

## SUPPORTING INFORMATION FILE

# Recoverable Ni-based catalyst for the selective hydrodeoxygenation of vanillin using isopropanol as a renewable LOHC

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## 1. General remarks.

Unless otherwise stated, all chemicals were purchased and used without any further purification.  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (NiAc),  $\text{Cu}(\text{NO}_3)_2$  (CuN),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (CoN),  $\gamma\text{-Al}_2\text{O}_3$ , NaOH and  $\text{NaBH}_4$  were purchased from Sigma-Aldrich.

The ultrasound irradiation was generated using the ultrasonic processor VCX750 (Sonics & Materials, Inc., Newton, CT, USA), operating at 20 kHz and having a 13 mm diameter tip. Catalytic reactions were performed in a 10 mL stainless steel reactor. GLC analyses were performed by using Hewlett-Packard HP 5890 SERIES II equipped with a capillary column DB-5MS (30 m, 0.32 mm), a FID detector, and helium as a gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 mass selective detector equipped with an electron impact ionizer at 70 eV. Metal content was measured using the MP-AES 4210 instrument. The XRD patterns were recorded with a Philips X'Pert PRO MPD diffractometer operating at 40 kV and 40 mA, with a step of  $0.017^\circ$  and a time per step of 30 s using Cu K $\alpha$  radiation and an X'Celerator detector.

The morphology and composition were examined by Field Emission Gun Electron Scanning Microscopy (FE-SEM) LEO 1525 ZEISS. Elemental composition and chemical mapping were determined using a Bruker Quantax EDS.

Transmission Electron Microscopy (TEM) images were obtained using a TALOS F200X G2 (Thermo-Fisher Scientific) at an accelerating voltage of 200 kV using a high-speed CETA camera operating at a camera resolution of  $4096 \times 4096$  pixels without any objective aperture. The samples were prepared by putting one drop of an ethanol dispersion of the catalyst powder on a copper grid pre-coated with a Formvar film and dried in air.

XPS analyses were performed in a custom-designed ultra-high vacuum chamber with a base pressure of  $10^{-10}$  mbar. A non-monochromatic magnesium source ( $h\nu = 1253.6$  eV, VSW-A10 model) was used as excitation radiation, coupled with a hemispherical electron/ion energy

analyzer (model VSW-HA100, equipped with a 16-channel detector). The Mg X-ray source was operated at 100 W (13 kV and 7.7 mA), and photoelectrons were collected along the surface normal; the angle between the analyser axis and the X-ray source was fixed at 54.5°. All spectra were acquired in Fixed Analyzer Transmission (FAT) mode with a pass energy of 44 eV. The calibration of XPS spectra was performed by setting the Al 2p 3/2 signal component to 75.0 eV [1,2].

Spectral analysis was conducted using CasaXPS software, employing a Shirley function for background subtraction. Spectral deconvolution was performed by applying a Gaussian/Lorentzian (GL) mix for Al 2p and a Lorentzian Asymmetric Lineshape (LA) for components in the Ni 2p region. Empirical sensitivity factors were used to determine semi-quantitative ratios [3].

#### **References:**

- [1] Kang H S, Siva Pratap Reddy M, Kim D S, Kim K W, Ha J B, Lee Y S, Choi H C and Lee J H 2013 Effect of oxygen species on the positive flat-band voltage shift in Al<sub>2</sub>O<sub>3</sub>/GaN metal-insulator-semiconductor capacitors with post-deposition annealing J. Phys. D. Appl. Phys. 46
- [2] Djebaili K, Mekhalif Z, Boumaza A and Djelloul A 2015 XPS, FTIR, EDX, and XRD analysis of Al<sub>2</sub>O<sub>3</sub> scales grown on PM2000 alloy J. Spectrosc. 2015
- [3] Wagner C D, Davis L E, Zeller M V, Taylor J A, Raymond R H and Gale L H 1981 Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis Surf. Interface Anal. 3 211–25

## 2. General procedures

### 2.1 Catalyst Preparation

Two series of catalysts were synthesized by means of an ultrasound-assisted co-precipitation method using NaOH (N) or NaBH<sub>4</sub> (B) as metal precipitant agent.

The first series of catalyst were carried out by adding 50 mL of 0.5 M NaOH dropwise to a metal salts solution with dispersed alumina (see table 1) under ultrasound irradiation for 30 minutes, at 50% of amplitude and a temperature of 25 °C. After each synthesis the precipitated was dried and calcined at 500 ° C for 1 h under static air.

The second series of catalyst were carried out by adding 50 mL of 0.1 M NaBH<sub>4</sub> dropwise to a metal salts solution with dispersed alumina (see table 1) under ultrasound irradiation for 15 minutes, at 50% of amplitude and a temperature of 10 °C. After each synthesis the precipitated was dried at 105°C for 2 h.

**Table S1.** List of the synthesized catalysts and conditions.

entry	catalyst	Metal Precursors			Support	Precipitant agent
		NiAc (g)	CuN (g)	CoN (g)	Al <sub>2</sub> O <sub>3</sub> (g)	
1	Ni/Al <sub>2</sub> O <sub>3</sub> -N	2.12	-	-	4.50	NaOH
2	NiCu/Al <sub>2</sub> O <sub>3</sub> -N	2.12	1.90	-	4	NaOH
3	NiCo/Al <sub>2</sub> O <sub>3</sub> -N	2.12	-	2.47	4	NaOH
4	CoCu/Al <sub>2</sub> O <sub>3</sub> -N	-	1.90	2.47	4	NaOH
5	Ni/Al <sub>2</sub> O <sub>3</sub> -B	2.12	-	-	4.50	NaBH <sub>4</sub>
6	NiCu/Al <sub>2</sub> O <sub>3</sub> -B	2.12	1.90	-	4	NaBH <sub>4</sub>
7	NiCo/Al <sub>2</sub> O <sub>3</sub> -B	2.12	-	2.47	4	NaBH <sub>4</sub>
8	CoCu/Al <sub>2</sub> O <sub>3</sub> -B	-	1.90	2.47	4	NaBH <sub>4</sub>

## 2.2 Catalyst characterization.

All obtained catalysts were fully characterized. MP-AES analyses determined the metal percentage, while XRD, FE-SEM-EDX, and TEM analyses were employed to give information about the chemical structure, morphology, and metal dispersion.

*General procedure for metal loading determination:* in a 10 mL volumetric flask, a certain amount of solid catalyst, ranging between 1 and 2 mg, was weighed and digested in 2 mL of aqua regia. After 2 h of stirring, the final volume was reached with Milli-Q water, the solution filtered, and the sample was analyzed by the MP-AES 4210 instrument.

**Table S2.** Catalysts loading.

entry	catalyst	Ni (wt %)	Cu (wt %)	Co (wt %)
1	Ni/Al <sub>2</sub> O <sub>3</sub> -N	7	-	-
2	NiCu/Al <sub>2</sub> O <sub>3</sub> -N	7	10	-
3	NiCo/Al <sub>2</sub> O <sub>3</sub> -N	8	-	6
4	CoCu/Al <sub>2</sub> O <sub>3</sub> -N	-	11	8
5	Ni/Al <sub>2</sub> O <sub>3</sub> -B	12	-	-
6	NiCu/Al <sub>2</sub> O <sub>3</sub> -B	10	11	-
7	NiCo/Al <sub>2</sub> O <sub>3</sub> -B	7	-	7
8	CoCu/Al <sub>2</sub> O <sub>3</sub> -B	-	10	9

Metal content measured by MP-AES analyses.

## 2.3. Catalytic test

In a 10 mL stainless steel reactor, the catalyst, vanillin (0.2 mmol), and 2 mL of IPA were consecutively added. The mixture was kept under stirring at a certain temperature. After the defined time, the reactor was cooled to room temperature, and the catalyst was separated by

filtration and washed with IPA. The conversion of vanillin and the product distribution were determined by GC and GC-MS analyses and are defined as follows:

$$\text{Conversion (\%)} = (C_{1i} - C_1) / C_{1i} \cdot 100$$

$$\text{Selectivity}_{\text{MMP}} (\%) = C_4 / (C_2 + C_3 + C_4) \cdot 100$$

Where  $C_{1i}$  is the initial vanillin concentration and  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are the concentrations of vanillin (**1**), vanillyl alcohol **2**, intermediate **3** and MMP (**4**), respectively.

#### **2.4. Typical procedure for vanillin HDO**

In a 10 mL stainless steel reactor, Ni/Al<sub>2</sub>O<sub>3</sub>-B (30 mol%, 29.3 mg), vanillin (0.2 mmol), and 2 mL of IPA were consecutively added. The mixture was kept under stirring at 180 °C for 15 h. After the selected time, the reactor was cooled to room temperature, and the catalyst was separated by filtration and washed with IPA. The conversion and selectivity were determined as reported in the catalytic test section 2.3.

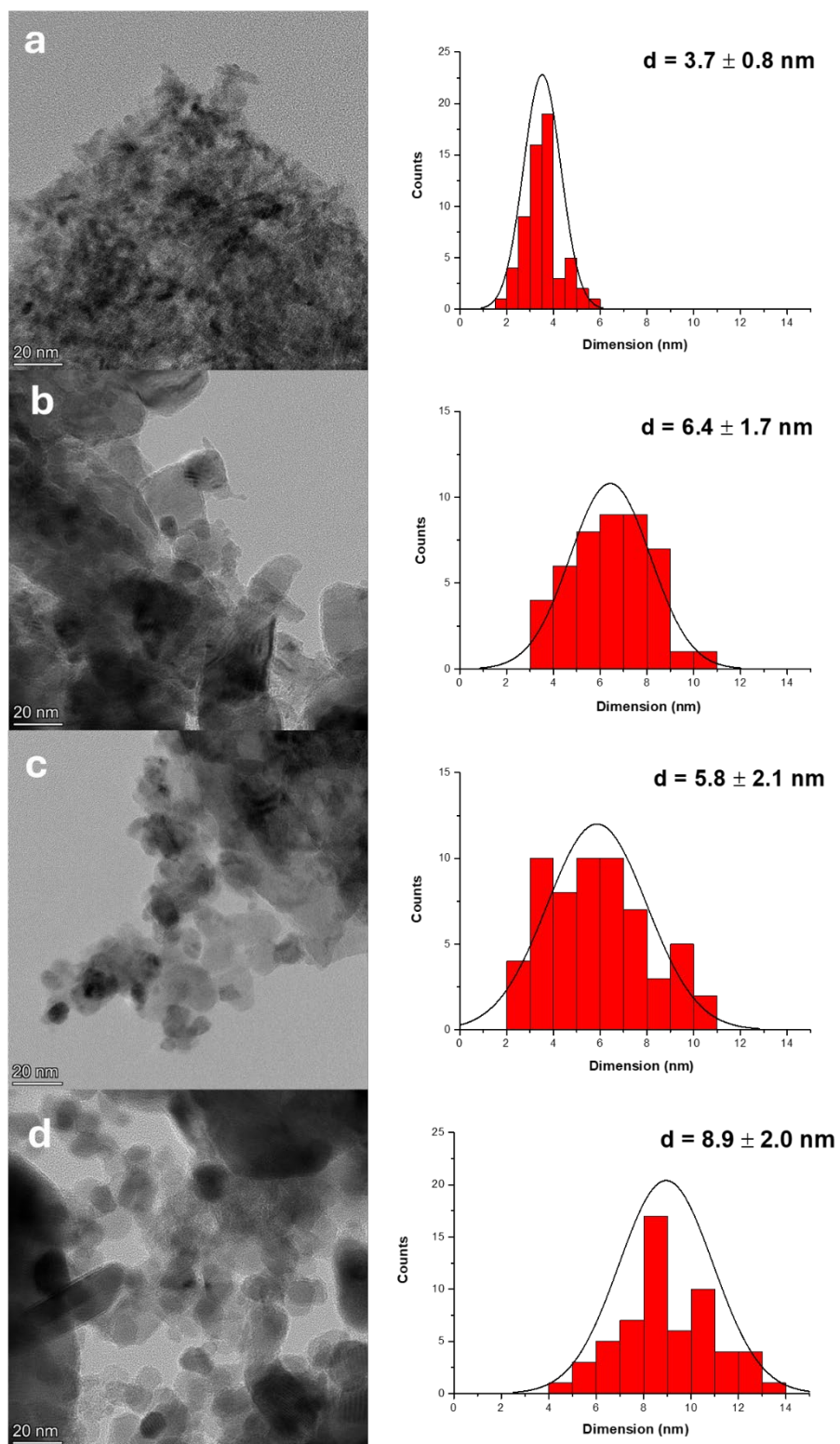
#### **2.5. Catalyst recycles**

After the reaction completion, the mixture was transferred into appropriate tubes, and the catalyst was recovered by centrifugation, washed with IPA (3 x 1 mL), and dried under vacuum at 80 °C for 1 h. The dried catalyst was reused under the optimized conditions.

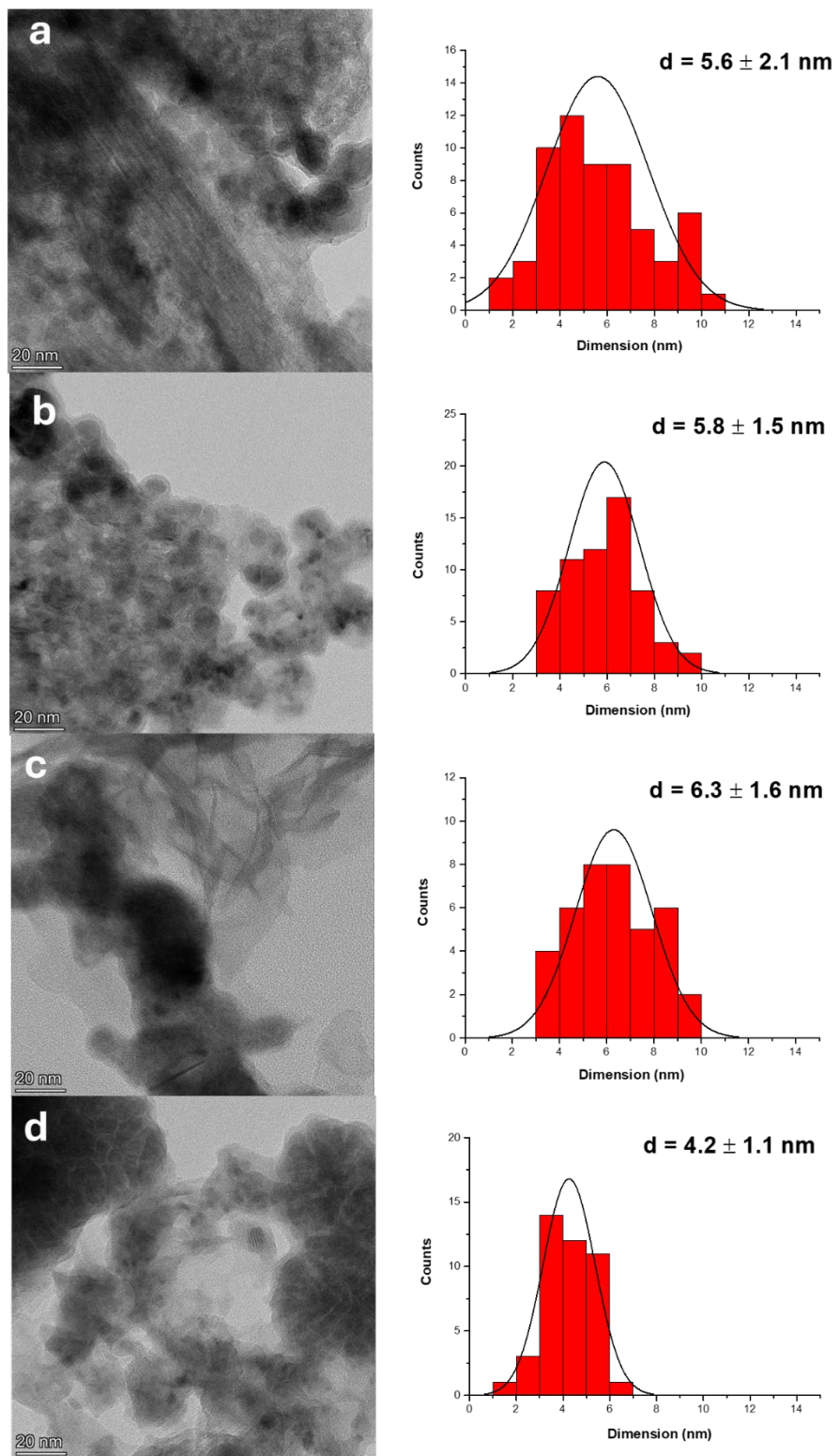
#### **2.6. Leaching measurement**

After the selected time, the catalyst was separated by filtration. The crude reaction mixture was dried under reduced pressure and digested in 2 mL of aqua regia. After 1 h at room temperature, the mixture was transferred to a 10 mL graduated flask and diluted with Milli-Q water to reach the final volume. If residual solid was present, it was filtered off, and the sample was analyzed by the MP-AES 4210 instrument.

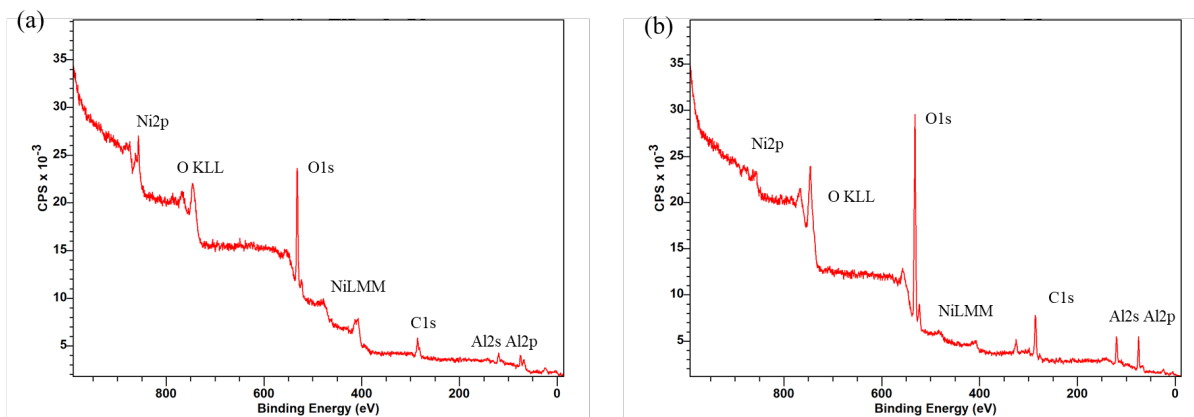
### 3. TEM images and XPS spectra



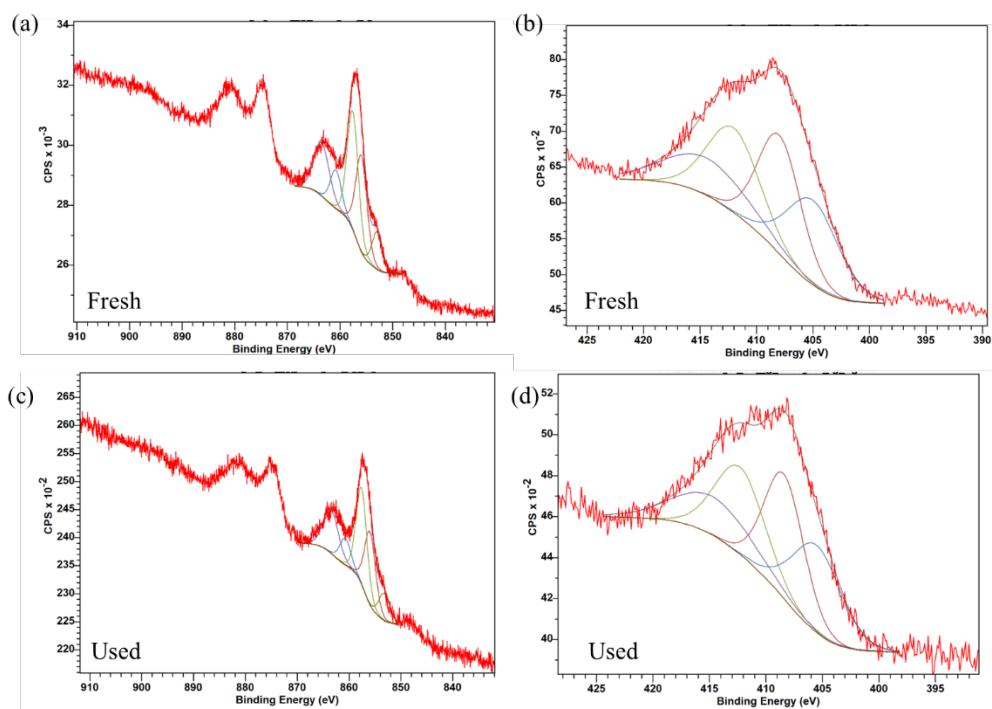
**Figure S1.** TEM images and size distributions of (a) Ni/Al<sub>2</sub>O<sub>3</sub>-N, (b) NiCu/Al<sub>2</sub>O<sub>3</sub>-N, (c) NiCo/Al<sub>2</sub>O<sub>3</sub>-N, (d) CoCu/Al<sub>2</sub>O<sub>3</sub>-N



**Figure S2.** TEM images and size distributions of (a) Ni/Al<sub>2</sub>O<sub>3</sub>-B, (b) NiCu/Al<sub>2</sub>O<sub>3</sub>-B, (c) NiCo/Al<sub>2</sub>O<sub>3</sub>-B, (d) CoCu/Al<sub>2</sub>O<sub>3</sub>-B

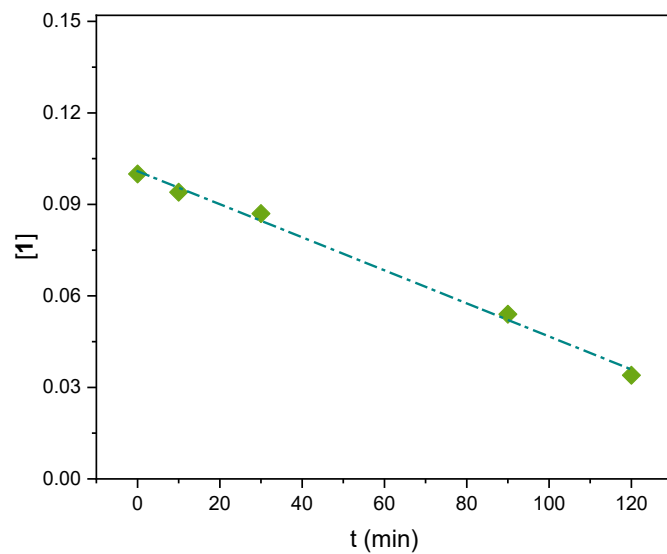


**Figure S3.** XPS spectra of catalysts: (a) survey-Ni/Al<sub>2</sub>O<sub>3</sub>-B fresh and (b) survey-Ni/Al<sub>2</sub>O<sub>3</sub>-B spent catalysts with respective peak assignments.



**Figure S4.** High-resolution XPS spectra in the Ni 2p region for Ni/Al<sub>2</sub>O<sub>3</sub>-B fresh (a) and Ni/Al<sub>2</sub>O<sub>3</sub>-B spent catalysts.

#### 4. Kinetic data



**Figure S5.** Kinetic profile for vanillin conversion during the time. Reaction condition: Ni/Al<sub>2</sub>O<sub>3</sub>-B (29 mg, 30 mol%), **1** (0.2 mmol), IPA (2 mL), 180°C.

Vanillin conversion follows the pseudo-zero-order kinetic trend

$$k = 5.418 \cdot 10^{-4}$$

$$R^2 = 0.994$$

## 5. Literature comparison

**Table S3.** Comparison of available catalysts for vanillin hydrodeoxygenation without H<sub>2</sub> pressure

Ref <sup>a</sup>	Catalyst	H-donor	Reaction condition	Vanillin Conv. (%)	MMP Sel. (%)
61	3Ni-Ce/C	EtOH	240 °C; 4 h	98	81
62	Ni <sub>2</sub> P@YSS	EtOH	180 °C; 3 bar N <sub>2</sub> ; 5 h	86	76
78	Cu/Cu-SiO <sub>2</sub>	IPA	140 °C; 20 bar N <sub>2</sub> , 10h	99	99
79	15 % Cu/AC-600	IPA	180 °C; 5 h	100	99
80	Cu/ZnAlSn-LDH	IPA	180 °C; 4 h; 1 bar N <sub>2</sub>	100	99
81	NiCu/BC	IPA	240 °C; 20 bar N <sub>2</sub> , 4 h	100	88
82	Au/Co <sub>3</sub> O <sub>4</sub> NR	IPA	240 °C, 4 bar N <sub>2</sub> , 3 h	99	99
83	UIO-66 <sub>def</sub>	IPA	150 °C; 9 h	>99	>99
84	Ni/MMT	IPA	180 °C; 10 bar N <sub>2</sub> , 2 h	>99	95
85	Ni <sub>2</sub> P@C-3	IPA	180 °C; N <sub>2</sub> , 3 h	100	95
<i>This work</i>	Ni/Al <sub>2</sub> O <sub>3</sub> -B	IPA	180 °C; 15 h	100	82

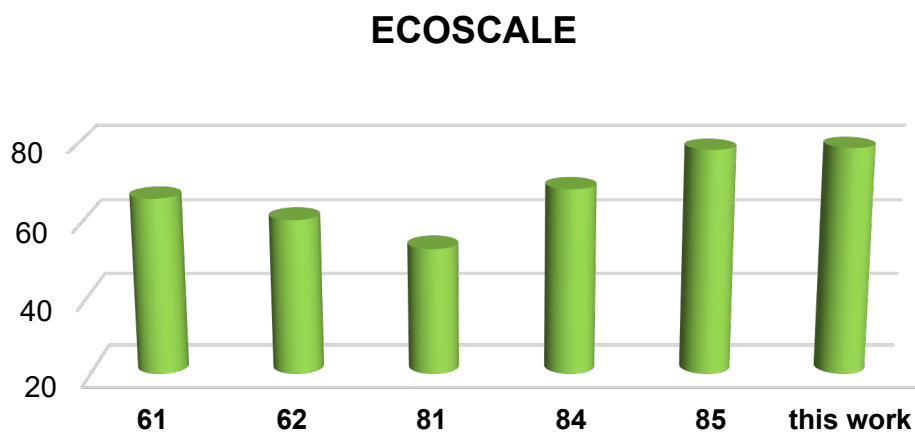
<sup>a</sup>References are referred to the main text.

## 6. Metrics calculation

**Table S4.** Comparison of Ni-containing catalysts for vanillin hydrodeoxygenation without external H<sub>2</sub> pressure

Ref <sup>a</sup>	Catalyst	AE	RME	SF	Ecoscale	VMR
61	3Ni-Ce/C	69.7	0.6	0.01357	66	0.5560
62	Ni <sub>2</sub> P@YSS	69.7	0.9	0.02003	60.5	0.5049
81	NiCu/BC	65.1	0.7	0.01514	53	0.5439
84	Ni/MMT	65.1	0.8	0.01764	68.5	0.5993
85	Ni <sub>2</sub> P@C-3	65.1	1.8	0.03738	78.5	0.6236
<i>This work</i>	Ni/Al <sub>2</sub> O <sub>3</sub> -B	65.1	1.4	0.03124	79	0.5868

<sup>a</sup>References are referred to the main text.



**Figure S6.** ECOSCALE values for the vanillin HDO using alcohols as LOHCs. Comparison of our work with Ni-based catalysts reported in Table S4. The calculation was adapted considering the general necessity of carrying out the process under an inert atmosphere and gas pressure.