Two-Step One-Pot Reductive Amination of Furanic Aldehydes Using CuAlO\textsubscript{x} Catalyst in a Flow Reactor

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Abstract: Aminomethylhydroxymethylfuran derivatives are well known compounds which are used in the pharmaceutical industry. Reductive amination of 5-hydroxymethylfurfural (HMF) derived from available non-edible lignocellulosic biomass is an attractive method for the synthesis of this class of compounds. In the present study, the synthesis of N-substituted 5-(hydroxymethyl)-2-furfuryl amines and 5-(acetoxymethyl)-2-furfuryl amines was performed by two-step process, which includes the condensation of furanic aldehydes (HMF and 5-acetoxymethylfurfural) with primary amines in methanol on the first step and the reduction of obtained imines with hydrogen in a flow reactor over CuAlO\textsubscript{x} catalyst derived from layered double hydroxide on the second step. This process does not require isolation and purification of intermediate imines and can be used to synthesize a number of aminomethylhydroxymethylfurans in good to excellent yield.

Keywords: reductive amination; 5-hydroxymethylfurfural; 5-acetoxymethylfurfural; Cu-based catalyst; Cu-Al mixed oxide; primary amines; imine hydrogenation; flow reactor

1. Introduction

N-Substituted 5-(hydroxymethyl)-2-furfuryl amines are an important class of compounds due to their usage in pharmaceutical industry for production of calcium antagonists, muscarinic agonists, cholinergic agents, carcinogenesis inhibitors, etc. (for instance, anti-hepatitis B virus drug and antihypertensives, Scheme 1) [1–3]. Generally, these structures are prepared by a Mannich-type reaction starting from furfural alcohol (or furfural), formaldehyde, and primary amines. However, harsh reaction conditions are usually required, that leads to a low yield of the target product [4–6]. Meanwhile, reductive amination of 5-hydroxymethylfurfural (HMF) derived from available non-edible lignocellulosic biomass is an attractive method for the synthesis of this type of amines [3,7–11].

![Scheme 1. Examples of N-substituted 5-(hydroxymethyl)-2-furfuryl amines with pharmaceutical activity.](image)

In general, the reductive amination of HMF is realized in the presence of noble metal-based catalysts such as dichlorobis(2,9-dimethyl-1,10-phenanthroline) ruthenium(II) complex [7], Pd/C [8], Au/TiO\textsubscript{2} [3], and Pd nanoparticles immobilized in a MOF/polymer composite [9] using batch reactors.
However, the high price and limited availability of precious metals are stimulated interest in catalysts based on earth-abundant elements. Chieffi et al. studied the reductive amination of HMF over carbon-supported Fe-Ni catalyst under flow conditions. However, the amines used were limited to 3-aminopropanol and alanine sodium and the yield of the target aminomethylhydroxymethylfuran (AMHMF) derivatives did not exceed 78% [11].

In our previous study [12], an environmentally friendly procedure has been developed for the synthesis of secondary amines through a two-step one-pot reductive amination of aromatic aldehydes with primary amines. The condensation of benzaldehyde derivatives (or furfural) with amines in methanol at room temperature gives imines, which are then hydrogenated in a flow reactor using Cu-Al mixed oxide (denoted hereafter as CuAlOx) derived from layered double hydroxide (LDH). In present work, we investigated the efficiency of this procedure for reductive amination of furanic aldehydes (HMF and 5-acetoxymethylfurfural) with primary amines via hydrogenation of the intermediate imines over CuAlOx catalyst in a flow reactor.

2. Results and Discussion

Methanol is a suitable solvent for the synthesis of N-substituted 5-(hydroxymethyl)-2-furfuryl amines, since it is a good solvent for both the condensation of aromatic aldehydes with primary amines and hydrogenation of imines [10,12,13]. We found that the reaction of HMF with aniline in low water methanol (0.02 wt% H2O) occurs at room temperature with imine yield of 98% (Table 1, entry 1) and time dependence of imine yield let us to see that equilibrium concentrations are reached within 2 h (Supplementary Materials, Figure S1). The use of ethanol instead of methanol leads to a decrease in the yield of imine 1a to 70% (Table 1, entry 2). Simultaneously, the yield of 1a in isopropanol is only 31% under the same reaction conditions (Table 1, entry 3).

| Table 1. Condensation of 5-hydroxymethylfurfural (HMF) with aniline 1. |
|---------------|----------------|-------------|
| Entry | Solvent | Yield, % |
| 1 | Methanol | 98 |
| 2 | Ethanol | 70 |
| 3 | Isopropanol | 31 |

1 Reaction conditions: HMF (0.05 M), aniline (0.05 M), batch reactor, T = 25 °C, 2 h. 2 GC yields.

The reaction mixtures obtained by condensation of HMF with primary amines were further hydrogenated over CuAlOx catalyst in a flow reactor at 100 °C and H2 pressure of 10 bar. Before each catalytic run, the CuO phase of CuAlOx was reduced in situ by hydrogen to metallic copper particles [12, 14]. The average size of copper crystallites in the reduced sample was about 7 nm [14] that is much smaller than in case of the supported Cu/Al2O3 catalysts with high copper content. Thus, CuAlOx material prepared by calcination of LDH precursor is a promising non-noble metal catalyst for hydrogenation reactions [12,14,15].

The hydrogenation of imine 1a, which is obtained by condensation of HMF and aniline in methanol, leads to the formation of AMHMF derivative 2a with the yield of 97% (Table 2, entry 1). In addition to 2a, undesired bis-(hydroxymethyl)furan 3 was observed among the reaction products. The use of ethanol or isopropanol instead of methanol leads to a strong drop in the yield of the target product (Table 2, entries 2 and 3) due to the much lower yield of imine in the first stage (Table 1). As a result, a greater amount of HMF is hydrogenated to 3. Raising the concentration of reactants in methanol to 0.2 M reduces the yield to 94% (Table 2, entry 4). However, an increase of reaction temperature...
to 120 °C at high reactant concentration leads to rise of the imine hydrogenation rate and allows synthesizing 2a with the yield of 98% (Table 2, entry 5).

The effect of primary amine structure on the formation of AMHMF derivatives was investigated by reductive amination of HMF with different aromatic and aliphatic amines over CuAlOx catalyst (Table 2, entries 1 and 6–16). Formation of 2b, 2c, and 2e with the excellent yield (95–97%) is observed for aromatic amines containing electron-donating substituent (CH3 and OCH3) in meta- and para-position (Table 2, entries 6, 7, and 9). It means that the rates of imine formation in the condensation of HMF with these compounds are similar to that in the reaction of HMF with aniline while using o-toluidine gives lower rate of imine formation due to steric hindrance created by methyl group in ortho-position [12]. A much longer period of time (16 h) is needed for the condensation of HMF with o-toluidine at the first stage to obtain 2d with the yield of 88% by imine hydrogenation over the CuAlOx catalyst at the second stage (Table 2, entry 8).

Introduction of F and Cl substituent in the para-position of aniline slightly decreases the yield of compounds 2 to 93–94% (Table 2, entries 10 and 11). At the same time, in the case of p-bromoaniline the significant drop in the yield of the target product to 60% was observed while imine amount in the final mixture was increased (Table 2, entry 12). It is worth to mention that reaction was performed at 110 °C that is higher than in case of other aromatic amines. This result can be explained by the steric hindrance created by bulky Br substituent during the diffusion of imine to active sites of CuAlOx [12]. It should be noted that hydrodehalogenated product practically did not form during the reaction.

Table 2. Two-step one-pot reductive amination of HMF with primary amines 1.

| Entry | R         | Step 1, h | T, °C | 2       | Yield, % 2 |
|-------|-----------|-----------|-------|---------|------------|
|       |           |           |       |         | 1  | 2  | 3  | 4  |
| 1     | Ph        | 3         | 100   | 2a      | n.d.        | 97 | 3  | n.d. |
| 2-6   | Ph        | 3         | 100   | 2a      | n.d.        | 74 | 26 | n.d. |
| 3-5   | Ph        | 3         | 100   | 2a      | n.d.        | 67 | 33 | n.d. |
| 6     | p-CH3C6H4 | 3         | 100   | 2b      | n.d.        | 97 | 3  | n.d. |
| 7     | m-CH3C6H4 | 3         | 100   | 2c      | n.d.        | 96 | 4  | n.d. |
| 8     | o-CH3C6H4 | 16        | 100   | 2d      | n.d.        | 88 | 12 | <0.5|
| 9     | p-CH2OC6H4| 3         | 100   | 2e      | n.d.        | 95 | 5  | n.d. |
| 10    | p-FC6H4   | 3         | 100   | 2f      | n.d.        | 94 | 6  | n.d. |
| 11    | p-ClC6H4  | 3         | 100   | 2g      | n.d.        | 93 | 7  | n.d. |
| 12    | p-BrC6H4  | 3         | 110   | 2h      | n.d.        | 22 | 60 | 16  |
| 13    | m-ClC6H4  | 3         | 100   | 2i      | n.d.        | 55 | 45 | n.d. |
| 14    | m-ClC6H4  | 16        | 100   | 2i      | n.d.        | 95 | 4  | 1   |
| 15    | o-ClC6H4  | 16        | 100   | 2j      | n.d.        | 52 | 42 | 6   |
| 16    | n-hexyl   | 3         | 100   | 2k      | n.d.        | 93 | 7  | n.d. |

1 Reaction conditions: HMF (0.05 M), primary amine (0.05 M), CuAlOx catalyst (165 mg), 10 bar H2, liquid flow rate of 0.5 mL min⁻¹, hydrogen flow rate of 30 mL min⁻¹. 2 The product yields were determined by 1H-NMR. 3 Ethanol was used as a solvent. 4 Isopropanol was used as a solvent. 5 Reactant concentrations were 0.2 M.

The position of electron-withdrawing substituent in aromatic amine has a strong effect on the reaction. The imine formation rate in the condensation of HMF with m-chloroaniline is much lower than with p-chloroaniline. As a result, the reaction of HMF with m-chloroaniline for 3 h on the first stage leads to formation of 2i in a low yield (Table 2, entry 13). However, carrying out the condensation of HMF and m-chloroaniline for 16 h allows obtaining 2i in 95% yield (Table 2, entry 14). At the same time, o-chloroaniline gave a moderate yield of 2j (52%) after the reaction with HMF on the first stage for
16 h (Table 2, entry 15). These observations are explained by a decrease in the nucleophilic properties of chloroanilines in the following order: p-chloroaniline > m-chloroaniline > o-chloroaniline.

Thus, the yield of 2 is determined by the imine formation at the first stage. Higher yield of the intermediate imine provides higher yield of AMHMF derivative. In the case of primary amines with weak nucleophilic properties (o-toluidine, m-chloroaniline, o-chloroaniline), a longer condensation time (16 h) is required to obtain compound 2 with a higher yield.

Using aliphatic hexylamine gave a slightly lower yield of AMHMF derivative than aniline (Table 2, entries 1 and 16) that can be explained by instability of intermediate imines containing alkyl substituent [16].

The time-on-stream measurements for reductive amination of HMF with aniline over the CuAlO catalyst were performed for ~3 h (Supplementary Materials, Figure S3). The yield of 2a (97%) remained unchanged meaning that the catalyst exhibits good stability during the reaction [12,14].

5-Acetoxymethylfurfural (AMF), which can be prepared from carbohydrates without isolating HMF, is less reactive, more stable and easily extracted from the aqueous reaction mixture. Therefore, AMF represents a good substitute for HMF [17–19]. Similar to HMF, AMF reacts with aniline in Introduction of methyl substituent in para-position of aniline decreases the yield of compound 6 to 96% (Table 3, entry 4). It is worth to mention that condensation of AMF with o-toluidine was performed for 16 h while temperature of following hydrogenation of obtained imine was raised to 90 °C. In the case of anilines with CH3O, F, and Cl substituents in para-position, AMHMF derivatives 6e, 6f, and 6g were obtained with the yield of 99, >98 and 97%, respectively (Table 3, entries 5–7). Simultaneously, the reaction of AMF with m-chloroaniline for 16 h at the first stage, followed by imine hydrogenation at 80 °C, allows synthesizing 6h with the yield of 96% (Table 3, entry 8). In contrast to aromatic amines, hexylamine gives only 82% yield of the AMHMF derivative due to hydrogenation of acetyl group in 6i (Table 3, entry 9).

**Table 3.** Two-step one-pot reductive amination of 5-Acetoxymethylfurfural (AMF) with primary amines.

| Entry | R         | Step 1, h | Yield, %  |
|-------|-----------|-----------|-----------|
| 1     | Ph        | 3         | 6a        | n.d. 99 <0.5 <1 n.d. |
| 2     | p-CH3C6H4 | 3         | 6b        | n.d. >99 n.d. <1 n.d. |
| 3     | m-CH3C6H4 | 3         | 6c        | <0.5 >98 n.d. 1 n.d. |
| 4     | o-CH3C6H4 | 16        | 6d        | n.d. 96 1 3 n.d.  |
| 5     | p-CH3OCH3 | 3         | 6e        | n.d. 99 0.5 <0.5 <0.5 |
| 6     | p-FC6H4   | 3         | 6f        | <0.5 >98 <0.5 1 n.d. |
| 7     | p-ClC6H4  | 3         | 6g        | <0.5 97 0.5 2 <0.5 |
| 8     | m-ClC6H4  | 16        | 6h        | n.d. 96 <0.5 2 2   |
| 9     | n-hexyl   | 3         | 6i        | n.d. 82 4 n.d. n.d. n.d. |

1 Reaction conditions: AMF (0.05 M), primary amine (0.05 M), CuAlO catalyst (165 mg), 80 °C, 10 bar H2, liquid flow rate of 0.5 mL min−1, hydrogen flow rate of 30 mL min−1. The product yields were determined by 1H-NMR.
2 T = 90 °C. 4 Compound 2k was also formed.
3. Materials and Methods

3.1. Chemicals

Aniline (99.8%), o-toluidine (99%), m-toluidine (99%), p-toluidine (99%), p-anisidine (99%), o-chloroaniline (>98%), m-chloroaniline (99%), p-chloroaniline (98%), p-fluoroaniline (98%), p-bromoaniline (>99%), n-hexylamine (99%), and 5-(acetoxymethyl)-2-furaldehyde (97%) from Acros Organics (Geel, Belgium), as well as 5-hydroxymethylfurfural (99%) from Sigma-Aldrich (St Louis, MO, USA), were used without additional purification. Methanol (99.8%) from J.T. Baker (Phillipsburg, NJ, USA), ethanol (99.9%) from J.T. Baker and isopropanol (99.5%) from Acros Organics were employed as a solvent.

3.2. Catalyst Preparation

Cu-Al layered double hydroxide was prepared by co-precipitation method at pH 9.0 and temperature of 70 °C using the mixture of copper (II) nitrate and aluminum nitrate as starting material and solution containing NaOH and Na$_2$CO$_3$ ([CO$_3^{2-}$]/[Al$^{3+}$] = 0.86, [OH$^-$] = 1.6([Al$^{3+}$] + [Cu$^{2+}$]) as precipitant agent. The aging of the obtained suspension was performed at 70 °C for 4 h. Afterwards, the precipitate was filtered, washed with hot water and dried at 110 °C for 14 h. The as-prepared LDH was calcined at 650 °C for 4 h to obtain desired CuAlO$_x$ catalyst [11,13] containing 47.2 wt% of Cu and 19.9 wt% of Al. The texture properties of CuAlO$_x$ were found to be as follows: BET specific surface area—68 m$^2$ g$^{-1}$ and total pore volume—0.15 cm$^3$ g$^{-1}$.

3.3. Characterization Techniques

The Cu and Al content was measured by atomic absorption spectroscopy on an Optima 4300 DV instrument (Perkin Elmer, Waltham, MA, USA). Textural characteristics were determined from nitrogen adsorption–desorption isotherms (77 K) obtained on a Micromeritics ASAP 2400 analyzer (Micromeritics, Norcross, GA, USA).

3.4. General Procedure for Reductive Amination of Furanic Aldehydes with Primary Amines

Depending on the nucleophilic properties of the amine, the solution of furanic aldehyde (0.05 M) and primary amine (0.05 M) in methanol was kept at 25 °C for 3 or 16 h. Then, the reaction mixture was mixed with H$_2$ and pumped through the flow reactor packed with the CuAlO$_x$ material. Catalytic experiments were performed in H-Cube Pro setup (Thalesnano, Budapest, Hungary) equipped with a 30 mm CatCart cartridge (CatCart®30, 0.30 mL empty volume) [11,13]. Before the catalytic run, the catalyst (0.165 g of 250–500 µm particles) was reduced by a mixture of hydrogen with methanol at 120 °C for 1 h (pressure of 10 bar, flow rates of methanol and H$_2$ were 0.5 and 30 mL min$^{-1}$, respectively). Afterwards, the reaction mixture was pumped through the reactor instead of pure solvent, and this point in time was chosen as the starting point of the experiment.

The reaction was carried out at temperature of 80–120 °C, H$_2$ pressure of 10 bar, liquid feed rate of 0.5 mL min$^{-1}$ and hydrogen flow rate of 30 mL min$^{-1}$ (inlet H$_2$/substrate molar ratio was 54). The use of a large excess of H$_2$ in the reaction medium is necessary to avoid the influence of external mass transfer on the reaction progress [13]. The performance of the catalyst was evaluated by analysis of the samples taken in the interval of 30–33 min from the beginning of the experiment. The composition of the reaction products was determined using $^1$H NMR spectroscopy in CDCl$_3$. The error in determining the yield is ±1%.

4. Conclusions

The two-step one-pot reductive amination of furanic aldehydes, including non-catalytic condensation of HMF (or AMF) with primary amines and the subsequent flow hydrogenation of the obtained imine over Cu-based catalyst derived from layered double hydroxide, was successfully
performed using methanol as a solvent. This inexpensive and environmentally friendly process can be utilized to obtain a wide range of N-substituted 5-(hydroxymethyl)-2-furfuryl amines and 5-(acetoxymethyl)-2-furfuryl amines in good to excellent yields (up to 98 and 99%, respectively). The proposed approach is a new method for the synthesis of aminomethylhydroxymethylfuran derivatives which can be used as pharmaceuticals or their precursors.

**Supplementary Materials:** The following are available online. Figure S1: The time dependence of imine yield in the condensation of HMF (0.05 M) and aniline (0.05 M) at room temperature; Figure S2: The time dependence of imine yield in the reaction between AMF (0.05 M) and aniline (0.05 M) in methanol at room temperature; Figure S3: Time dependence of 2a yield in the two-step one-pot reductive amination of HMF (0.05 M) with aniline (0.05 M) at 100 °C; 1H-NMR spectra of the final reaction mixtures.

**Author Contributions:** A.L.N. planned and designed the experiments, performed the catalytic activity tests, and wrote the manuscript. M.V.B. performed the catalyst synthesis and revised the manuscript. V.I.B. supervised the project. All authors discussed the results and approved the final version of the manuscript.

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