Reductive Amination of Furanic Aldehydes in Aqueous Solution over Versatile Ni₆AlOₓ Catalysts

Hangkong Yuan, Jerry-Peng Li, Fangzheng Su, Zhen Yan, Bright T. Kusema, Stéphane Streiff, Yongji Huang, Marc Pera-Titus, and Feng Shi

INTRODUCTION

Furanic aldehydes (X-furfural with X = H, CH₂OH) are important chemicals readily accessible from carbohydrates (hexoses or pentoses) contained in lignocellulosic biomass. In particular, furfural (FF) is a versatile platform chemical for the production of fuel additives, solvents, polymers, surfactants, perfumes, and agrochemical ingredients. The current world production of FF is estimated at 280 kton/year with the largest plant being based in the Dominican Republic with a capacity of 35 kton/year. Likewise, 5-hydroxymethyl furfural (HMF) has attracted great interest in recent years with extensive research on its production and further transformation as a platform chemical. Unlike FF, no industrial production of HMF is available today. However, as key intermediate for FDCA, production, HMF is on a fast track for commercialization. Likewise, 5-hydroxymethylfurfural (HMF) has attracted great interest in recent years with extensive reaction conditions. Besides, 5-hydroxymethylfurfural could react with a library of primary and secondary amines with yields in the range 76–88%. The catalyst could be easily recycled and reused without apparent loss of activity in four consecutive runs.

ABSTRACT: We disclose in this study a Ni₆AlOₓ catalyst prepared by coprecipitation for the reductive amination of biomass-derived aldehydes and ketones in aqueous ammonia under mild reaction conditions. The catalyst exhibited 99% yield toward 5-aminomethyl-2-furylmethanol in the reaction of 5-hydroxymethyl furfural with ammonia at 100 °C for 6 h under 1 bar H₂. The catalyst was further extended to the reductive amination of a library of aromatic and aliphatic aldehydes and ketones with a yield in the range 81–90% at optimized reaction conditions. Besides, 5-hydroxymethylfurfural could react with a library of primary and secondary amines with yields in the range 76–88%. The catalyst could be easily recycled and reused without apparent loss of activity in four consecutive runs.

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reducing agent followed by the reduction of the furan ring with Raney Ni. Hara and co-workers reported a highly active and durable Ru/Nb2O5 catalyst for the RA of carbonyl compounds containing reduction-sensitive functional groups to primary amines.16,17 Ru/ZrO2 was also developed for the RA of 5-methylfurfural with aqueous NH3, leading to 5-methylfurfurylamine with 61% yield. The coexistence of Ru and RuO2 on the surface of Ru/ZrO2 provided both strong Lewis acid and metal hydrogenation sites. The cooperation between both sites led to an excellent performance for the production of primary amines.18 Finally, Co-assisted RA of HMF using a variety of amines in methanol/water (1:1 v/v) could proceed fast over Au/TiO2.19

Ni is known as an active non-noble metal for the direct amination of alcohols and the RA of aldehydes and ketones.20,21 Herein, a series of Ni6AlO14 catalysts were easily prepared by coprecipitation of starting precursors and were further employed in the RA of furanic aldehydes with aqueous NH3. More importantly, the Ni/Al molar ratio could be easily tuned by adjusting the relative amount of the starting precursors in the synthesis solution.

RESULTS AND DISCUSSION

Figure 1 plots the X-ray diffraction (XRD) patterns of the different Ni6AlO14 catalysts prepared in this study. The catalysts were prereduced ex situ before analysis. The patterns suggest that finely crystallized metal Ni is formed on Ni6AlO14, especially at high Ni loading, as can be inferred from the characteristic Ni(111), Ni(200), Ni(220), Ni(311), and Ni(222) reflections appearing at 44°, 53°, 77°, 93°, and 98°, respectively (Ni, JCPDS card no: 04-0850, Fm3m cubic unit cell). Unexpectedly, metal Ni is stable after air exposure, suggesting potential encapsulation by alumina or passivation, especially at higher Ni content. Additional reflections are also visible at 37°, 43°, 63°, 76°, and 79°, which can be assigned to NiO(111), NiO(200), NiO(220), NiO(311), and NiO(222), respectively (NiO, JCPDS card no: 47-1049, Fm3m cubic unit cell). By decreasing the Ni/Al molar ratio, the reflections ascribed to either alumina or the spinel NiAl2O4 can be discerned, suggesting the presence of amorphous aluminum oxides or hydroxides.

Figure 2 shows representative transmission electron microscopy (TEM) micrographs of Ni6AlO14 after reduction at 450 °C for 2 h under H2 flow. Because the catalyst was prepared by the coprecipitation method, it is difficult to distinguish Ni/NiO nanoparticles on the catalyst surface. The average particle size of the catalyst ranges from 10 to 30 nm. The magnified TEM micrographs of Ni6AlO14 reveal the presence of highly crystalline Ni/NiO nanoparticles.

The surface composition of the Ni6AlO14 catalysts was analyzed by X-ray photoelectron spectroscopy (XPS). Figure 3 plots representative XPS spectra of the Ni 2p, Ni 3p, and Al 2p core levels for Ni6AlO14. Additional spectra for the remaining catalysts can be found in the Supporting Information (Figures S1–S5). The deconvoluted Ni 2p core level (Figure 3a) can be assigned to two spin–orbit coupling levels for the Ni 2p3/2 and Ni 2p1/2 states. Both states show a main band in the range 855.7–856.9 eV (Ni 2p3/2) and 873.4–874.5 eV (Ni 2p1/2) corresponding to Ni2+, whereas the small band (<5% surface) at 852.0–853.4 eV (Ni 2p3/2) and 871.2–872.5 eV (Ni 2p1/2) can be attributed to Ni0.23...
Ni10AlO

The BET surface area, average pore size, and pore volume for Ni10AlO

nanoparticles are expected to be mostly exposed on the opposite trend is observed for the highly Ni-loaded catalysts, whereas Ni and NiO

When NH3 is added to the reaction system at 1 bar H2, 5-

dimethanol (THFMA) is obtained with 95% yield (entry 2).

°

92% yield (entry 1). At 100°

The Ni content from 0.51 cm³/g for Ni1AlO

hydrogenation and RA of HMF over Ni6AlO

line with the XRD patterns, these results can be interpreted by desorption at −196°C. In parallel, the average pore size increases from 3.8 nm for Ni1AlO

We conducted a first series of catalytic tests for the hydrogenation and RA of HMF over Ni6AlO

(4.0 vs 1.6), whereas the (Ni/Al)b bulk ratios show similar values (5.5 vs 5.1). In line with the XRD patterns, these results can be interpreted by a partial encapsulation of Ni and NiO nanoparticles by alumina for Ni6AlO, Ni5AlO, and Ni4AlO, whereas Ni and NiO nanoparticles are expected to be mostly exposed on the alumina surface for Ni3AlO, Ni4AlO, and Ni10AlO.

Table 1 (columns 2–4) also lists the Brunauer–Emmett–Teller (BET) surface area, average pore size, and pore volume of the different catalysts measured by Ni adsorption/desorption at −196°C. The BET surface area decreases gradually with the Ni content from 273 m²/g for Ni1AlO to 81 m²/g for Ni10AlO. Likewise, the pore volume declines with the Ni content from 0.51 cm³/g for Ni1AlO to 0.30 cm³/g for Ni10AlO. In parallel, the average pore size increases from 3.8 nm for Ni1AlO to 7.3 nm for Ni10AlO.

We conducted a first series of catalytic tests for the hydrogenation and RA of HMF over Ni6AlO (Table 2). Ni6AlO can efficiently catalyze the hydrogenation of HMF into 2,5-furandimethanol (FMA) at 70°C and 10 bar H2 with 92% yield (entry 1). At 100°C, 2,5-tetrahydrofurandimethanol (THFMA) is obtained with 95% yield (entry 2). When NH3 is added to the reaction system at 1 bar H2, 5-aminomethyl-2-furfmethanol (FAA) is generated as main product with 98% yield at the expense of FMA and THFMA (entry 3). At higher H2 pressure (10 bar) and temperature (150°C), 5-aminomethyl-2-tetrahydro-furfmethanol (THFAA) is obtained as main product with 95% yield (entry 4) at the expense of FAA. FAA is fast generated during the initial 3 h reaction and becomes gradually hydrogenated to THFAA during the first 10 h at full HMF conversion (Figure 4).

With these results in hand, we explored the performance of the Ni6AlO catalysts toward FAA formation in the RA of HMF with NH3 at 100°C for 6 h under 1 bar H2 (Table 3). Ni6AlO exhibits low HMF conversion (65%) and FAA yield (32%) together with a poor mass balance (70%). FAA issued from HMF hydrogenation is generated as minor byproduct with only 2.3% yield. An increase of the Ni/Al molar ratio to 2 and 4 enhances moderately the HMF conversion, the FAA yield, and the mass balance. The best performance is achieved when the nominal Ni/Al molar ratio is set at either 6 or 8, resulting in full HMF conversion and 99% FAA yield together with 99% mass balance. FAA only appears as trace byproduct. A further increase of the Ni/Al molar ratio to 10 leads to a slight decline of the FAA yield (96%) at full HMF conversion with 96% mass balance. For comparison, the RA of HMF with NH3 was also studied over a NiO catalyst prereduced at 450°C.

| catalyst   | BET area (m²/g) | pore size (nm) | pore volume (cm³/g) | (Ni/Al)b | (Ni/Al)c |
|------------|----------------|---------------|---------------------|----------|----------|
| Ni1AlO     | 275            | 3.8           | 0.51                | 0.9      | 3.8      |
| Ni2AlO     | 277            | 4.0           | 0.55                | 1.6      | 4.0      |
| Ni3AlO     | 203            | 4.0           | 0.41                | 3.0      | 4.0      |
| Ni4AlO     | 133            | 5.5           | 0.36                | 5.1      | 5.5      |
| Ni5AlO     | 115            | 6.2           | 0.36                | 7.2      | 6.2      |
| Ni6AlO     | 81             | 7.3           | 0.30                | 8.9      | 7.3      |

*Measured by ICP–OES. bMeasured by XPS. Measured by N2 adsorption/desorption at −196°C.

| entry | NH3/HMF ratio (mol/mol) | H2 pressure (bar) | total pressure (bar) | T (°C) | time (h) | product | yield (%) |
|-------|--------------------------|-------------------|----------------------|--------|---------|---------|-----------|
| 1     | 10                       | 10.5              | 70                   | 6      | FMA     | 92      |
| 2     | 10                       | 12.5              | 100                  | 6      | THFMA   | 95      |
| 3     | 49:1                     | 5.0               | 100                  | 6      | FAA     | 98      |
| 4     | 49:1                     | 25.0              | 150                  | 16     | THFAA   | 95      |

*Other reaction conditions: 1 mmol of HMF, 50 mg of cat, 1 bar H2, and 3 mL of H2O.
aldehydes, the RA of ketones is often challenging because of fur-ther used for expanding the reaction scope.

99% FAA yield at full HMF conversion while keeping the other these tests, a catalyst loading in the range 40–50 mg afforded 99% FAA yield at full HMF conversion while keeping the other reaction conditions unchanged. This catalyst loading was further used for expanding the reaction scope.

In a next step of our study, we assessed the catalytic performance of Ni_6AlO_x in the RA of a series of aldehydes and ketones with NH_3 (Table 5). FF can be aminated to give FAM (dimer), which can be produced by hydrolysis and retro-
dol condensation of cellulose, can be transformed into ethanolamine with 85% yield by reaction at 80 °C for 3 h under 5 bar H_2 (entry 9).

We also explored the credentials of Ni_6AlO_x for preparing HMF-derived amines (Table 6). The reaction of HMF with primary and secondary amines can afford the corresponding secondary and tertiary amines in good yield by reaction at 100 °C for 6 h under 3 bar H_2. Aromatic amines such as benzylamine and aniline can react with HMF to produce the corresponding secondary amines with 76 and 85% yield (entries 1 and 2), respectively. A secondary amine such as morpholine can also react with HMF to generate the tertiary amine with high yield (88%, entry 3). Finally, a yield >80% of secondary amines can be achieved with aliphatic amines such as 1-butylamine and ethanolamine (entries 4 and 5).

More importantly, we found that Ni_6AlO_x could catalyze the RA of HMF with NH_3 toward FAA in a gram-scale synthesis with high yield. As shown in Scheme 1, by stirring a mixture of 3 g of HMF and 30 mL of aqueous NH_3 (28 et %) at 90 °C for 12 h under 10 bar H_2 over Ni_6AlO_x, FAA can be obtained with 81% isolated yield.

Finally, we explored the catalyst recycling and reuse using the same operation conditions as in Table 2 (entry 3). The catalyst can be separated and reused in four consecutive runs without apparent loss of activity (Figure 5). Nonetheless, after the fifth and sixth runs, a drop in the HMF conversion is observed, which can be ascribed to a progressive catalyst loss during operation as the turnover number (TON) of the catalyst measured with respect to the bulk Ni keeps almost unchanged at a value of 2.3 mmol FAA/mmol Ni. Noticeably, the catalytic performance can be recovered if the lost catalyst, that is, 20 mg, is compensated by the addition of fresh Ni_6AlO_x. The catalyst keeps its integrity during operation, as can be deduced by the comparison of the XRD patterns and XPS spectra of the Ni 2p, Ni 3p, and Al 2p core levels before and after the first and fifth runs (Figures S6–S8). However, after the fifth run, characteristic reflections ascribed to γ-alumina can be distinguished at 25°, 34°, 37°, 54°, 65°, and 67°, which can be assigned to AL(111), AL(220), AL(311), AL(400), AL(511), and AL(440) (γ-Al_2O_3). JCPDS no: 10-0425, Fd3m cubic unit cell), respectively. This observation suggests a partial recrystallization of the initially amorphous alumina phase during the reaction. The (Ni/Al)_b ratio of the fresh and spent catalyst after the fifth run as analyzed by ICP–OES is 5.2 and 4.9, respectively, suggesting a slight leaching of nickel during the reaction.

■ CONCLUSIONS

Along this study, we have demonstrated that Ni_6AlO_x formulations can behave as efficient and versatile catalysts for the RA of a broad series of biomass-derived aldehydes and ketones in aqueous ammonia at mild reaction conditions. By tuning the Ni/Al molar ratio, Ni_6AlO_x was found to be an optimal formulation. This catalyst offered high selectivity and yield to primary amines by reacting carbonyl compounds with aqueous ammonia. In particular, FF and HMF could react with a variety of primary and secondary amines to afford highly substituted amines. The catalyst could be easily recycled and reused without apparent loss of activity in four consecutive runs.

| catalyst | HMF conversion (%) | FAA yield (%) | FMA yield (%) | mass balance (%) |
|----------|--------------------|--------------|--------------|-----------------|
| Ni_6AlO_x | 65 | 32 | 2.3 | 70 |
| Ni_5AlO_x | 74 | 38 | 1.5 | 66 |
| Ni_4AlO_x | 93 | 85 | 0.6 | 92 |
| Ni_3AlO_x | 100 | 99 | 0.1 | 99 |
| Ni_2AlO_x | 100 | 99 | 0.1 | 99 |
| Ni_AlO_x | 100 | 96 | 0.1 | 96 |
| NiO | 91 | 33 | 3.2 | 45 |
| Raney-Ni | 100 | 48 | 5.6 | 53 |

Table 4. RA of HMF with NH_3 toward FAA in a gram-scale synthesis with high yield. Reaction conditions: 1 mmol of HMF, 49:1 NH_3/HMF, 3 mL of H_2O, 50 mg of cat, 1 bar H_2, and 6 h.

| catalyst loading (mg) | HMF conversion (%) | FAA yield (%) | mass balance (%) |
|-----------------------|--------------------|--------------|-----------------|
| 10 | 100 | 2 | 2 |
| 20 | 79 | 26 | 47 |
| 30 | 88 | 82 | 94 |
| 40 | 100 | 99 | 99 |
| 50 | 100 | 99 | 99 |

Table 4. Influence of the Ni_6AlO_x Loading on the RA of HMF.

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Table 5. RA of Different Carbonyl Compounds over Ni$_6$AlO$_x$.

| Entry | Substrate | Product | H$_2$ pressure (bar) | T (°C) | Time (h) | Yield (%)$^b$ |
|-------|-----------|---------|---------------------|-------|---------|--------------|
| 1$^a$ | ![Substrate Image](image1) | ![Product Image](image2) | 1                   | 100   | 6       | 99           |
| 2     | ![Substrate Image](image3) | ![Product Image](image4) | 4                   | 100   | 5       | 90           |
| 3     | ![Substrate Image](image5) | ![Product Image](image6) | 3                   | 100   | 6       | 86           |
| 4     | ![Substrate Image](image7) | ![Product Image](image8) | 3                   | 100   | 6       | 81           |
| 5     | ![Substrate Image](image9) | ![Product Image](image10) | 2                   | 100   | 10      | 82           |
| 6     | ![Substrate Image](image11) | ![Product Image](image12) | 3                   | 80    | 3       | 83           |
| 7     | ![Substrate Image](image13) | ![Product Image](image14) | 3                   | 100   | 5       | 89           |
| 8     | ![Substrate Image](image15) | ![Product Image](image16) | 3                   | 80    | 3       | 84           |
| 9$^c$ | ![Substrate Image](image17) | ![Product Image](image18) | 5                   | 80    | 3       | 85           |

$^a$Reaction conditions: 1 mmol of the substrate, 49:1 NH$_3$/aldehyde, 50 mg of cat, and 3 mL of H$_2$O. $^b$Isolated yields in entries 1–5 and GC yields in entries 6–9. $^c$0.5 mm mol of the substrate.

Table 6. RA of HMF with Primary and Secondary Amines over Ni$_6$AlO$_x$.$^a$

| Entry | Substrate | Product | Yield (%) |
|-------|-----------|---------|-----------|
| 1$^b$ | ![Substrate Image](image19) | ![Product Image](image20) | 76        |
| 2$^b$ | ![Substrate Image](image21) | ![Product Image](image22) | 85        |
| 3     | ![Substrate Image](image23) | ![Product Image](image24) | 88        |
| 4$^c$ | ![Substrate Image](image25) | ![Product Image](image26) | 86        |
| 5$^c$ | ![Substrate Image](image27) | ![Product Image](image28) | 82        |

$^a$Reaction conditions: 1 mmol of HMF, 1.2 mmol of the amine, 40 mg of cat, 100 °C, 3 bar H$_2$, and 6 h. $^b$100 °C. $^c$Co-solvent (1 mL of H$_2$O + 2 mL of ethanol) was used due to insolubility of fatty amines in H$_2$O.

Figure 5. Recycling test of Ni$_6$AlO$_x$ in the RA of HMF. Reaction conditions as in Table 2 (entry 3). The experiment at run 7 was conducted by adding 20 mg of the catalyst to compensate the catalyst loss along runs 1–6.

Scheme 1. Scale-Up Synthesis of FAA from the RA of HMF.
stirred until complete dissolution. Then, aqueous Na₂CO₃ (20 mL, 1.25 M) was added dropwise and the mixture was stirred for 5 h, followed by centrifugation and washing with deionized water until neutral pH was reached. Finally, the solid was dried at 100 °C in air for 5 h, calcined at 450 °C for 4 h, and reduced at 450 °C for 2 h under 10 cm³(STP)/min H₂ flow using a 10 °C/min heating ramp. The Ni/Al ratio in the formulations was tuned by adjusting the Ni/Al molar ratio in the system. A NiOₓ catalyst was also prepared using the same protocol, but without addition of the Al(NO₃)₃·9H₂O precursor.

RaneyNi was prepared according to a previous study. Briefly, 10.0 g of Ni–Al alloy (50:50 w/w) was slowly added to an aqueous solution of NaOH (6.0 M, 50 mL) under stirring over ice water and a controlled temperature in the range 10–20 °C for 1 h, followed by 30 min at room temperature and heating to 90 °C under stirring for 2 h until no H₂ bubbles were observed. Then, the mixture was cooled down to room temperature and the final black precipitate was washed with distilled water until pH 7 and kept in water or ethanol.

Catalyst Characterization. The bulk metal composition of the catalysts was quantified by ICP analysis using an Activa (HORIBA Jobin-Yvon) Optical Emission Spectrometer. Before the measurements, the samples were dissolved using a mixture of inorganic acids (H₂SO₄, HNO₃, and HF).

TEM was carried out using a Tecnai G2 F30 S-Twin Field microscope operating at 300 kV equipped with energy-dispersive X-ray spectroscopy analysis in the scanning TEM mode. For TEM inspection, the prereduced catalysts were suspended in ethanol by ultrasonication and deposited on carbon-coated copper grids.

The XRD patterns were measured using a STADIP-automated transmission diffractometer (STOE) equipped with an incident-beam curved Ge monochromator with Cu Kα radiation and operated at 40 kV and 150 mA. XPS was used for measuring the surface composition of the catalysts on a Kratos Axis Ultra DLD apparatus equipped with a hemispherical analyzer and a delay line detector. The adventitious C₁s binding energy (285.0 eV) was used as an internal reference. The XRD patterns were measured using a STOE (STADIP) equipped with a pressure gauge and a safety valve. In a typical test, the reactor was charged with 1 mmol of HMF, 3 mL of NH₃·H₂O (28 wt %) solution and 50 mg of the prereduced catalyst. The reactor was sealed and evacuated by applying vacuum followed by H₂ charging. The reactor was then placed on a hot plate equipped with a magnetic stirrer at the desired temperature, the pressure was equilibrated, and the reaction was conducted at variable times.

The reactant (HMF) and the N-products were analyzed and quantified using an Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt % phenyl groups and an FID detector, using dioxane as the internal standard. Besides, the isolated yields were measured by flash column chromatography. The ¹H NMR spectra were measured using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (¹H) and 100 MHz (¹³C). All the spectra were recorded in CD₃OD.

The HMF conversion, the selectivity and yield to N-products, the mass balance, and the TON (FAA) were defined as follows:

\[ \text{Conversion} \, (\%) = 1 - \frac{n_{\text{HMF}}}{n_{\text{HMF,0}}} \]  
\[ \text{Selectivity} \, (i) \, (\%) = \frac{n_i}{n_{\text{HMF,0}} - n_{\text{HMF}}} \]  
\[ \text{Yield} \, (i) \, (\%) = \frac{n_i}{n_{\text{HMF}}} \]  
\[ \text{Mass balance} \, (\%) = 1 - \left[ \text{conversion} \, (\%) - \sum_i \text{yield} \, (i) \, (\%) \right] \]  
\[ \text{TON (FAA)} = \frac{n_{\text{FAA, yield}}}{n_{\text{Ni}} \text{(bulk)}} \]  

where \( n_{\text{HMF}} \) and \( n_{\text{HMF,0}} \) refer to the initial and final HMF mole number, respectively, \( n_i \) indicates the mole number of the N-products, and \( n_{\text{Ni}} \text{(bulk)} \) refers to the mole number of bulk Ni in the reactor.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03516.

Collection of deconvoluted XPS spectra of the Ni 2p, Ni 3p, and Al 2p core levels of the fresh NiₓAlO₉, NiₓAlOₓ, NiₓAlO₉, NiₓAlOₓ, and NiₓAlOₓ and XPS spectra and XRD patterns of the spent NiₓAlO₉ after the first and fifth run (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: marc.pera-titus-ext@solvay.com (M.P.-T.).
*E-mail: fshi@licp.cas.cn (F.S.).

ORCID
Marc Pera-Titus: 0000-0001-7335-1424
Feng Shi: 0000-0001-5665-4933

Notes
The authors declare no competing financial interest.

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