

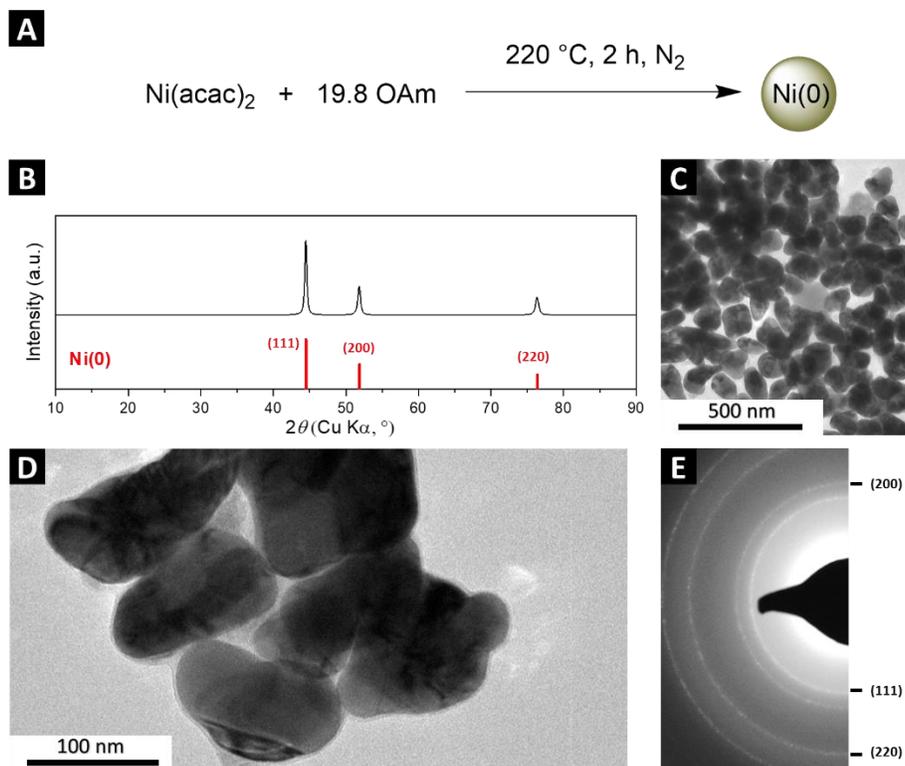
## Supporting Information

# Nickel Carbide (Ni<sub>3</sub>C) Nanoparticles for Catalytic Hydrogenation of Model Compounds in Solvent

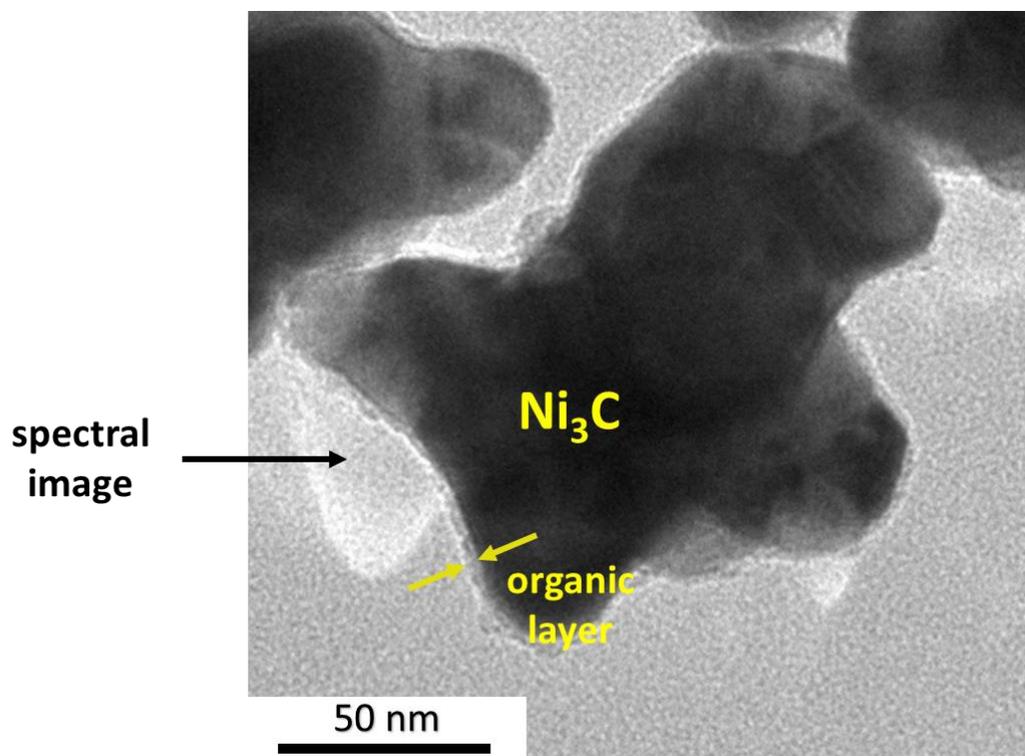
*Rémi F. André,<sup>1</sup> Léna Meyniel,<sup>1</sup> Sophie Carencó,<sup>1,\*</sup>*

<sup>1</sup> Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière  
Condensée de Paris (LCMCP), 4 place Jussieu, 75005 Paris, France

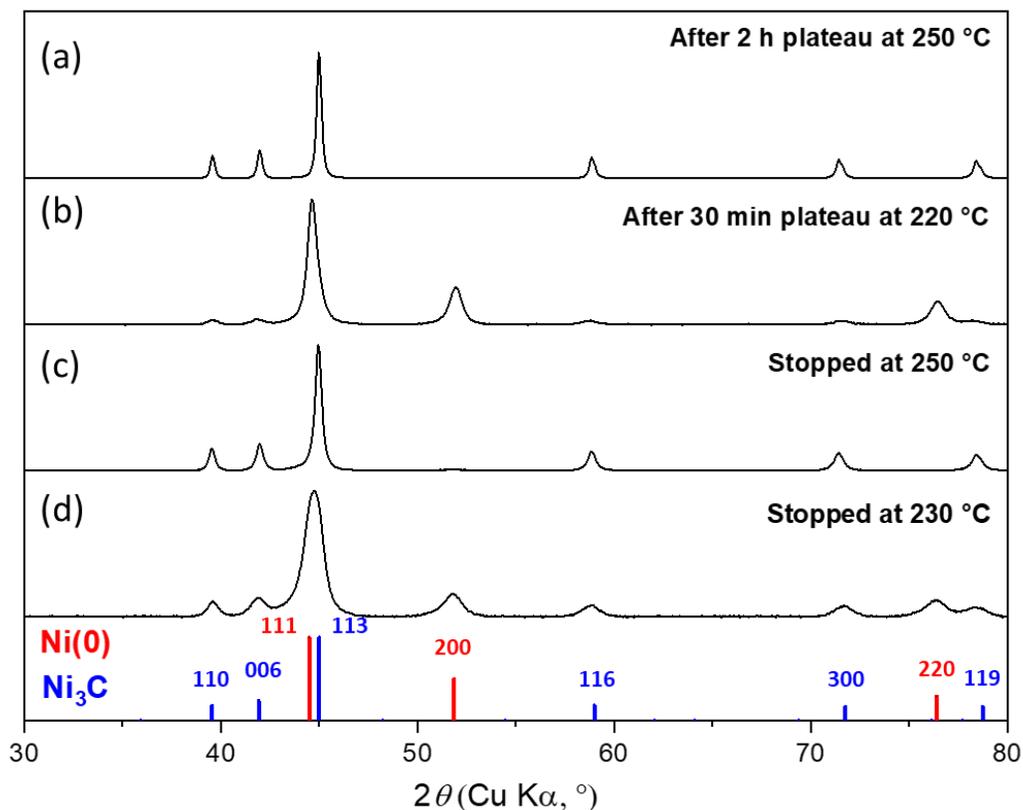
\*Corresponding author. E-mail: [sophie.carenco@sorbonne-universite.fr](mailto:sophie.carenco@sorbonne-universite.fr)



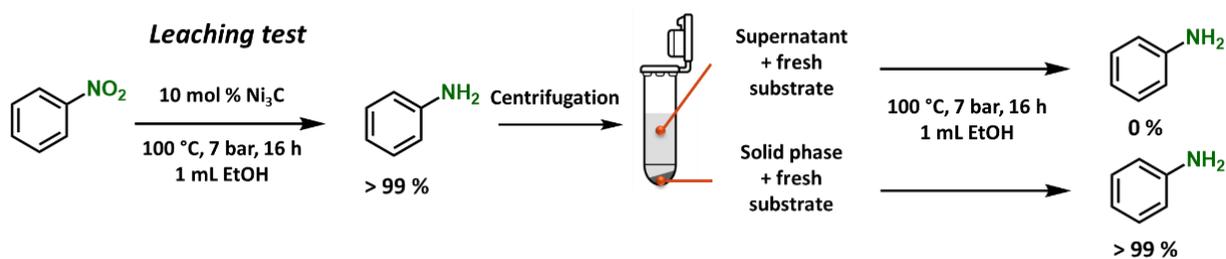
**Figure S1. Nickel nanoparticles formation and characterization.** (A) Synthesis of nickel nanoparticles, (B) XRD pattern (Ni: PDF N°03-065-2865), (C-D) corresponding TEM images and (E) SAED pattern with (hkl) attributions.



**Figure S2. Nickel carbide nanoparticle TEM image.**



**Figure S3. XRD pattern of the Ni<sub>3</sub>C nanoparticles** synthesized (a) at 250 °C during 2 h, (b) at 220 °C during 30 min, (c) when the heating ramp was stopped at 250 °C, (d) when the heating ramp was stopped at 230 °C.



**Figure S4. Leaching test on nitrobenzene hydrogenation.** Reaction conditions: solvent (1 mL), substrate (2 mmol), Ni<sub>3</sub>C (12.5 mg, 10 mol % [Ni]), H<sub>2</sub> (7 bar), 16 h.

### Calculations for the percentage of surface atoms on the NPs.

Considering a sphere of radius  $r$ , composed of a material of density  $\rho$ , the Avogadro's number  $N_A$  and the molar mass of the elementary unit  $M$ , we can estimate the number of atoms in the sphere:

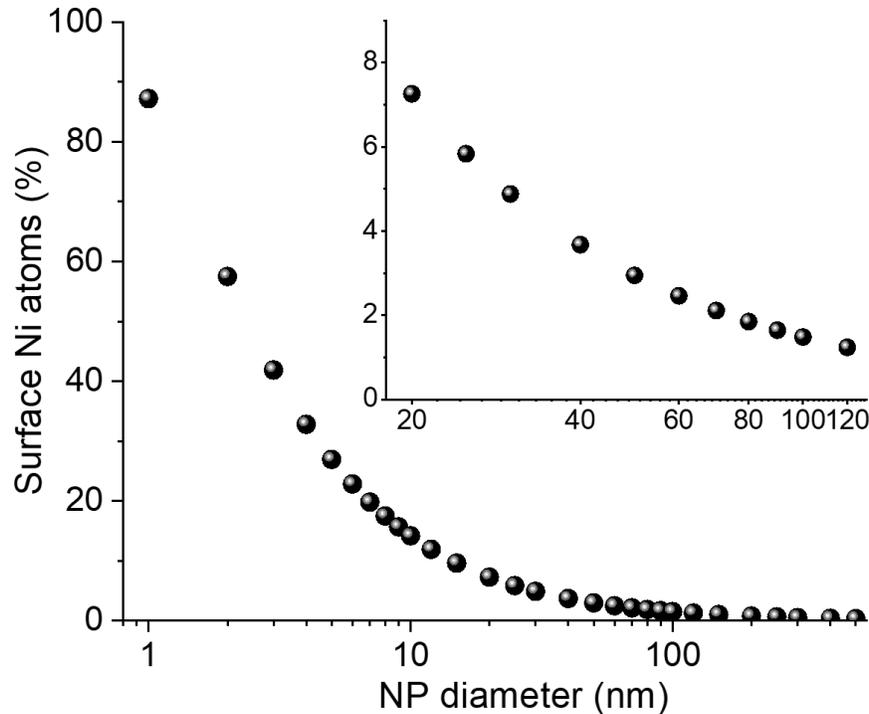
$$n_{Ni\ atoms} = N_A \cdot \frac{\rho}{M} \cdot \frac{4}{3} \pi r^3$$

The number of atoms in the subsurface region corresponds to the number of atoms in a sphere of radius  $r - d_{Ni}$  with  $d_{Ni}$  the metallic diameter of nickel:

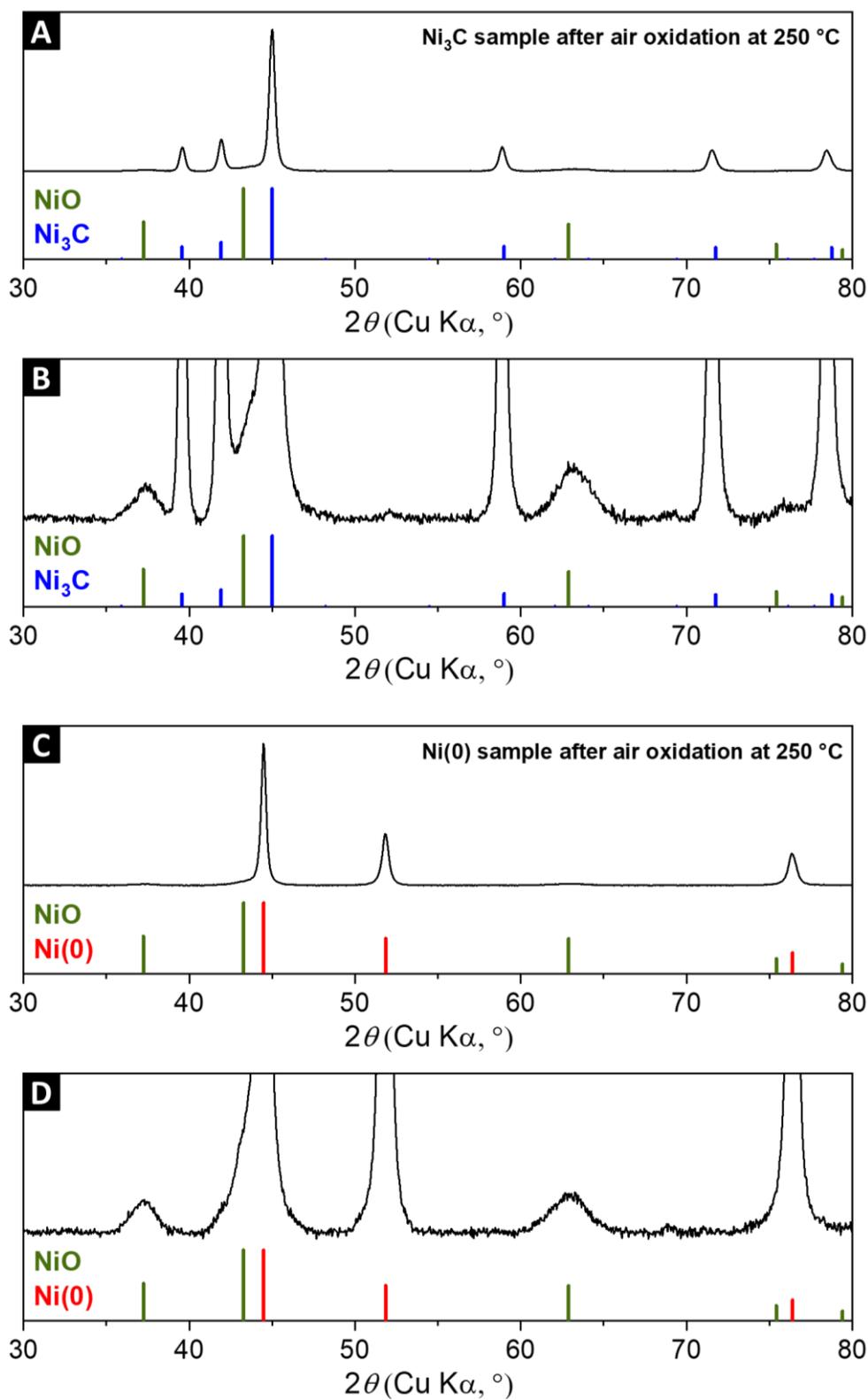
$$n_{Ni\ subsurface\ atoms} = N_A \cdot \frac{\rho}{M} \cdot \frac{4}{3} \pi (r - d_{Ni})^3$$

The percentage of surface atoms is finally given by:

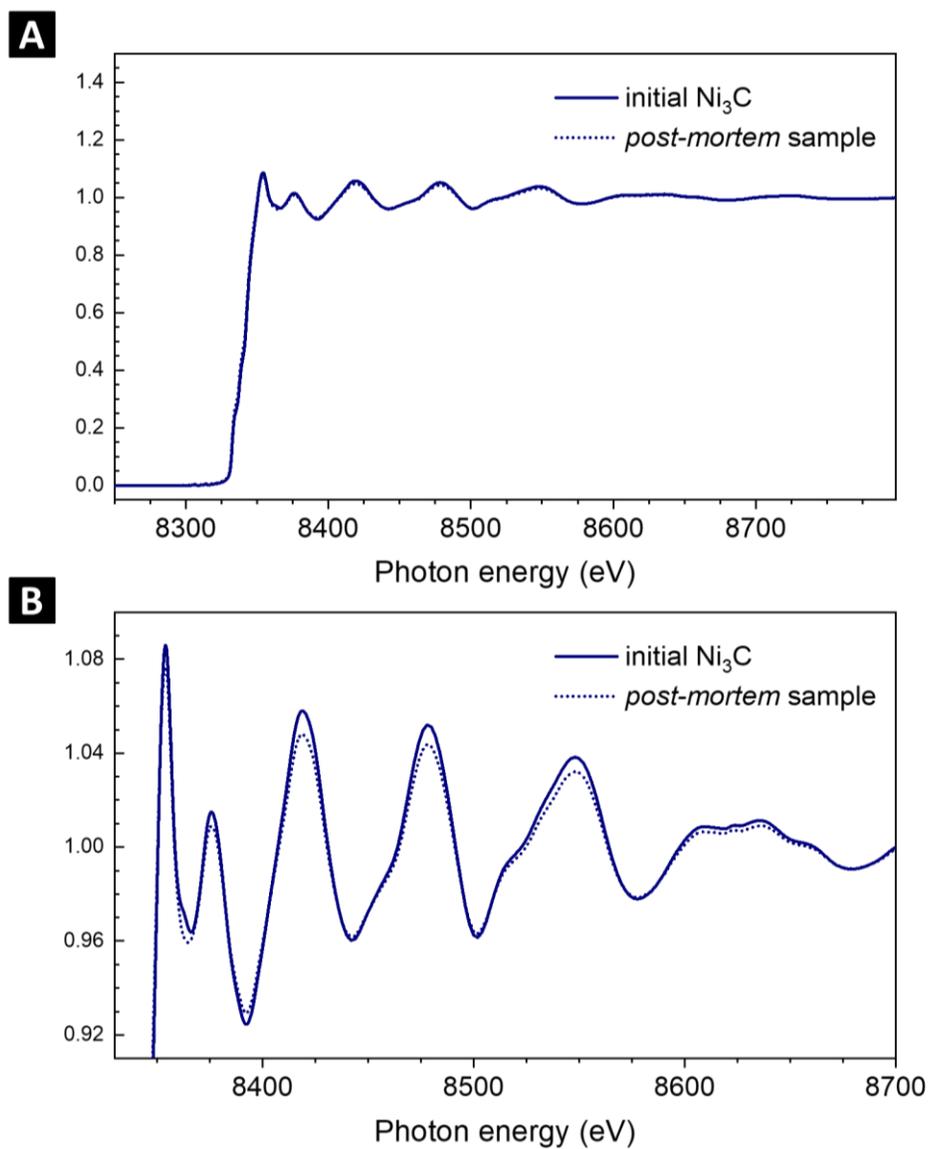
$$\%_{Ni\ surface} = 100 \frac{n_{Ni\ atoms} - n_{Ni\ subsurface\ atoms}}{n_{Ni\ atoms}} = 100 \left( 1 - \left( 1 - \frac{d_{Ni}}{r} \right)^3 \right)$$



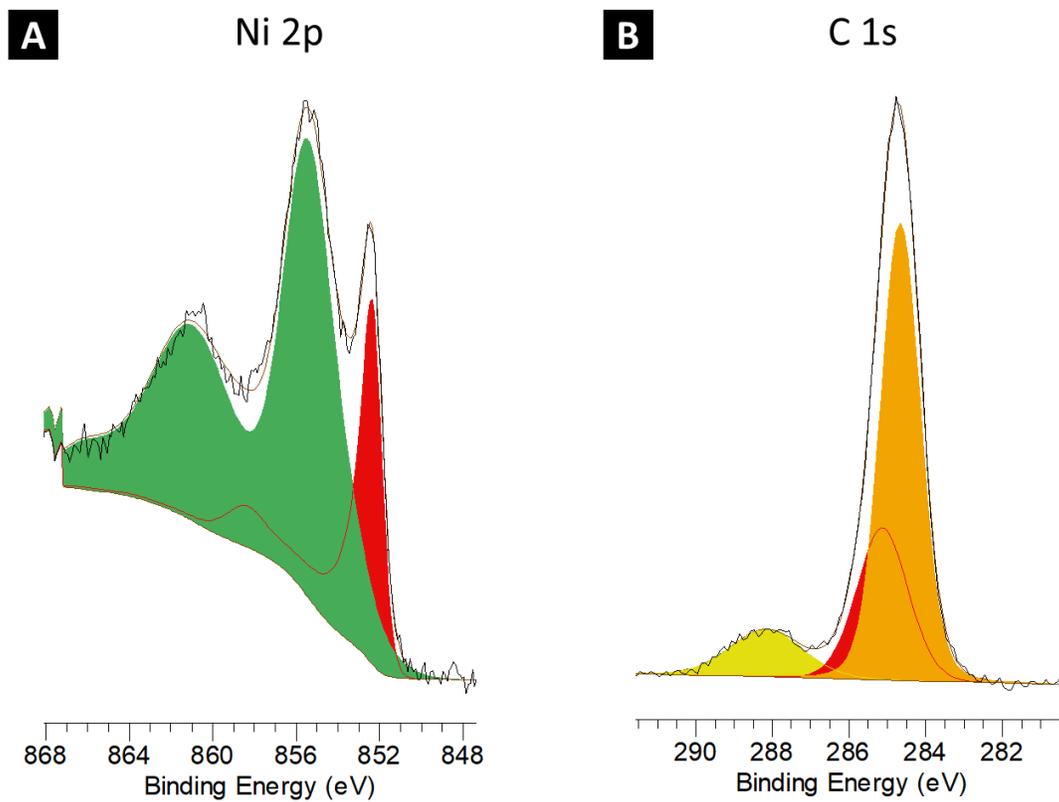
**Figure S5. Percentage of surface Ni atoms** as a function of the nanoparticle diameter (insight: zoom on the 20-120 nm region). The metallic diameter for nickel was taken as 0.248 nm.



**Figure S6. X-Ray Diffractograms after air oxidation at 250 °C during 2 h.** (A)  $\text{Ni}_3\text{C}$  sample with (B) a zoom on the  $\text{NiO}$  peaks. (C)  $\text{Ni}(0)$  sample with (D) a zoom on the  $\text{NiO}$  peaks.



**Figure S7. X-Ray Absorption spectra of Ni<sub>3</sub>C NPs before (solid line) and after (dotted line) catalysis.** (A) Full spectrum and (B) zoom on the EXAFS region. Catalysis conditions: hydrogenation of nitrobenzene in iPrOH at 4 bar H<sub>2</sub> and 100 °C for 16 h.



**Figure S8.** XPS spectra of the Ni(0) nanoparticles after 6 months of air exposure. (A) Ni 2p region (green: Ni<sup>2+</sup>, red: Ni(0)). (B) C 1s region (yellow : C<sub>oxidized</sub>, red: C<sub>sp3</sub>, orange: C<sub>sp2</sub>).

## Substrate screening

NMR-spectra were recorded by using Bruker AVANCE-III (300 MHz) in CDCl<sub>3</sub> at 298 K. Chemical shifts are given in parts per million (ppm,  $\delta$ ), referenced to the solvent peak of CDCl<sub>3</sub>, defined at  $\delta = 7.26$  ppm, or to the mesitylene peak at 6.78 ppm if aromatic peaks prevent the use of the CDCl<sub>3</sub> peak. Coupling constants are quoted in Hz (J). <sup>1</sup>H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

For the substrate screening, the reactions were performed at 100 °C under 7 bar of H<sub>2</sub> in a 25 mL Büchi glass batch reactor with a catalytic charge of 10 mol % of [Ni] (12.5 mg of Ni<sub>3</sub>C), 1 mL of ethanol and 2 mmol of substrate. The two hydrogenations of nitrile were performed in a mixture EtOH:NH<sub>3</sub> (aq) 28 % (v:v) (1:1).

**Styrene** hydrogenation in *ethylbenzene*.  $\delta$  7.38–7.13 (m, 5 H), 2.64 (q, J = 7.6 Hz, 2 H), 1.23 (t, 3 H). Conversion of 100 % of the reagent.

**Octene** hydrogenation in *octane*.  $\delta$  1.32 (m, 12 H), 0.94 (t, J = 6.7 Hz, 6 H). Conversion of 100 % of the reagent.

**Phenylacetylene** hydrogenation in *ethylbenzene*.  $\delta$  7.38–7.13 (m, 5 H), 2.64 (q, J = 7.6 Hz, 2 H), 1.23 (t, 3 H). Conversion of 100 % of the reagent.

**Diphenylacetylene** hydrogenation in *1,2-diphenylethane* (A, 74 %), *cis-stilbene* (B, 24 %) and *trans-stilbene* (C, 2 %). A  $\delta$  7.32–7.14 (m, 10 H), 2.92 (s, 4 H). B  $\delta$  7.32–7.14 (m, 10 H), 6.60 (s, 2 H). C  $\delta$  7.32–7.14 (m, 10 H), 7.11 (s, 2 H). Conversion of 100 % of the reagent.

No hydrogenation recorded for *naphthalene*.

*Benzaldehyde* hydrogenation in *benzyl alcohol*.  $\delta$  7.36–7.11 (m, 5 H), 4.63 (s, 2 H). Conversion of 100 % of the reagent.

*Furfural* hydrogenation in *furfuryl alcohol*.  $\delta$  7.67 (m, 1 H), 6.31 (m, 1 H), 6.25 (m, 1 H), 4.56 (s, 2 H). Conversion of 80 % of the reagent.

*Trans-cinnamaldehyde* hydrogenation in *3-phenylpropan-1-ol*.  $\delta$  7.36–7.11 (m, 5 H), 3.64 (t,  $J = 7.2$  Hz, 2 H), 2.68 (t,  $J = 7.8$  Hz, 2 H), 1.87 (q,  $J = 7.5$  Hz, 2 H). Conversion of 100 % of the reagent.

*Octanal* hydrogenation in *octanol*.  $\delta$  3.60 (t,  $J = 6.7$  Hz, 2 H), 1.54 (q,  $J = 6.7$  Hz, 2 H), 1.26 (m, 2 H), 0.86 (t,  $J = 6.5$  Hz, 3 H). Conversion of 100 % of the reagent.

*Trans-octenal* hydrogenation in *octanol*.  $\delta$  3.60 (t,  $J = 6.7$  Hz, 2 H), 1.54 (q,  $J = 6.7$  Hz, 2 H), 1.26 (m, 10 H), 0.86 (t,  $J = 6.5$  Hz, 3 H). Conversion of 100 % of the reagent.

*Acetophenone* hydrogenation in *1-phenylethanol*.  $\delta$  7.38–7.06 (m, 5 H), 4.83 (q,  $J = 6.4$  Hz, 1 H), 3.32 (br, 1 H), 1.44 (d,  $J = 6.4$  Hz, 3 H). Conversion of 100 % of the reagent.

*Benzophenone* hydrogenation in *benzhydrol*.  $\delta$  7.37–7.18 (m, 10 H), 5.8 (s, 1 H). Conversion of 36 % of the reagent.

*Chalcone* hydrogenation in *dihydrochalcone* (A, 60 %) and *1,3-diphenylpropan-1-ol* (B, 40 %). A  $\delta$  7.94 (d,  $J = 7.7$  Hz, 2 H), 7.54 (t,  $J = 7.4$  Hz, 2 H), 7.43 (t,  $J = 7.6$  Hz, 2 H), 7.36–7.11 (m, 4 H), 3.29 (t,  $J = 7.6$  Hz, 2 H), 3.05 (t,  $J = 7.6$  Hz, 2 H). B  $\delta$  7.36–7.11 (m, 10 H), 4.67 (dt,  $J = 5.7$  Hz, 1.8 Hz, 1 H), 2.80–2.58 (m, 2 H), 2.17–1.95 (m, 2 H). Conversion of 100 % of the reagent.

No hydrogenation recorded for *butanone*.

No hydrogenation recorded for *methyl benzoate*.

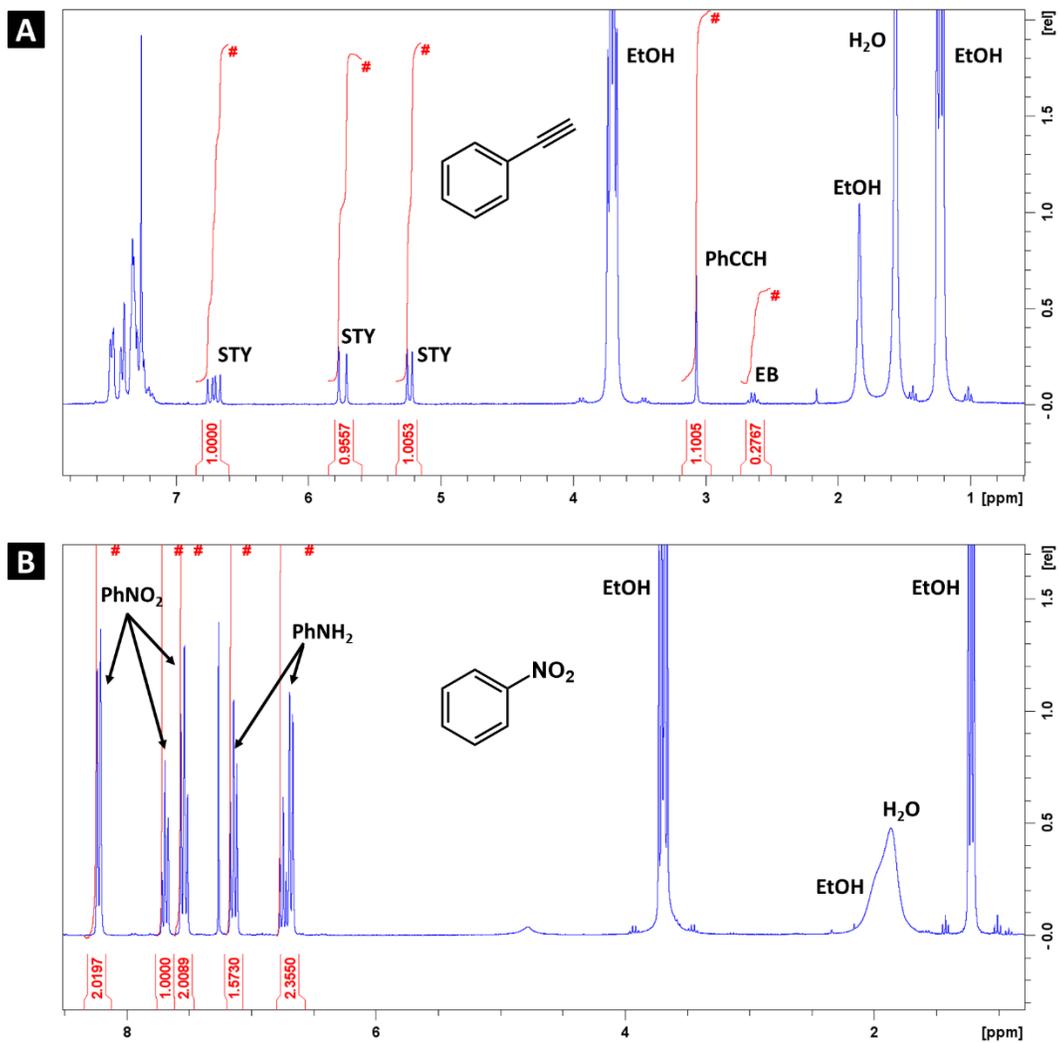
No hydrogenation recorded for *ethyl caproate*.

*Nitrobenzene* hydrogenation in *aniline*.  $\delta$  7.14 (t, J = 7.8 Hz, 2 H), 6.74 (t, J = 7.5 Hz, 1 H), 6.68 (d, J = 7.8 Hz, 2 H), 1.90 (br, 2 H). Conversion of 100 % of the reagent.

*p-nitrotoluene* hydrogenation in *p-toluidine*.  $\delta$  6.95 (d, J = 8.0 Hz, 2 H), 6.60 (d, J = 8.0 Hz, 2 H), 2.22 (s, 3 H). Conversion of 100 % of the reagent.

*Benzonitrile* hydrogenation in *benzylamine*.  $\delta$  7.38–7.18 (m, 5 H), 3.84 (s, 2 H), 2.30 (br, 2 H). Conversion of 100 % of the reagent.

*Butyronitrile* hydrogenation in *butylamine*.  $\delta$  2.66 (t, J = 6.8 Hz, 2 H), 1.47–1.27 (m, 4 H), 0.89 (t, J = 7.2 Hz, 3 H). Conversion of 100 % of the reagent.



**Figure S9.** Typical  $^1\text{H}$  NMR spectra obtained for (A) phenylacetylene and (B) nitrobenzene hydrogenation. STY = styrene and EB = ethylbenzene.