We were pleased to see that in the presence of 2-pentanone, 25% of furanic amine was obtained and that from 2-heptanone 57% of furanic amine was observed showing that this strategy can be applied to other ketones than MIBK. However, a full study has to be performed for each ketone in order to improve the yield.

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Table 5. Catalytic conversion of furfural to furanic amine by one-reactor, two-step process^[a]

| Entry | Ketone | | Catalyst | Time | | NH ₃ / g | H ₂ /bar | Yield / % | | Carbon balance / % |
|------------------|----------|-------------|------------|-----------------|-----------------|---------------------|---------------------|----------------------------|---------|--------------------|
| | Reagent | | | 1 st | 2 nd | | | Unsaturated furanic ketone | Amine | |
| 1 | 1a | - | Ru/C | | 14 | 0.3 | 15 | < 1 (2a) | 95 (2b) | 95 |
| 2 | Furfural | MIBK | Ru/C + A26 | 4 | 16 | 0.3 | 15 | 7 (2a) | 71 (2b) | 78 |
| 3 | Furfural | MIBK | Ru/C + A26 | 4 | 24 | 0.3 | 15 | 6 (2a) | 70 (2b) | 76 |
| 4 | Furfural | MIBK | Ru/C + A26 | 4 | 16 | 0.3 | 30 | 3 (2a) | 74 (2b) | 77 |
| 5 | Furfural | MIBK | Ru/C + A26 | | 14 | 0.3 | 15 | 18 (2a) | 9 (2b) | 27 |
| 6 ^[b] | Furfural | 2-pentanone | Ru/C + A26 | 1.5 | 6 | 0.3 | 15 | 33 | 25 (3b) | 58 |
| 7 ^[b] | Furfural | 2-heptanone | Ru/C + A26 | 1.5 | 14 | 0.3 | 15 | 23 | 57 (4b) | 80 |

[a] The furfural conversion was 100 % for all the reactions. (1st) All runs were carried out at 100 °C in 1 g EtOH with 162 mg furfural while keeping the molar ratio of ketone:furfural – 1:1 and the mass ratio of base/furfural 40 wt%, 30 mg Ru/C; (2nd) the reductive amination reactions were all following the first step of aldol condensation by inserting NH₃ and H₂. [b] not optimized result.

In summary, we demonstrated that a new family of furan-derived primary amines could be selectively prepared (95%) from bio-derived ketones using NH₃ as a nitrogen source, molecular H₂ as a reducing agent and commercially available Ru/C as catalyst. This system efficiently catalyzed the hydrogenation of C=C bonds together with the reductive amination of carbonyl groups at mild reaction conditions. Besides, the catalyst remains stable during the reaction for at least 4 consecutive runs. We also demonstrated that furfural could be directly converted into furan-derived primary amines by a one-reactor two-step process, achieving a high yield of 74% and that it can be extended to other ketones than MIBK (not optimized results). Thus our present work leads to the production of opens a new avenue for producing biomass-derived amines from products of biomass processing with potential application as biosolvents or biosurfactants. Also, this work provides a toolbox that enables the conversion of furfural into the desired amine. The deposition of ruthenium species over a multifunctional support, the design of a continuous flow process and the transposition of the current results to a variety of amines are topics under investigation.

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Keywords: Amines • Biomass • Catalyst • Furfural • Ketones

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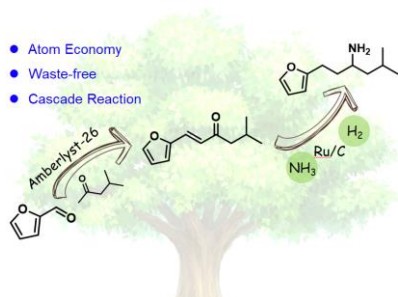
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Catalytic conversion of furfural to primary amines with high yield (74%) by a one-reactor two-step process in the presence of Amberlyst 16 and Ru/C based catalysts. The hydrogenation of C=C bonds together with the reductive amination of carbonyl groups at mild reaction conditions were performed using ammonia and hydrogen.