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Supporting Information

Continuous Reductive Amination of Biomass-Derived Molecules over Carbonized Filter Paper-Supported FeNi Alloy

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1. Materials

Iron(III) nitrate nonahydrate (>99%), benzaldehyde (98%), levulinic acid (LA, >98%) were purchased by Acros; nickel(II) nitrate hexahydrate and L-Leucine (≥ 99) were purchased by Roth; furfural (>99%)**,** 5-(hydroxymethyl)-2-furaldehyde (99%), aniline (99.5%), β-Alanine (Bioreagent) and phenethylamine (PEA, 99%) by Aldrich; 3-amino-1-propanol (99%) and L-Alanine (99%) by Alfa Aesar; nitrobenzene (99%) by Fluka; glycine (GR for analysis) by Merck KGaA. All chemicals used were reagent grade and used as supplied.

2. Characterization techniques

XRD measurements were performed on a Bruker D8 diffractometer using Cu $K\alpha_1$ radiation (λ= 1.5418 Å) and a scintillation counter (KeveX Detector). Crystalline size was calculated from XRD pattern using Scherrer Equation,

$$d = K\lambda/(B\cos\theta)$$

where *K* is the constant with value between 0.85 and 0.9, λ is the wavelength of the X-ray (Cu $K\alpha_1$), B is the line broadening at half the maximum intensity (FWHM) in radians, θ is the Bragg angle and *d* the particle size. Reference patterns were obtained from the ICDD PDF-4+ data base (2013 edition). GC-MS analysis was performed using an Agilent Technologies 5975 gas chromatograph equipped with a MS detector and a capillary column (HP-5MS, 30 m, 0.25 mm, 0.25micron). The temperature program used to monitor the reaction on model compounds started with an isothermal step at 50 °C for 2 min, the temperature was then increased to 300°C with a rate of 30°C/min and maintained for 1 min. Qualitative and quantitative analysis were performed with MS library NIST 08 database with a retention index allowance of ± 100. The unknown levulinic acid (LA) concentration was calculated preparing a calibration curve using standard levulinic acid solutions at different concentrations and showed linearity (r^2 = 0.995) between the range of concentrations of interest. The metal content in the catalyst was analyzed using an ICP OES Optima 2100 DV from Perkin Elmer.
^{1}H- and ^{13}C-NMR spectra were measured on a Bruker Spectrospin 400 MHz Ultrashield Spectrometer in deuterated solvents, with chemical shifts referenced to the residual solvent signals unless otherwise stated. For quantification, the proton spectra were recorded using 32 scans and a recycle delay of 1s.
SEM images were performed on a LEO 1550 Gemini instrument. The samples were loaded on carbon coated aluminium holder and measured without any additional coating. TEM images were recorded using a Zeiss EM 912Ω microscope operated at an acceleration voltage of 120 kV.

3. CFP supported FeNi powders preparation

3.4g of lab-grade cellulose filter paper (Macherey-Nagel, ø 55 mm) were impregnated with 7.2 mL of a $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution {mass balance *g* cellulose/ *g* [$Ni(NO_3)_2 \cdot 6H_2O$ + $Fe(NO_3)_3 \cdot 9H_2O$] = 0.76; *n* Fe/*n* Ni= 0.7; overall concentration 1.8M}. The loaded cellulose filter paper was dried overnight at room temperature and then heat-treated at 800 °C for two hours (10°C/min) under nitrogen flux (*n* Fe/*n* Ni= 0.7, calculated by inductively coupled plasma-optical emission spectroscopy).

4. Catalytic tests

All the reactions were performed using a H-Cube Pro™ reactor equipped with a hydrogen feed (generated in situ) and a liquid feed. Solutions containing the amine and the corresponding carbonyl compound were freshly prepared at the desired concentration, and directly pumped, if not otherwise stated, through a 70mm column packed with the carbon supported FeNi powder (~600 mg) using a HPLC pump. The residence time was controlled by adjusting the flow rate. In this study flow rates of 0.1-0.5 mL min^{-1} were used. The hydrogen produced in situ was mixed with the eluent at $10<PH_2<85$ bar before reaching the packed cartridge. After equilibrating the system at the desired temperature (25<T<150 °C), samples from the eluate were collected and analyzed by GC-MS or NMR. For Table 3 the uncorrected GC conversion and selectivity were calculated as follows:

Conversion: $1 - \frac{A_4}{A_2+A_3+A_4+A_5} \times 100$ (eq.1)

Selectivity: $\frac{A_5}{A_3+A_5} \times 100$ (eq.2)

with A_2 corresponding to the area of PEA, A_3 to the area of the ethylphenethyl amine by-product, A_4 to the area of the imine obtained from the condensation of PEA and LA, A_5 to the area of the corresponding hydrogenated amine.

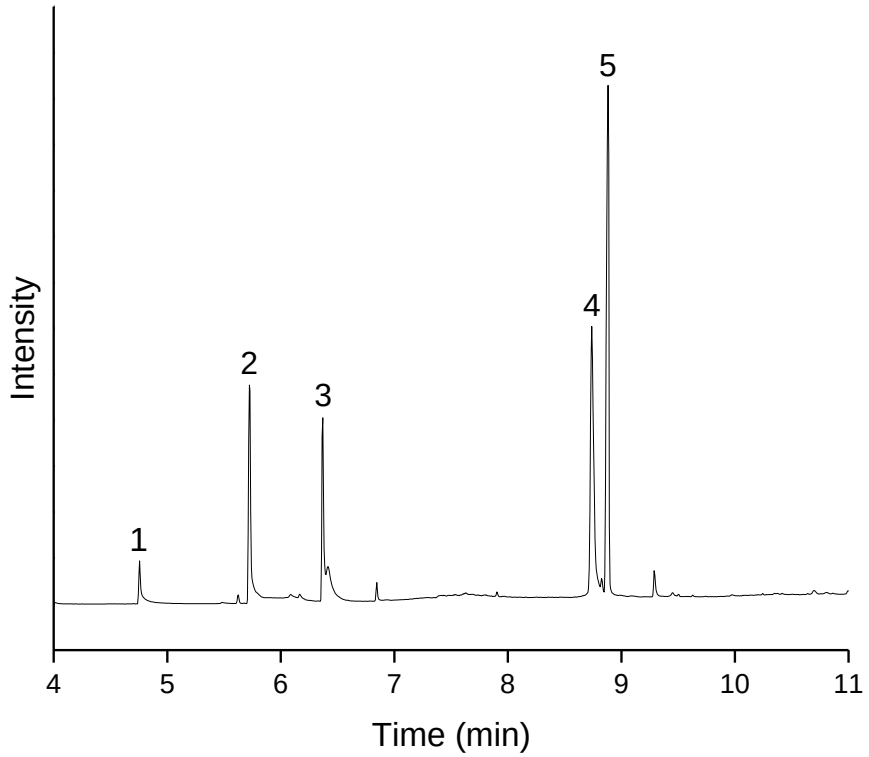

Fig. S1. Exemplary GC-MS spectrum of the imine compound used in Table 3, entry 1, obtained by condensation of levulinic acid with phenethylamine (mole ratio 1:1). Peak 1: γ-valerolactone; Peak 2: phenethylamine; Peak 3: ethylphenethyl amine, Peak 4: imine; Peak 5: amine.

5. Imine preparation from amino acids

When amino acids were employed for reductive amination reactions the preparation of the corresponding imine was performed as described in the following.

Amino acid (40 mmol) was suspended in methanol and a solution of NaOH (1 eq.) in methanol (40 mL) was added dropwise. The mixture was stirred until complete dissolution, and then the solvent was evaporated *in vacuo* to afford a transparent gel. At this point we employed two different procedures in order to afford the required imine:

- In the case of alanine the gel was diluted in EtOH at the desired concentration followed by the addition of hydroxymethylfurfural (40 mmol). The resulting light brown solution is stirred for 3h before the catalytic experiments.
- For Glycine, Leucine and b-Alanine the gel was dissolved in an EtOH/H_2O mixture (25:1 v/v) and subsequently furfural (40 mmol) was added. The solvent was slowly removed under reduced pressure at 50 °C using a rotary evaporator. The residue was freeze-dried to remove the residual water and an analytical sample was collected to assess the formation of the imine via ^{1}H-NMR analysis (see Fig. S2 for an exemplary ^{1}H spectrum). Thus, the compound was dissolved in MeOH

and stirred for 3h before the continuous hydrogenation reactions.

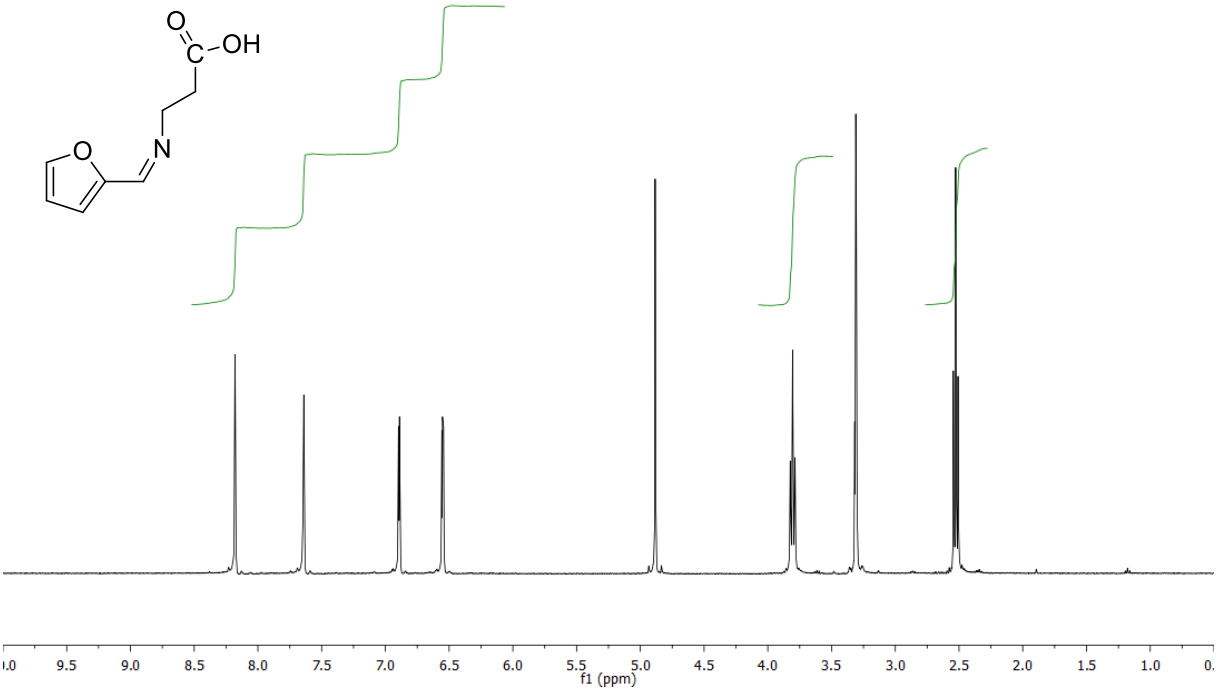

Fig. S2. Exemplary ^{1}H spectrum of the imine compound used in Table 2, entry 3, obtained by condensation of furfural with β-alanine. ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.18 (broad s, 1H), 7.64 (d, *J* = 1.8 Hz, 1H), 6.89 (d, *J* = 3.5, 1H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.81 (td, *J* = 7.3, 1.3 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H).

6. Biorefinery experiments

The acidic hydrolysis of the biomass was performed following literature known procedures without further optimizations. Briefly, glucose (540 mg) was loaded in a Teflon lined, stainless steel autoclave (Parr Instruments, 45 ml) followed by 0.5 M H_2SO_4 (15 mL). The autoclave was placed into an oven and the reaction was heated up to 220 °C for 8 hours, then allowed to cool to room temperature. The solution was filtered and the volume of the solution was measured. The final water phase was extracted three times with 2-MeTHF and the levulinic acid content was quantified by GC-MS (39% mol yield) thus, phenethylamine (PEA, 17 mM) was added to the LA solution (34 mM) and reacted at a flow rate of 0.1 mL/min, 85 bar H_2 and 150 °C. The so obtained pyrrolidone was extracted with acidic water (0.1M HCl) and characterized by GC-MS (see Fig. S1) and ^{13}C NMR (see Fig. S2). ^{13}C NMR (100 MHz; C_4D_8O) δ 20.1, 27.9, 30.5, 34.9, 42.5, 54.0, 126.9, 129.1, 129.6, 140.6, 173.9. EI-MS (m/z): $[M]^+$ calcd. for $C_{13}H_{17}NO$: 203,13, found, 203.1.

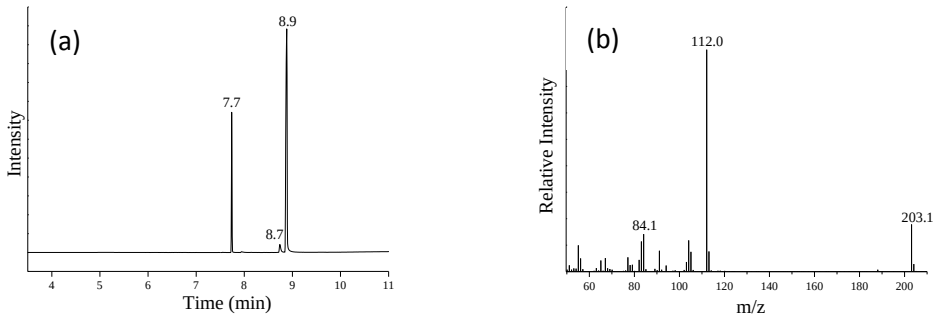

Fig. S3 a) GC chromatogram of crude 5-methyl-1-phenethylpyrrolidin-2-one [retention time = 8.9 min; residual imine retention time = 8.7 min; butylated hydroxytoluene stabilizer retention time = 7.7 min.] b) Mass spectrum of 5-methyl-1-phenethylpyrrolidin-2-one obtained by reductive amination of LA and PEA and successive acid water extraction.

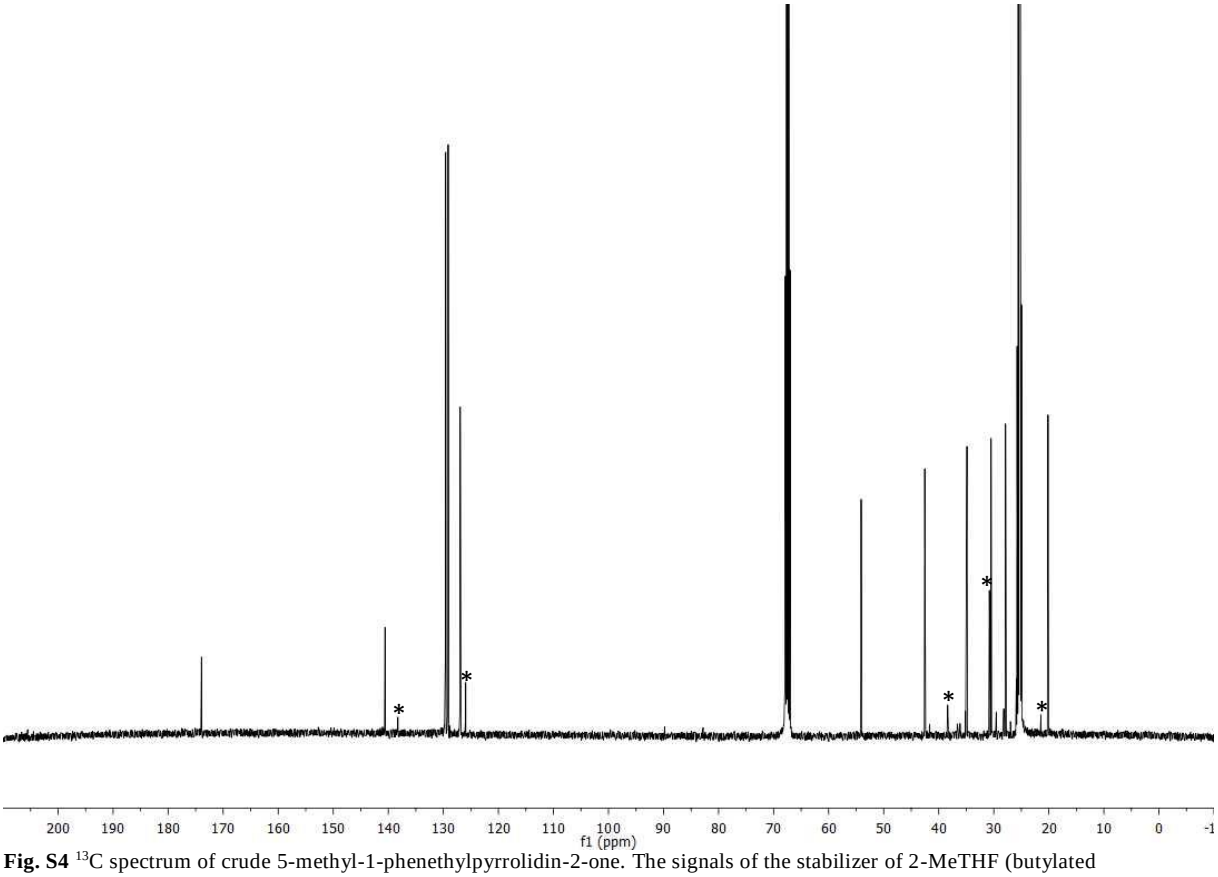

Fig. S4 ^{13}C spectrum of crude 5-methyl-1-phenethylpyrrolidin-2-one. The signals of the stabilizer of 2-MeTHF (butylated hydroxytoluene, BHT) are marked with an asterisk.

7. TEM and SEM analysis

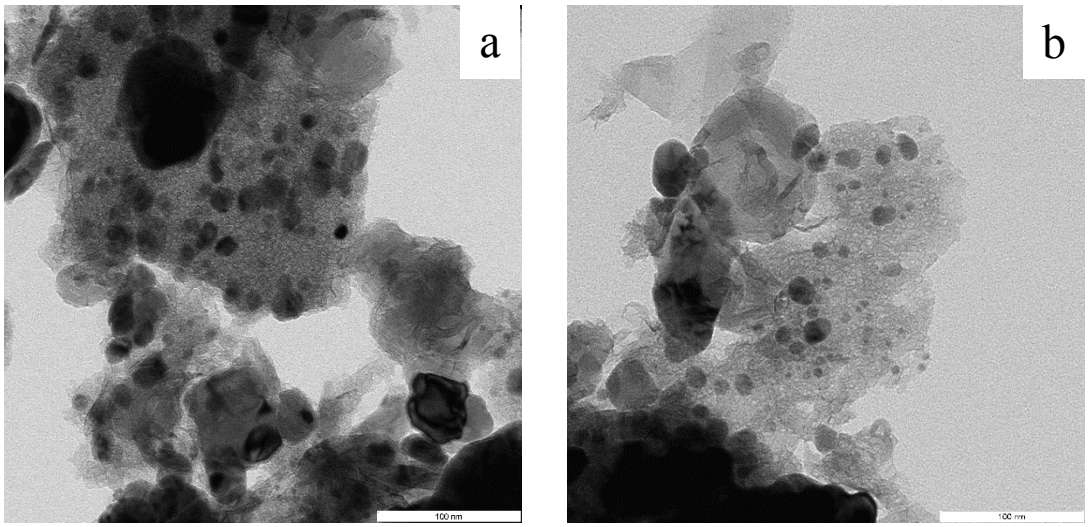

Fig. S5. TEM images of the carbonized filter paper supported FeNi alloy: a) as synthesized, b) after 60 h of catalytic experiments. The average size distribution value of FeNi alloy nanoparticles was 27 (pre-catalysis) and 26 nm (post-catalysis).

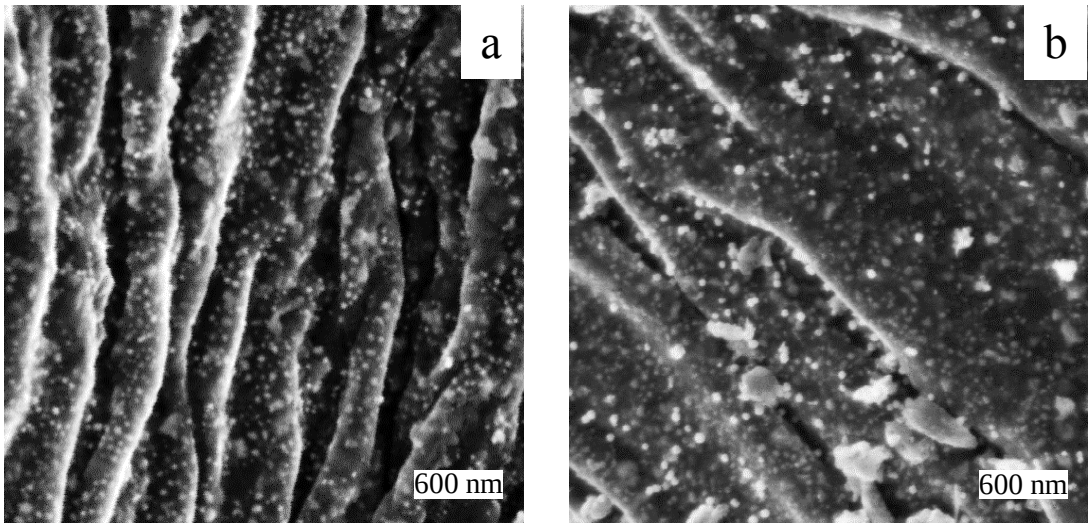

Fig. S6. SEM images of the carbonized filter paper supported FeNi alloy: a) as synthesized, b) after 60 h of catalytic experiments. The average size distribution value of FeNi alloy nanoparticles was 32 (pre-catalysis) and 31 nm (post-catalysis).