Valorization of lignin waste from hydrothermal treatment of biomass: towards porous carbonaceous composites for continuous hydrogenation

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1. Materials

Iron(III) nitrate nonahydrate (>99%) was purchased by Acros; nickel(II) nitrate hexahydrate was purchased by Roth; phenylacetylene (98%) was purchased by Alpha and nitrobenzene (99%) by Fluka; Lindlar catalyst was purchased by Sigma-Aldrich. The rye straw was provided by TU Hamburg (41.2% Cellulose, 21.1% Hemicellulose, 19.5% Lignin, 18.1% Others) and was ground to a maximum size limit of 0.8 mm for easier processing.

2. Characterization techniques

Nitrogen sorption measurements were accomplished with N_2 at 77 K after degassing the samples at 150 ° C under vacuum for 20 hours using a Quantachrome Quadrasorb SI porosimeter. The apparent surface area was calculated by applying the Brunauer–Emmett–Teller (BET) model to the isotherm data points of the adsorption branch in the relative pressure range $p/p_0 < 0.3$. The pore size distribution was determined using the non-local density functional theory (NLDFT).
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 aluminum holder and sputter-coated in case of the ML and CDL. TEM images were recorded using a Zeiss EM 912Ω microscope operated at an acceleration voltage of 120 kV. 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 line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, 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). 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. FT-IR spectra were recorded on a Thermo Scientific FT-IR spectrometer (Nicolet™ iS5 Spectrometer equipped with an iD5 ATR accessory). TG measurements were performed by using a Netzsch TG 209 F1 Libra at heating rate of 10 K min^{-1} under nitrogen at 20 mL/min.

3. General procedure for the hydrothermal treatment of biomass in autoclave, isolation of lignin, demineralization process and catalyst preparation.

A 1L stainless steel autoclave equipped with an overhead mechanical stirrer was charged with rye straw (40.7 g). $Ba(OH)_2$ (96 g) and water (350 mL) were added and the autoclave was sealed. A stirring of 100 rpm was applied. The reactor was heated up to 225 °C over a period of 1 hour during which, an endogenous pressure of ca. 30 bar is reached. Thus, the reaction was cooled down to rt, and the crude mixture was filtered. The solid filtrate (20.6 g) was dried in the vacuum oven, part of it (19.2 g) was heat-treated at 800 °C under N_2 (10 °C/min), washed with aqueous HCl 1 N (20 mL/g) then with an excess of water, filtered and dried overnight at 50 °C in vacuum (16% of the initial weight was retained). 1.5 g of the obtained powders were impregnated with 1.92 g of $[Fe(NO_3)_3{\cdot}9H_2O]$ and 1.92 g of $[Ni(NO_3)_2{\cdot}6H_2O]$ (nNi/nFe= 1.4) previously dissolved in ethanol and then stirred for 5 h. At this point the solution was heated up to 80°C as long as the ethanol was evaporated. The dried powder were heat-treated at 800 °C under N_2 (10 °C/min) affording 3.3 g of the product.

4. Catalytic tests

All the reactions were performed using a H-Cube Pro™ flow reactor. The hydrogen was generated in situ by the electrolysis of water within an electrolytic cell and then mixed with a solution of the reactant at the desired concentration. The solutions of the starting materials were pre-heated and then pumped through a 70mm column packed with the desired catalyst [FeNi-CDL (290 mg), or CDL (110 mg) or Lindlar catalyst (290 mg)] using a HPLC pump. The residence time was controlled by adjusting the flow rate. In this study a flow rate of 0.3-0.5 mL min^{-1} was used. The hydrogen produced in situ was mixed with the eluent at 1-50 bar before reaching the packed cartridge. After equilibrating the system at the desired temperature (25<T<150 °C) over a period of 10-20 minutes, samples from the eluate were collected and analyzed by GC-MS.

5. Figures

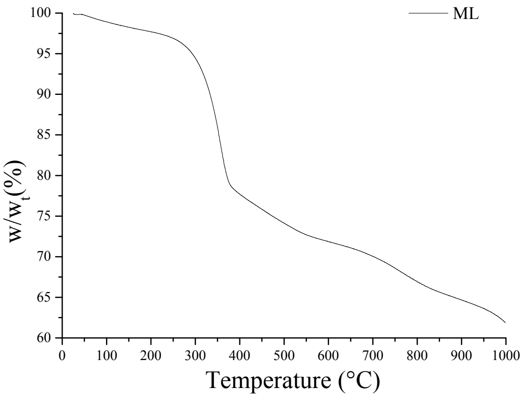

Fig. S1 TGA of the ML (recorded under nitrogen atmosphere, 10 °C/min).

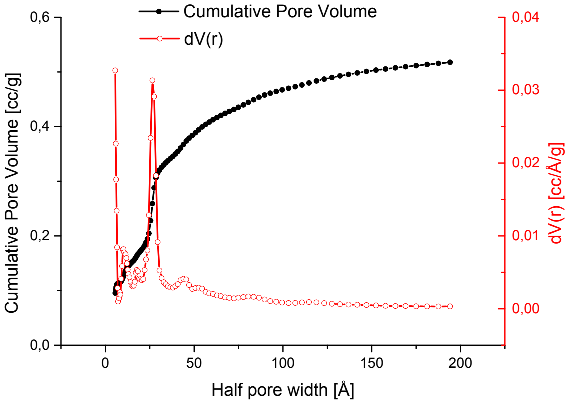

Fig. S2 Pore size distributions of CDL.

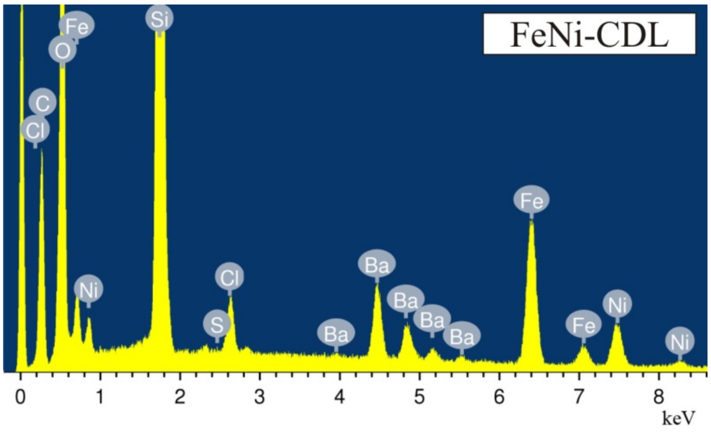

Fig. S3 EDX spectrum of FeNi-CDL corresponding to SEM analysis in Fig. 3.

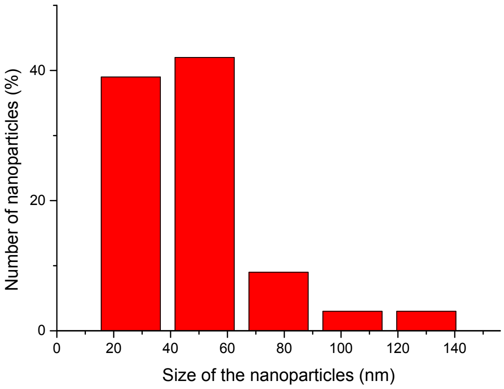

Fig. S4 Average size distribution of non-aggregated FeNi alloy nanoparticles calculated by TEM analysis (high magnification image of Fig. 5b).

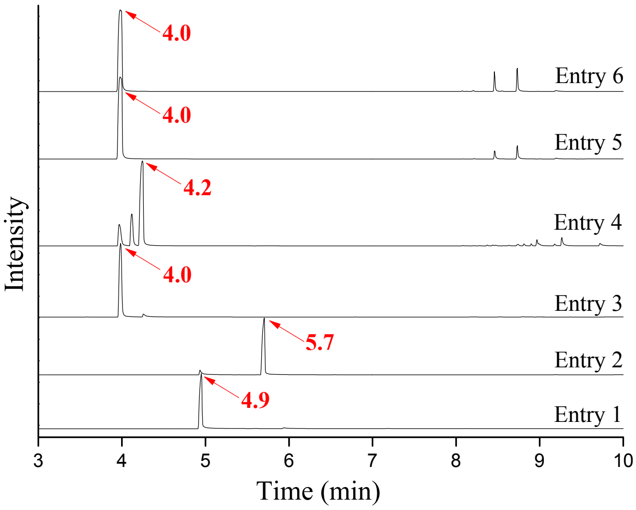

Fig. S5 GC chromatograms relative to entries 1-6 of Table 1. The retention time of the main product are labeled in red.

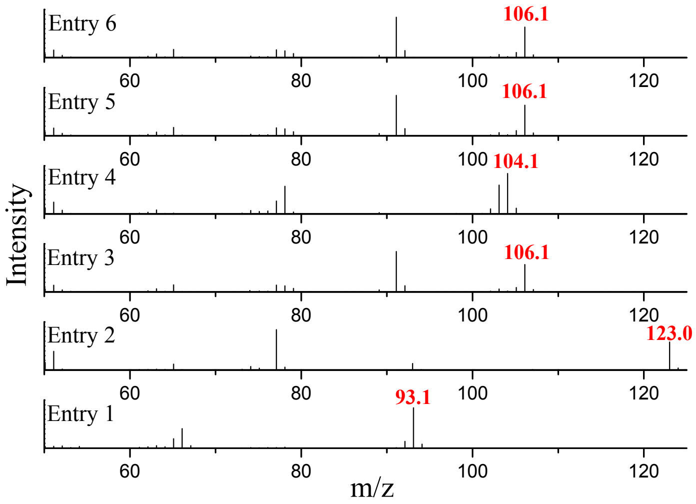

Fig. S6 Mass spectra relative to entries 1-6 of Table 1. The m/z value of the main product are labeled in red.

6. Tables

Table S1. Sample compositions obtained from the elemental analysis of the ML, CDL, FeNi-CDL and ICP-OES analysis of the FeNi-CDL

	Elemental analysis					**ICP analysis**			
Sample	**C% mass**	**N% mass**	**H% mass**	**S% mass**	**C/N**	**Ba mass%**	**Si mass%**	**Fe mass%**	**Ni mass%**
ML	16.62	0.14	2.42	0.96	103.45				
CDL	21.67	0.26	1.80	1.01	87.50				
FeNi-CDL	10.52	0.27	0.98	0.90	19.77	8	16	14	22