Supporting Information

One-pot synthesis of Ni-NiFe$_2$O$_4$/carbon nanofibers composites from biomass for selective hydrogenation of aromatic nitro compounds

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Experimental Section

Materials. The biomass used in this work is fir sawdust, a naturally abundant lignocellulosic biomass waste. Prior to use, the biomass was first washed to remove the impurity particles and dried at 378 K overnight. Afterwards, the sawdust was crushed through a high-speed rotary cutting mill, and the biomass with the particle size smaller than 120 mesh were collected. The elemental composition and proximate analysis of the sawdust were reported in our previous work.[1]

The precursor for the Ni-mCNFs was the Ni, Fe-preloaded biomass, and prepared in a biosorption process employing sawdust as adsorbent at ambient temperature. Briefly, 10.0 g of sawdust and 1,000 mL aqueous solution with 10 mmol L^{-1} of $FeCl_3$ and 10 mmol L^{-1} $NiCl_2$ were mixed in a flask and shaken in a constant temperature oscillator at 200 rpm for 300 min. Thereafter, the water in the mixture was evaporated under reduced pressure. Finally, the solid residue was dried again at 378 K to remove the moisture and the Fe, Ni-preloaded biomass with a Fe, Ni contents of approximately 1.0 mmol g^{-1} was obtained.

Other chemicals, including nitrobenzene, p-nitrophenol, p-chloro-nitrobenzene, p-nitro-benzaldehyde, and methanol, etc., were analytically pure and purchased from Sinopharm Chemical Reagent Co., Shanghai, China, and used as received.

Synthesis of the Ni-NiFe$_2$O$_4$/carbon nanofibers composites. The Ni-NiFe$_2$O$_4$/CNFs was synthesized by direct pyrolysis of $NiCl_2$ and $FeCl_3$-preloaded biomass under anaerobic condition, which was conducted in a pyrolyzed reactor described previously.[2] Briefly, 5.0 g of the $NiCl_2$/$FeCl_3$-preloaded biomass was

placed in the feed pipe under a 400 mL min^{-1} of N_2 flow (maintaining for 20 minutes to remove air from the pyrolysis system). Once the temperature rose to the desired value (e.g., 873 K), the biomass was feed into the quartz tubular reactor through a piston for pyrolysis. The volatiles produced in the pyrolysis process were swept out by a N_2 flow of 200 mL min^{-1}, and condensed by cold ethanol to obtain bio-oil. When the fast pyrolysis process was accomplished, the solid residue remained in the heating zone for another 1 h for further carbonization. Finally, the reactor was moved out of the heating zone and cooled under the N_2 flow (200 mL min^{-1}) to room temperature, and the Ni-NiFe$_2$O$_4$/CNFs were obtained.

Characterization. The Ni contents of the Ni-NiFe$_2$O$_4$/CNFs were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, Perkin-Elmer Co., Waltham, MA, USA) after a preliminary digestion performing with concentrated sulfuric acid and hydrogen peroxide in an oil-bath at 473 K. The surface morphology of the Ni-NiFe$_2$O$_4$/CNFs was observed by scanning electron microscopy (SEM, Sirion 200, FEI electron optics company, USA) and transmission electron microscopy (TEM, JEOL-2100F, Japan). The texture features of the Ni-NiFe$_2$O$_4$/CNFs were analyzed by N_2 adsorption-desorption isotherms, which were conducted at 77 K with a Micromeritics Gemini apparatus (ASAP 2020 M+C, Micromeritics Co., USA). Specific surface areas of the Ni-NiFe$_2$O$_4$/CNFs were calculated by the Brunauer, Emmett, and Teller (BET) method, while their pore volumes were calculated by the amount of nitrogen adsorbed at a relative pressure of 0.99. The Raman analysis of the Ni-NiFe$_2$O$_4$/CNFs was performed in a Laser Raman

spectrometer (LabRamHR, HORIBA Jobin Yvon. Co., France). The radiation source was a laser operating at a wavelength of 514 nm and a power of 25 mW. X-ray diffraction (XRD) analysis of the Ni-NiFe$_2$O$_4$/CNFs was performed in an 18 kW rotating anode X-ray diffractometer (MXPAHF, Rigaku, Japan) using nickel-filtered Cu Kα radiation source (30 kV/160 mA, λ=0.154056 nm). The samples were scanned from 20° to 80° with the scan rate (2θ) of 0.02° per second. The diffraction peaks were assigned to the corresponding crystalline phases by comparison with the powder diffraction files from Joint Committee on Power Diffraction Standards (JCPDS). The surface composition and chemical state of the Ni-NiFe$_2$O$_4$/CNFs were studied by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed in a Constant Analyzer Energy (CAE) mode (70 eV pass energy for survey spectra and 20 eV for high resolution spectra) through a Thermo VG-Scientific spectrometer (ESCALAB250, USA) with a monochromatized Al Ka radiation (1486.92 eV).

Catalytic hydrogenation reaction. The catalytic activities of the Ni-NiFe$_2$O$_4$/CNFs were evaluated by hydrogenation of nitrobenzene with H$_2$ at different pressures. Typically, 0.1 g of the Ni-NiFe$_2$O$_4$/CNFs catalyst was mixed with 100 mL of absolute methanol containing 123 mg (1 mmol) of nitrobenzene and transferred into a 100-mL zirconium autoclave reactor. Then the reactor was sealed and flushed with H$_2$ for 5 times to remove the air. Afterwards, the autoclave reactor was filled with H$_2$ to desired pressures (e.g., 0-5 MPa), and the temperature increased from room temperature to 423 K within 30 min and maintained for 120 min. The hydrogenation was performed at 423 K with continuously stirring. When the reaction was completed,

the reactor was cooled to room temperature in a water bath and vented the H_2 to ambient pressure. The reaction mixture was then separated with a extern magnet and the liquid was analyzed with a gas chromatography (Model 1690, Kexiao Co., Hangzhou, China) equipped with a capillary column (1.0 μm, 50 m, and 0.25 mm) and a flame ionization detector. The conversion of reactant and selectivity of products were calculated using the following equations (Eqs. 1-2):

$$\text{Conversion (\%)} = \frac{C_{r0} - C_{rt}}{C_{r0}} \times 100\% \tag{1}$$

$$\text{Selectivity (\%)} = \frac{C_{pt}}{C_{r0} - C_{rt}} \times 100\% \tag{2}$$

where C_{r0} is the initial concentration (mmol) of the reactant, C_{rt} is the concentration (mmol) of reactant at time t (min), and C_{pt} is the concentration (mmol) of the product at time t (min). The separated catalyst was washed with absolute methanol several times and dried at 343 K overnight. The dried catalyst was then used in another hydrogenation reaction. After 7 times reused, the regenerated catalyst was analyzed with XRD and XPS to evaluate its stability.

Reference

1.   Liu, W.-J.; Tian, K.; Jiang, H.; Zhang, X.-S.; Ding, H.-S.; Yu, H.-Q., Selectively Improving the Bio-Oil Quality by Catalytic Fast Pyrolysis of Heavy-Metal-Polluted Biomass: Take Copper (Cu) as an Example. *Environmental Science & Technology* **2012,** *46*, 7849-7856.
2.   Liu, W.-J.; Zeng, F.-X.; Jiang, H.; Yu, H.-Q., Total recovery of nitrogen and phosphorus from three wetland plants by fast pyrolysis technology. *Bioresource Technology* **2011,** *102*, (3), 3471-3479.

Table S1. The Texture Feature (Surface Area, Pore Volume and Sizes) of the Ni-NiFe$_2$O$_4$/CNFs.

Items	Values
Single point surface area (m^2 g^{-1})	359.8
BET surface area (m^2 g^{-1})	348.4
t-Plot micropore area (m^2 g^{-1})	290.1
t-plot external surface area (m^2 g^{-1})	58.3
total pore volume (cm^3 g^{-1})	0.21
t-Plot micropore volume (cm^3 g^{-1})	0.13
average pore size (nm)	2.40
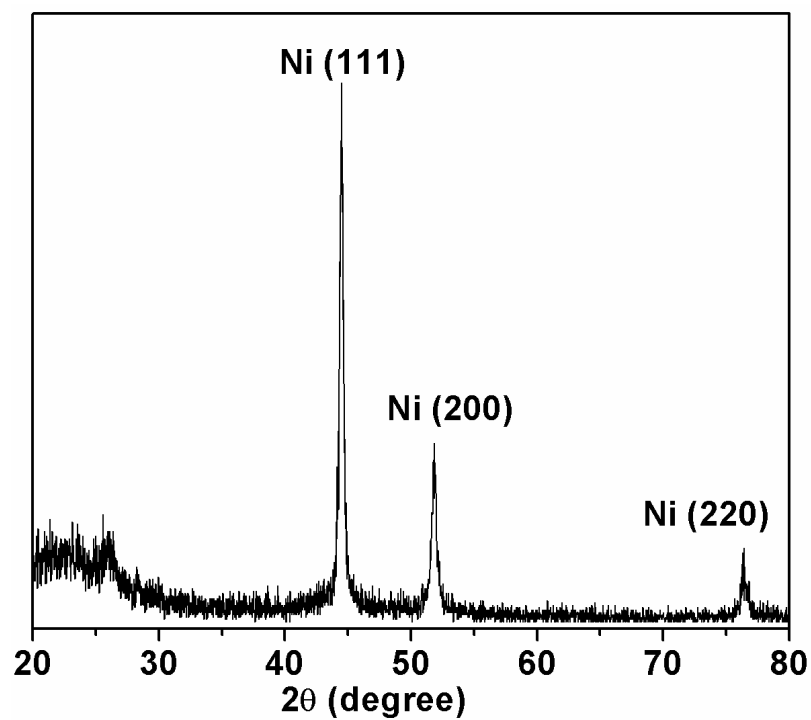
Fig. S1. XRD pattern of the amorphous carbon supported Ni metallic NPs prepared from NiCl$_2$ preloaded biomass.
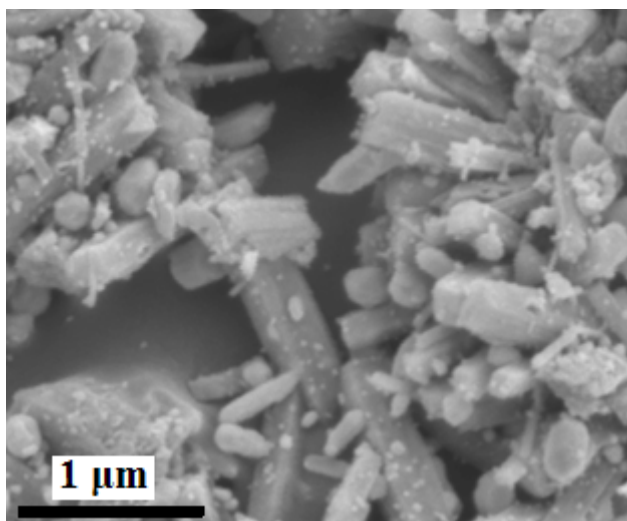
Fig. S2. SEM images of the amorphous carbon supported Ni metallic NPs prepared from $NiCl_2$ preloaded biomass.
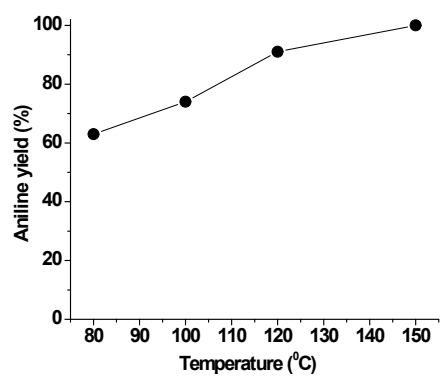
Fig. S3. The yield of aniline at different temperatures (H_2 pressure 1.5 MPa)
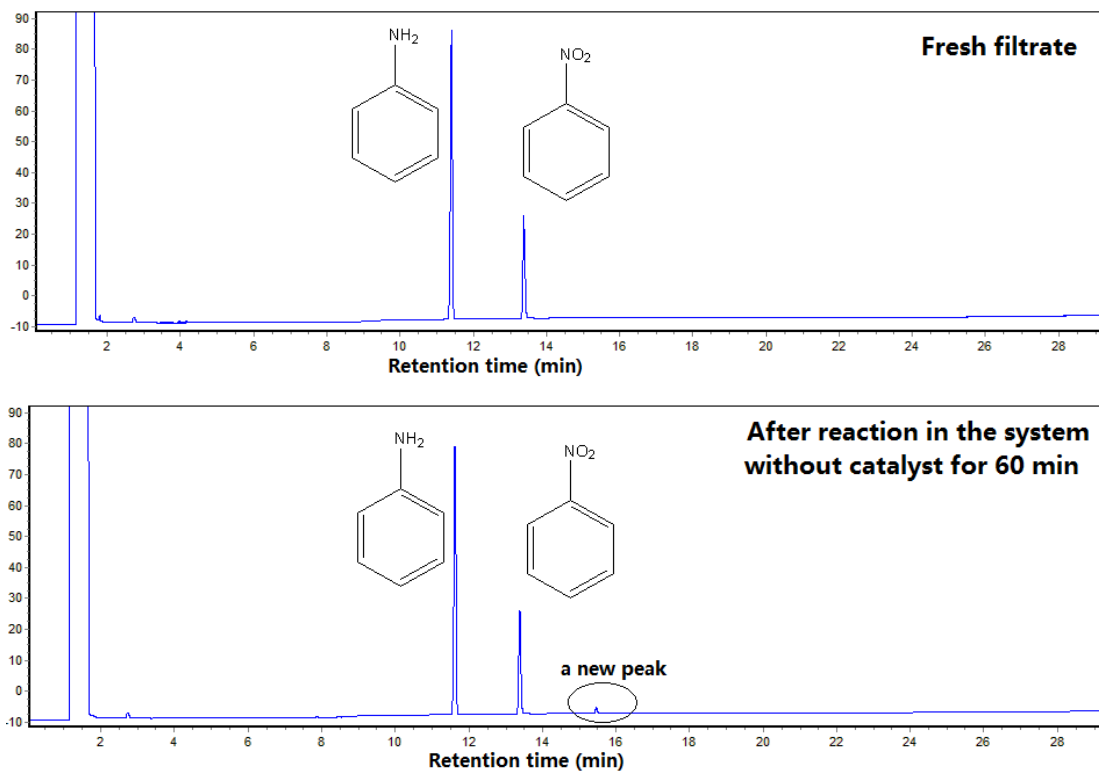
Fig. S4. The GC spectra of the filtrate.

This phenomenon can be explained that in the catalytic system, the H_2 can be activated by the catalyst to form the active H atoms, and the nitrobenzene can react with these activated H atoms preferentially to form the final product, aniline. While in the system without catalyst (after filtration), the H_2 cannot be activated to form the active H atoms, and therefore, the nitrobenzene cannot further convert to the aniline. However, it still has some aniline which formed in the catalytic system (before filtration), and this aniline can react with the nitrobenzene in the system without hydrogenation catalyst. Form the GC spectra of the filtrate (Fig. S3), it can be seen that in the fresh filtrate which is just obtained from the catalyst system, there are only two main compounds found, i.e., the nitrobenzene and aniline, confirming that there are no detectable azoxybenzene or azobenzene byproducts in the catalytic system. While in the filtrate after reaction in the system without catalyst for 60 min, there is a new small peak found, which may be attributed to the product formed in the reaction between the nitrobenzene and aniline.
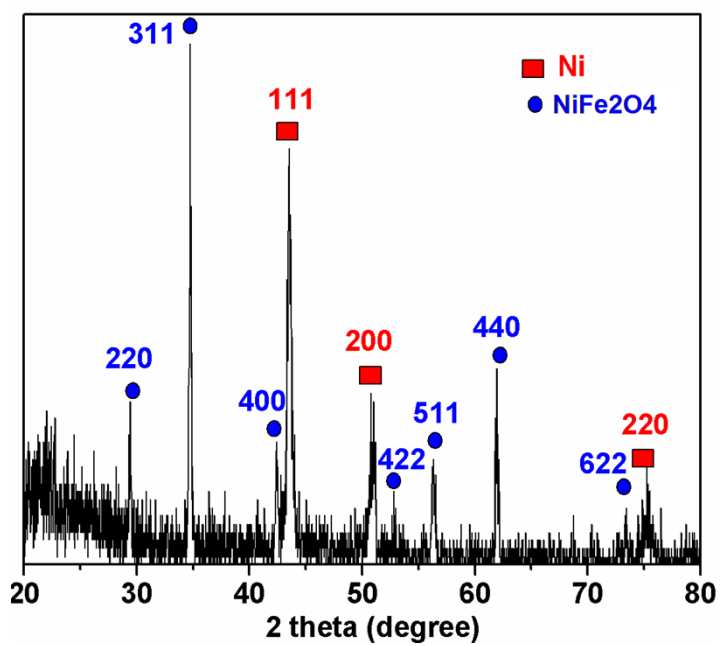
Fig. S5. XRD patterns of the Ni-mCNFs catalyst after 7 times cyclic reused.