Supplementary Materials

Cu-Pd bimetallic nanoalloy anchored on N-rich porous organic polymer for high-performance hydrodeoxygenation of biomass-derived vanillin[†]

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Characterization Techniques:

Powder X-ray diffraction (PXRD) patterns of different samples were recorded with a Bruker D8 Advance X-ray diffractometer operated at a voltage of 40 kV and a current of 40 mA using Ni-filtered Cu K α (λ =0.15406 nm) radiation.

Synchrotron powder diffraction experiments were carried out with photons of wavelength 0.7 Å using the x-ray diffraction beamline of the Elettra Synchrotron radiation facility, Trieste. Samples were loaded in glass capillary of 300 micron inner diameter to serve as the target. Diffracted signals were collected using a Dectris Pilatus 2M hybrid-pixel area detector. Powder diffraction patterns were obtained from the diffraction images by integration using the Fit2D package while the GSAS software package is used for the structural analysis.

Copper K-edge x-ray absorption fine structure measurements were performed in transmission mode at the XAFS beamline of the Elettra Synchrotron radiation facility, Trieste. Pellets for the XAFS measurements were prepared by homogeneously mixing the sample with an insert matrix, boron nitride to obtain an x-ray absorption edge close to one. Measurements on the copper foil is done using the standard readily available at the beamline. Standard data analysis procedure was used to extract the extended x-ray absorption fine structure (EXAFS) signal from the measured absorption spectra using the Demeter package.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source. Spectra were recorded using an aluminium anode (Al K_{α}=1486.6 eV) operating at 72W and a spot size of 400 mm. Prior to the XPS measurements, all the samples were treated in a 10 vol% H₂/Ar flow at 200°C for 4 h.

High Resolution Transmission electron microscopy (HR-TEM) images were recorded in a JEOL JEM 2010 transmission electron microscope with operating voltage 200 kV equipped with a FEG. Field emission scanning electron microscopic images of samples were obtained using a JEOL JEM 6700 field emission scanning electron microscope (FE-SEM). Nitrogen sorption isotherms were obtained using a Quantachrome Autosorb 1C surface area analyzer at 77 K. Prior to the measurement, the samples were degassed at 433 K for approximately 6 h in high vacuum. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) in the relative pressure (P/P_0) range of 0.01-0.1. The total pore volumes and pore size distribution curves were obtained from the adsorption branches using nonlocal

density functional theory (NLDFT) method. FT IR spectra of the samples were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. Thermogravimetry (TGA) analyses of the all samples were carried out using a TGA Instruments thermal analyzer TA-SDT Q-600 under nitrogen atmosphere with a heating rate of 10°C min⁻¹ from 25 to 600°C. Solid-state ¹³C CP-MAS NMR studies were performed using a Bruker Avance III HD 400 MHz NMR spectrometer. Transmission electron microscope high-annular dark-field scanning (HAADF-STEM) and energy-dispersive X-ray mapping images were obtained with a TECNAI G2 F20 equipped with an EDX detector. X-ray photoelectron spectroscopy (XPS) was performed on an Omicron nanotech operated at 15 kV and 20 mA with a monochromatic Al K α X-ray source. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC and Agilent 6890 GC system equipped with a flame ionization detector were used for analysis of catalytic reactions. The loading amounts of Pd and Cu were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP-6500DUO, Thermo Fisher Scientific).

Entry	Catalyst	Con (%)	Selectivity (%)		References
			-OH	-CH ₃	
1	Pd@CN _{0.132}	65	31	69	[1]
2	Pd@NH ₂ -UiO-66	100	0	100	[2]
3	Pd/SO ₃ H-MIL-101(Cr)	96.6	9.1	90.9	[3]
4	Pd/NPC-ZIF-8	100	0	100	[4]
5	Pd-MIL-101	100	0	100	[5]
6	Pd-POP	96.5	1.8	98.2	[6]
7	Pd ₅₀ Ag ₅₀ /Fe ₃ O ₄ /N-rGO	100	0	98	[7]
8	Pd/MSMF	>99.5	45.8	54.2	[8]
9	Au-Pt/CeO ₂	100	0	99.8	[9]
10	Ni-NCB-900	74.4	35.4	64.6	[10]
11	Co@NC-700	95.7	0	100	[11]

 Table S1: Comparison in vanillin hydrodeoxygenation (HDO) activity over different supported catalysts

12	Pd/CN-CF	99	2	98	[12]
13	Cu ₃ Pd ₁ @BBA-1	99.3	0	93.6	Our Work

First we have compared the catalytic performance of our catalyst based on the obtained selectivity of the desired product 2-methoxy-4-methylphenol. The survey reports indicated that N-doped carbon-supported Pd catalyst Pd@CN0.132 and Pd/MSMF provided vanillin conversion with 69% and 54.2% 2-methoxy-4-methylphenol selectivity, respectively.^{1,8} Additionally, superior catalytic performance for MOF based catalysts including Pd@NH2-UiO-66, Pd/SO₃H-MIL-101(Cr), Pd/NPC-ZIF-8 and Pd-MIL-101 showed outstanding catalytic performance but the durability of the catalyst in terms of recyclability does not show an impressive result (catalyst could be recycled for only three to six successive runs).²⁻⁵ And also structure degradation of the framework has also been took place after catalytic run of the previously mentioned catalysts. On the other hand, Kim and co-workers have investigated the hydrodeoxygenation of vanillin over $Pd_{50}Ag_{50}/Fe_{3}O_{4}/N$ -rGO catalyst but the catalyst suffers from the use of expensive both Pd and Ag as noble-metals in high contents and tedious job including multistep catalyst synthesis procedure.⁷ Similar kind of thing is observed for the use of both expensive catalyst as Au-Pt for HDO of vanillin.⁹ Xia and co-workers have achieved very moderate vanillin conversion (74.4%) with low selectivity of the desired product (64.6%) employing non-noble metal based catalyst Ni/NCB-900. And also in this case a drastic drop in the desired product selectivity has been found on multiple catalyst reuse.¹⁰ Xia *et al.* have observed a remarkable outcome of the catalytic result when they have used Co@NC-700 catalyst but it still suffers from the catalyst stability on multiple reuse which is important for further implementation in industry.¹¹ Although Pd/CN-CF has served some fruitful result for catalytic applications but the catalyst synthesis procedure is included multi-step and use of hydrogen gas at high temperature.¹²

Table S2: Comparison of the ca	atalyst performance	based on the same	e standard,	such as	TOF
and MMP productivity based on	the metal.				

Catalyst Used	TOF (s^{-1})	MMP Productivity (mol _{MMP} g _{catalyst} ⁻¹ h ⁻¹)
Cu@BBA-1	0.069	4.37
Pd@BBA-1	0.141	5.40
Cu ₁ Pd ₁ @BBA-1	0.211	10.16
Cu ₃ Pd ₁ @BBA-1	0.287	14.94
Cu ₁ Pd ₃ @BBA-1	0.270	11.38
Cu ₄ Pd ₁ @BBA-1	0.229	12.76
Cu ₅ Pd ₁ @BBA-1	0.196	11.44

TOF= Turn Over Frequency; MMP= 2-methoxy-4-methylphenol.

Materials	C (%)	H (%)	N (%)
Cu@BBA-1	72.853	6.419	2.678
Pd@BBA-1	76.062	6.770	2.292
Cu ₁ Pd ₁ @BBA-1	38.23	3.61	0.75
Cu ₃ Pd ₁ @BBA-1	39.97	3.52	0.65
Cu ₄ Pd ₁ @BBA-1	33.60	3.25	0.55
Cu ₅ Pd ₁ @BBA-1	37.87	3.46	0.68
Cu ₁ Pd ₃ @BBA-1	34.01	3.18	0.30

Table S3: Elemental (C, H & N) analysis of the respective monometallic and bimetallic samples

Table S4: Inductively coupled plasma mass spectrometry (ICP-MS) analysis results of the bimetallic Cu-Pd nanoalloy.

Catalyst	Cu-content (mmolg ⁻¹)	Pd-content (mmolg ⁻¹)
Cu@BBA-1	0.385	NA
Pd@BBA-1	NA	0.296
$Cu_1Pd_1@BBA-1$	0.432	0.346
$Cu_3Pd_1@BBA-1$	0.512	0.223
Cu ₄ Pd ₁ @BBA-1	0.592	0.136
Cu ₅ Pd ₁ @BBA-1	0.672	0.086
Cu ₁ Pd ₃ @BBA-1	0.145	0.507



Figure S1: Distribution of products based on substrate to catalyst molar ratio (S/C)

For practical applications, both high yield and low cost are required. We have conducted the vanillin HDO reaction varying substrate/catalyst molar ratio from 260 to 360 (Figure S1, SI). We have achieved 97.4 and 95.3% vanillin conversions, respectively, with S/C molar ratio of 265 and 280, respectively. But in these cases we have observed the formation of several side products (over hydrogenation products) diminishing the selectivity of desired product 2-methoxy-4-methylphenol. We have found best result when the S/C ratio is 294. In this case 99.3% conversion with a high 2-methoxy-4-methylphenol selectivity of 93.6% was obtained at 140°C. In contrast, a decrease in vanillin conversion along with the desired product selectivity has been observed with the increase of S/C molar ratio about 365. In this case vanillin alcohol is appeared with 18.3% selectivity, suggesting all the initially formed vanillin alcohol do not undergo complete hydrogenolysis reaction.



Figure S2: Kinetic profile diagram (fitted with experimental data) of all catalysts.



Figure S3: Thermogravimetric (TGA) analysis data of all the respective samples.

In order to further investigate thermal stability and presence of confined guest molecules, we have conducted Thermogravimetric (TGA) analysis (Figure S3, SI). The TGA curve is associated with the two respective weight losses, first one is at lower temperature range (100-200°C) and second one is at higher temperature range (400-500°C). We have observed around 10% weight loss at the in the region 200°C, which could be explained to the removal of surface bound or the intercalated water absorbed in the internal pores or due to the loss of coordinated solvent molecules. After reaching 400°C temperature region, a huge weight loss (32%-37%) took place, which corresponds to the decomposition of the organic fragments.

Figure S4 below presents the measured synchrotron powder diffraction patterns of the Pd@BBA-1 (a), Cu₃Pd@BBA-1 (b) and Cu@BBA-1 (c) systems. We have also included the structural refinement results in all the cases (solid lines). Pd@BBA-1 data is found to be well described the *fcc* structure (space group Fm-3m, Pd at 4a (0.0, 0.0, 0.0) Wyckoff position) with a lattice parameter 3.891 Å, except for some weak peaks mostly originating from the minor crystalline oxide phase. Compared to this, the Cu@BBA-1 sample is found to have an additional phase which is found to be well described by the Cu₂O crystal lattice (space group: Pn-3m, Cu (0.5, 0.5, 0.5) and O (0.25, 0.25, 0.25) with the cubic unit cell parameter 4.254 Å. This phase is found to have a weight of 80%. The pure metallic phase in the Cu@BBA-1 was found to be the of the standard *fcc* structure (space group Fm-3m, Cu at 4a (0.0, 0.0, 0.0))

Wyckoff position) with a lattice parameter 3.609 Å. As described in the main text, the diffraction data evidenced the alloying in the Cu₃Pd@BBA-1 sample. The diffraction pattern is found to be reasonably well described by the *fcc* structure (space group Fm-3m, Cu and Pd at 4a (0.0, 0.0, 0.0) Wyckoff position with occupation respectively 0.66667 and 0.33333) with a lattice parameter 3.758 Å. Unlike the diffraction pattern of Pd@BBA-1, the calculated intensities does not described well the observed one in case of the Cu₃Pd@BBA-1 which may be due to the strong interaction of the nanoalloy with the matrix thus modifying its local structure. This is in agreement with the EXAFS observations. This structural diversity from the expected average crystal periodicity may have a bearing on the high performance of this system.



Figure S4: X-ray diffraction patterns of Pd@BBA-1 (a), Cu₃Pd@BBA-1 (b) and Cu@BBA-1 (c) obtained using a wavelength of 0.7 Å. Symbols represent the experimental data, solid lines denote the refined results and the vertical bars indicate the Bragg positions.



Figure S5: FT-IR analysis data of all the respective samples.

The broad absorption bands located at 3420 cm⁻¹ is responsible for the presence of $-NH_2$ groups in the porous organic polymer BBA-1 unit of Cu@BBA-1, Pd@BBA-1 and Cu₃Pd₁@BBA-1, respectively. The bands appeared at around 1604 cm⁻¹ and 1502 cm⁻¹ could be attributed to the aromatic C=C bonds stretching vibrations. The absorption bands centered at the region 2918 cm⁻¹, could be assigned to the characteristic sp³ C-H bond vibrations (benzyl carbon and hydrogen bond) in all the respective monometallic and bimetallic materials.





Figure S6: Particle size distribution histogram profiles of the respective catalysts.

Figure S7: XPS survey spectra of the respective catalysts.

Cu K-edge XANES provides rich information on the unoccupied electronic states and the local structure. Figure S8 presents the XANES data of the Cu@BBA-1 and Cu₃Pd@BBA-1 samples, which evidences clear difference between the two. A pure Cu nano system is expected to show a similar XANES spectra as that of a bulk except for the huge damping of the near-edge features and a variation in the pre-edge intensity. In case of Cu@BBA-1, the near-edge features are found to be completely different which is understandable considering the diffraction results showing the presence of another major phase. This is further confirmed by the large shift of the absorption edge in comparison to the metallic foil. Compared to this the Cu₃Pd@BBA-1 is found to be more close to the bulk foil, similar continuum resonance peak, except for a shift (broad feature around 9028 eV) and double structured main peak (8995 eV). Present results indicate that the nanoalloying permits to keep the metallicity at atomic scale which may be main factor to have a higher catalytic performance for the Cu₃Pd system.



Figure S8: copper K-edge XANES data of Cu₃Pd@BBA-1 and Cu@BBA-1 together with that of a standard metallic copper foil.

Figure S9 presents the Cu K-edge EXAFS oscillations of a copper foil, Cu@BBA-1 and Cu₃Pd@BBA-1. Large k range obtained reveals the high quality of the EXAFS data. Huge damping in the EXAFS oscillations for the Cu@BBA-1 and Cu₃Pd@BBA-1 compared to a bulk system Cu foil (note the y-scale) is characteristic of the nanostructuring.



Figure S9: copper K-edge EXAFS oscillations from metallic Cu foil, Cu@BBA-1 AND Cu₃Pd@BBA-1. Notice the difference in the y scale.



Figure S10: Possible hydrodeoxygenation pathway of Vanillin and the various reactions are involved to produce different products fragments.

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