Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

FeNi nanoparticles with carbon armor as sustainable hydrogenation catalyst: towards biorefineries

Gianpaolo Chieffi,[a] Cristina Giordano,[a] Markus Antonietti,[a] Davide Esposito*[a]

[a] Max-Planck-Institute of Colloids and Interfaces, 14424 Potsdam, Germany.

*Corresponding Author

E-Mail: davide.esposito@mpikg.mpg.de

Table of Contents

1. Materials

Iron(III) nitrate nonahydrate (>99%), benzaldehyde (98%), 2-cyclohexen-1-one (97%), cyclohexanone (99.8%), levulinic acid (>98%), α-terpinene (90%) were purchased by Acros; nickel(II) nitrate hexahydrate was purchased by Roth; methanesulfonic acid (≥99.5%), DMSO (≥99.9%), styrene, furfural (>99%), D-(+)-glucose, D-(+)-xylose, D-(-)-fructose by Aldrich; phenylacetylene (98%) was purchased by Alpha; nitrobenzene (99%) by Fluka and benzonitrile (99%) by Merck. All chemicals used were reagent grade and used as supplied.

2. Characterization

Nitrogen sorption experiments were performed using Quantachrome Quadrasorb at the temperature of liquid nitrogen. All the samples were degassed at 150 °C for 20 hours before measurements and analyzed with a QuadraWin software (version 5.11). SEM images were performed on a LEO 1550 Gemini instrument. Energy dispersive X-ray (EDX) analysis was performed on a JEOL (JSM – 7500 F) instrument with an Oxford Instruments X-MAX 80mm^2 detector. 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. High resolution TEM measurements were recorded on a CM200FEG (Philips) microscope, operated at 200 kV and equipped with a field emission gun. XRD measurements were performed on a Bruker D8 diffractometer using Cu Kα_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 Kα_1), B is the full width high maximum, FWHM (in radians) of the peak due to size effect, θ is the Bragg angle and d the particle size. Reference patterns were obtained from the ICDD PDF-4+ data base (2011 edition). Elemental analysis was performed as combustion analysis using a Vario Micro device. 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 analysis was performed with MS library NIST 08 database with a retention index allowance of ± 100.

HPLC analysis was performed using Agilent 1200 series equipped with a Phenomenex Rezex ROA-Organic Acid H+ (8 % cross-linked sulfonated styrene-divinylbenzene; length 300 mm, 7.8 mm i.d., flow 0.4 mL/min) using isocratic aqueous H_2SO_4 (5 mM) as eluent and RI (refractive index) as detector. Quantification was performed by external standard method. Calibration curves were prepared using solution of the analytes at different concentrations. The curves showed linearity in the range of concentrations of interest (correlation coefficient $R^2 \geq 0.998$). Reactions were carried out multiple times and showed good reproducibility.

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 $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution [mass balance [*g* cellulose/(*g* $Ni(NO_3)_2 \cdot 6H_2O$ + $Fe(NO_3)_3 \cdot 9H_2O$)] = 0.76), *n* Ni/*n* Fe= 1.4, overall concentration 1.8M]. The loaded cellulose filter paper loaded was dried overnight at room temperature and then heat-treated at 800 °C for two hours (10°C/min) under nitrogen flux.

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 of the starting materials at the desired concentration were pumped through a 70mm column packed with CFP supported FeNi powders (0.77 g), using a HPLC pump. The residence time was controlled by adjusting the flow rate. In this study a flow rate of 1 mL min^{-1} or 0.3 mL min^{-1} was used. The hydrogen produced in situ was mixed with the eluent at 10 or 50 bar before reaching the packed cartridge. After equilibrating the system at the desired temperature ($25<T<150$ °C) over a period of 20 minutes, samples from the eluate were collected and analyzed by GC-MS or HPLC (RI).

5. Figures

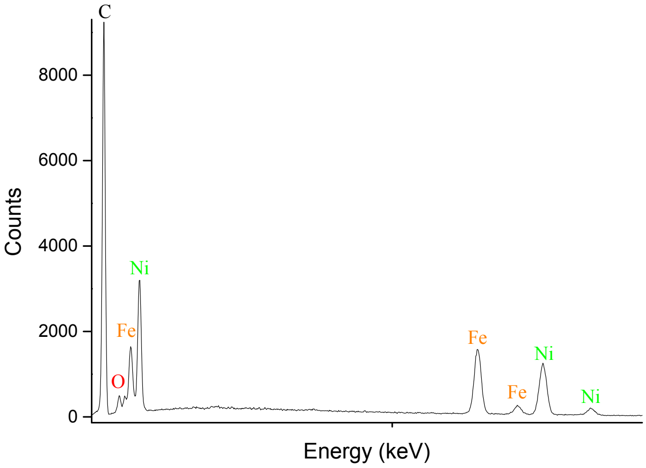

Fig. S1 EDX spectrum of CFP supported FeNi alloy.

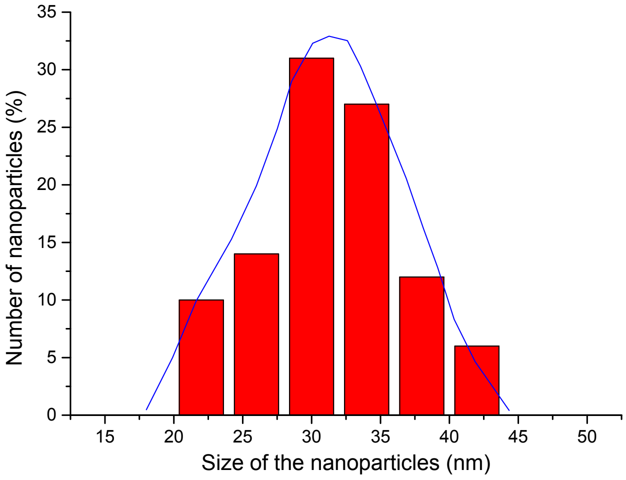

Fig. S2 Bar diagram with its fitting curve of the diameter distribution of FeNi alloy nanoparticles calculated by SEM analysis.

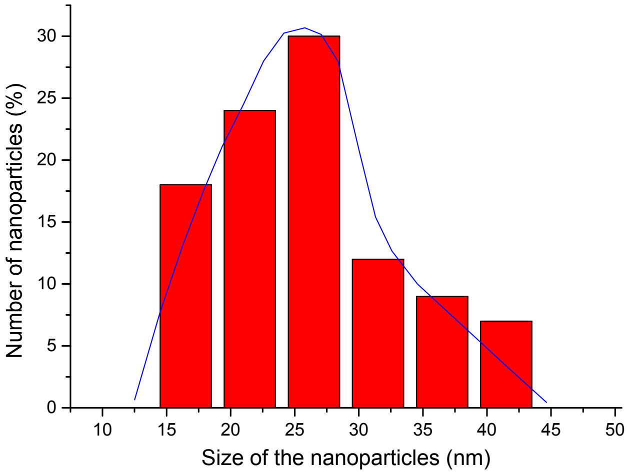

Fig. S3 Bar diagram with its fitting curve of the diameter distribution of FeNi alloy nanoparticles calculated by TEM analysis.

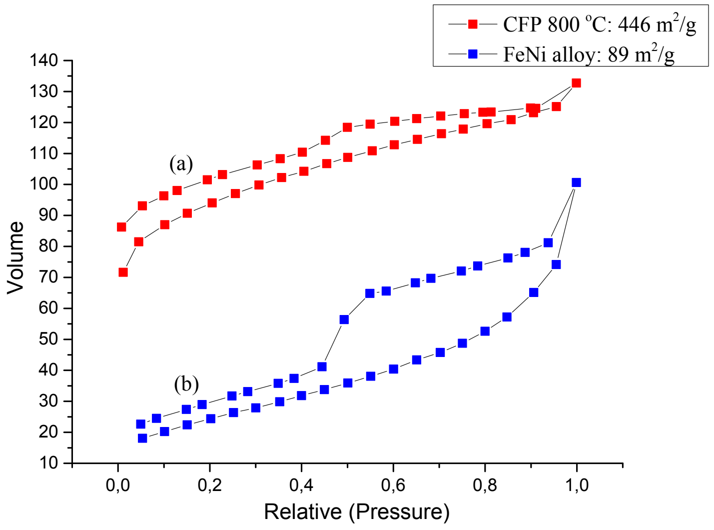

Fig. S4 Nitrogen absorption analysis of the annealed at 800 °C (10 °C/min) for 2h under nitrogen flux cellulose filter paper (a) and of the CFP supported FeNi alloy (b).

6. HMF synthesis and hydrogenation

Fructose (0.5 g, 2.8 mmol) and methane sulfonic acid (0.18 mL, 2.8 mmol) were dissolved in DMSO (2 mL) in a round-bottom flask and heated at 100 °C for 1 hour. The reaction was allowed to cool to room temperature, then a saturated aqueous solution of $NaHCO_3$ was added until the pH became neutral. The solution was extracted with ethylacetate. The GC chromatogram in Figure S5 (a) of the extracted solution showed a peak at a retention time (RT) of 6.79 min relative to the presence of HMF as confirmed by the corresponding mass spectrum (b) (molecular peak of HMF at m/z 126). Traces of DMSO were found at lower RT (3.87 min).

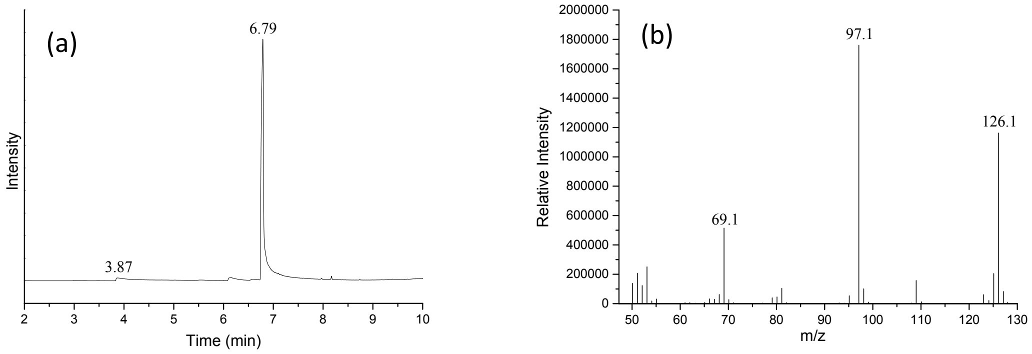

Fig. S5 GC chromatogram (a) and mass spectrum (b) of HMF obtained by acid-catalysed dehydration of fructose in DMSO followed by extraction with ethylacetate.

The organic layer was concentrated in vacuum affording crude HMF (2.1 mmol, 0.21 mL) which was redissolved in ethanol (0.1 M solution) for the hydrogenation using the conditions described above. The GC chromatogram of the main hydrogenated product 2,5-BHF (a) (RT = 6.74 min) and the corresponding mass spectrum (b) (molecular peak of 2,5-BHF at m/z 128) are reported in Figure S6. Finally, the activity of the catalyst was checked hydrogenating phenylacetylene at the same conditions of entry 1. The conversion of phenylacetylene was quantitative and its selectivity toward ethylbenzene remained >99%.

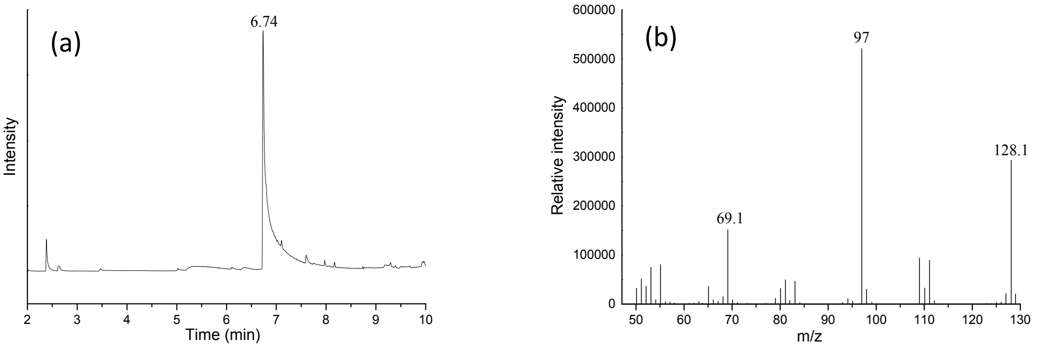

Fig. S6 GC chromatogram (a) and mass spectrum (b) of 2,5-BHF obtained by hydrogenation of HMF using the CFP supported FeNi catalyst.

7. Time on stream experiments

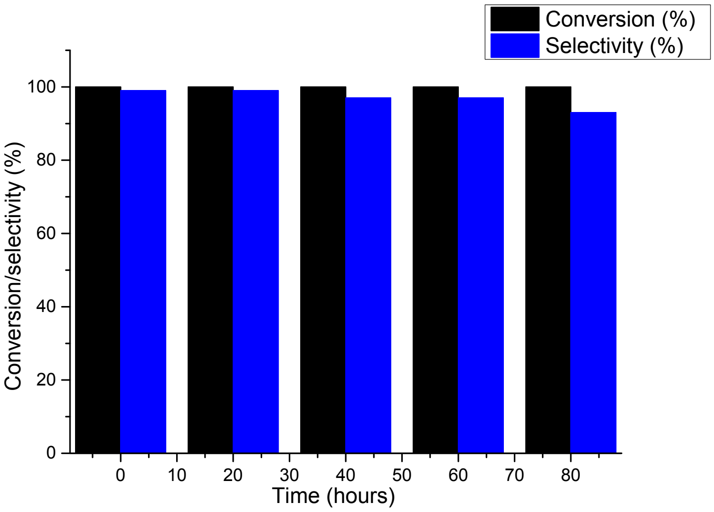

Fig. S7 Conversion and selectivity to ethylbenzene versus time on stream evaluated for the continuous-flow high pressure hydrogenation of phenylacetylene.