Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Efficient non-noble Ni-Cu based catalysts for the valorization of palmitic acid through decarboxylation reaction

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Catalyst characterization:

The surface area, pore volume and distribution of the pore size were determined by nitrogen adsorption/desorption at 77.35 K using a TriStar II Plus and a 3Flex apparatus from Micromeritics. Preliminary degassing of the samples was performed at 150 °C for 45 min. The specific surface area was evaluated using the Brunauer, Emmet and Teller (BET) method. In addition, the pore size distribution and the pore volume were calculated according to the Barrett-Joyner-Halenda (BJH) formula taking into account the desorption branch.

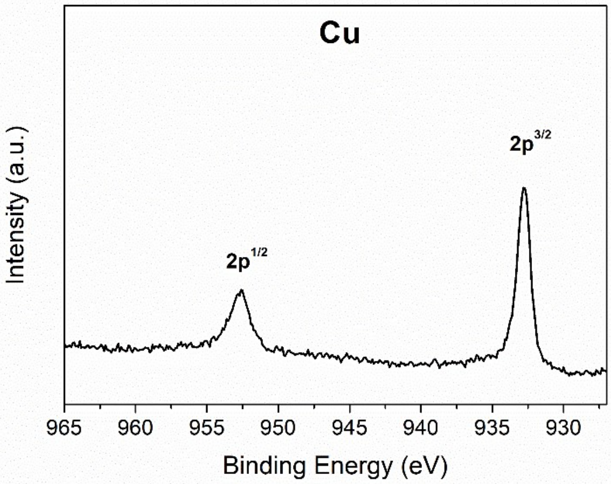
Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was performed using Agilent 720-ES ICP-OES equipment combined with Vulcan 42S automated digestion system. Owing to their difficulty to be totally dissolved in *aqua regia*, the catalysts were calcined to remove the carbon prior the analysis: 30 mg of catalysts were calcined at 350 °C (temperature rate of 5 °C/min) in a ceramic crucible under air, for 3 h. Then, the solid samples were digested using *aqua regia* that was distributed for each sample by the robot before heating for 2 h up to 50 °C (this step was repeated 3 times).

Transmission electron microscopy (TEM) images were recorded on electron microscope FEI Tecnai G2 20 (TEM) equipped with an Energy-dispersive X-ray spectroscopy (EDX) micro-analysis, a Gatan energy filter (EELS), precession and electron tomography systems and an Orius CCD camera. This microscope uses a voltage of 200 kV for the acceleration of electrons. The samples were prepared by placing a drop of the particles dispersion in ethanol onto a carbon coated copper grid. The average Au nanoparticle size was determined taking into account at least 300 particles.

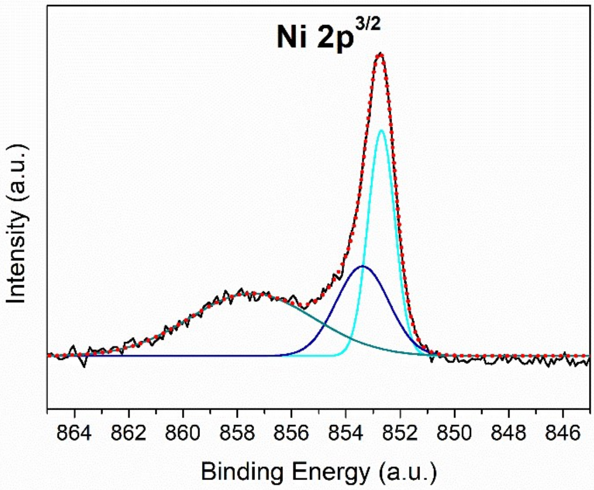
X-ray powder diffraction (XRD) of catalysts was recorded on a D8 Discover X-Ray Diffractometer from Bruker using a X-Ray tube in Cu (Kα) radiation (λ=1.54060 Å). The diffraction angle 2θ was in the 10-70° range with steps of 0.02° per second. For the interpretation of the XRD spectrum obtained, Diffrac Eva software was used and for the identification of the crystalline phase, reference standards were measured. The average crystallite size of the metals particles in the catalyst was determined by the Scherrer equation.

X-ray photoelectron spectroscopy (XPS) spectra were collected on a high-performance hemispheric analyzer VG Escalab 220 XL spectrometer "1996" and on a XPS Kratos, Axis UltraDLD "2009" with monochromatic Al Kα (hν = 1486.6 eV) radiation as the excitation source. For interpretation the calibration of the XPS spectra was made using the carbon C 1s reference of 284.8 eV.

The H_2-TPR (Temperature programmed reduction with H_2) analyses were performed on an automated AutoChem II 2920 Chemisorption Analyzer from Micromeritics. At first, 40 mg of catalyst were weighted and inserted into a glass reactor. Then, the sample was flushed with a mixture gas of 5 vol.% H_2 in Ar at room temperature. While the gas was flowing (100 mL/min), the temperature of the sample was increased linearly at a ramp rate of 5 °C/min up to 750 °C and then kept at this temperature for 1 h. Finally, the consumption of hydrogen by adsorption/reaction was monitored to get quantitative information on the reducibility of the species present in the catalyst.



a)



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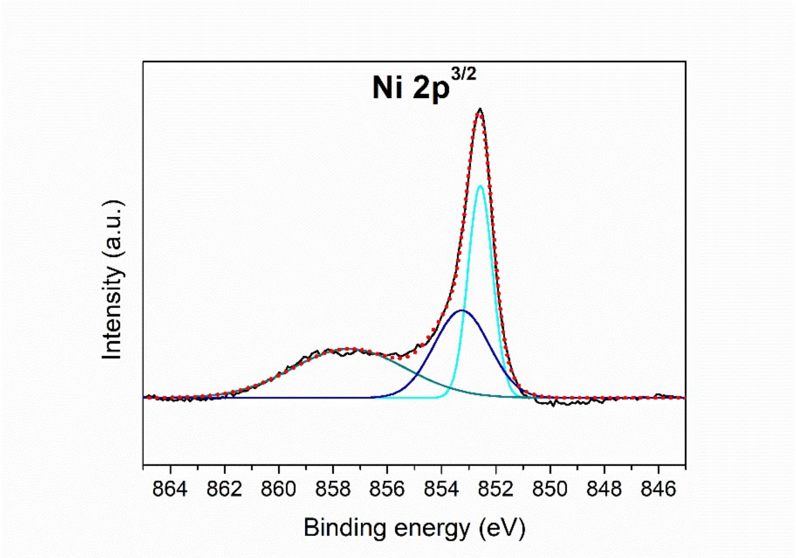

c)

Fig. S1. a) XPS spectra in the Cu 2p and (b) Ni 2p region for the monometallic 10%Cu/C bimetallic Ni-Cu catalysts after activation and (f) in the Ni 2p3/2 region for 10%Ni10%Cu/C catalyst.

Table S1. DCX of PA into *n*-PD using commercial 5%Pd/C and 5%Pt/C catalysts in comparison with 10%Ni10%Cu/C catalyst. Reaction conditions: T = 320°C, operating pressure = 40 bar, t = 6 h, stirrer speed = 600 rpm; PA loading = 0.197 mmol. X: conversion), $S_{n\text{-PD}}$: *n*-PD selectivity, $Y_{n\text{-PD}}$: *n*-PD yield, CB: carbon balance.

Catalyst	X%	$S_{n\text{-PD}}$%	$Y_{n\text{-PD}}$%	CB%	catalyst amount (mg)
5%Pd/C-act	100	51	51	51	
5%Pt/C-act	81	87	70	90	12.8
10%Ni10%Cu/C	76	87	66	87	
5%Pd/C-act	100	66	66	66	
5%Pt/C-act	81	87	70	90	26.0
10%Ni10%Cu/C	100	89	89	89	
5%Pd/C-act	100	84	84	84	
5%Pt/C-act	100	89	89	89	52.0
10%Ni10%Cu/C	100	94	94	94	
5%Pd/C-act	100	91	91	91	
5%Pt/C-act	100	91	91	91	75.0
10%Ni10%Cu/C	100	95	95	95	

Table S2. DCX of PA into *n*-PD using commercial 5%Pd/C and 5%Pt/C catalysts: Effect of the reduction of the catalyst with H_2. Reaction conditions: T = 320°C, operating pressure = 40 bar, t = 6 h, stirrer speed = 600 rpm; catalyst amount = 12.8 mg, PA loading = 0.197 mmol. X%: conversion), $S_{n\text{-PD}}$: *n*-PD selectivity, $Y_{n\text{-PD}}$: *n*-PD yield, CB: carbon balance. 5%Pd/C and 5%Pt/C: as-prepared catalysts were used; 5%Pd/C-act and 5%Pt/C-act: catalysts were activated under hydrogen at 350 °C for 2 h before the catalytic test.

Catalyst	X%	$S_{n\text{-PD}}$	$Y_{n\text{-PD}}$	CB
5%Pd/C	91	31	28	37
5%Pd/C-act	100	51	51	51
5%Pt/C	92	33	30	38
5%Pt/C-act	81	87	70	79
10%Ni10%Cu/C	76	87	66	87