Environmentally-friendly preparation of natural hollow carbon sphere derived from biomass puffball for in-situ upgrading of lignin-derived vanillin

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Catalyst characterization: N_2 adsorption-desorption isotherms of Ni_xCu_y/BC catalysts were carried out at -196 ℃ using a Micromeritics ASAP 2460 apparatus to obtain the parameter of surface area, pore volume and pore size distribution. Powder X-ray diffraction (XRD) patterns of Ni_xCu_y/BC catalysts were carried out on a Rigaku Smart Lab SE using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan speed of 10° min^{-1} and a scan range of 30-80° at 30 kV and 15 mA. Raman spectroscopy was carried out to study the degree of graphitization by a WITec alpha300R using a laser excitation wavelength of 532 nm. Scanning electron microscopy (SEM) was investigating by employing a ZEISS Gemini SEM 300. high-resolution transmission electron microscopy (HRTEM) images of the Ni_xCu_y/BC catalysts were studied by a FEI Talos F200S. X-ray photoelectron spectroscopy (XPS) was performed to study the element states of the Ni and Cu by employing a Thermo Scientific K-Alpha with Al-Kα as the photon source. H_2-temperature programmed reduction (H_2-TPR) and NH_3-temperature programmed desorption (NH_3-TPD) were studied on a Micromeritics

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The density functional theory (DFT) was calculated by the first principle and Perdew Burke ernzerhof (PBE) formula. The plane-wave basis set was used to expand the smooth part of the wave functions with a cutoff kinetic energy of 450 eV. The sufficiently large vacuum region of 18 Å was employed to make sure the periodic images were separated. The convergence criterion of the electronic self-consistent loop was 10^{-5} eV and the atomic structures were optimized until the residual forces were below 0.03 eV $Å^{-1}$.

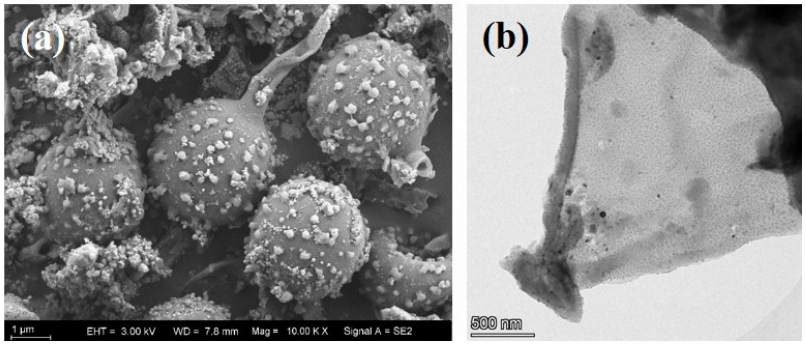


Fig. S1 (a-b) SEM and HRTEM images of puffball-based biochar.

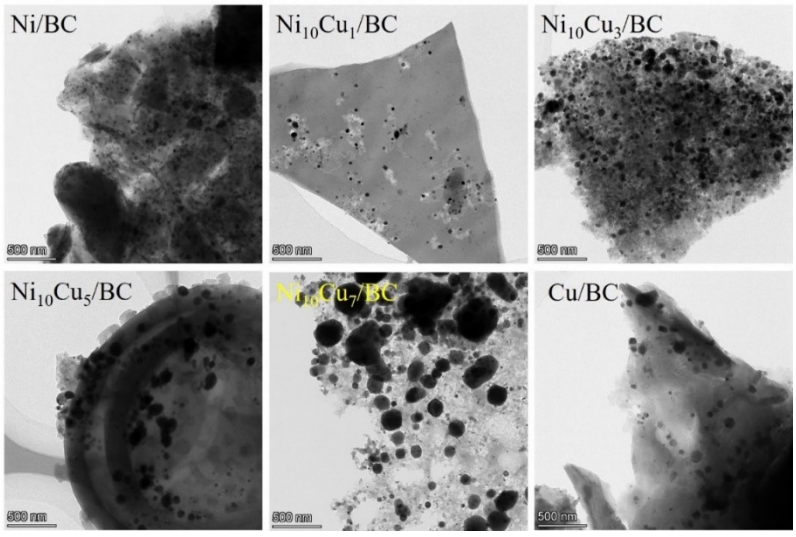


Fig. S2 HRTEM images of all Ni_xCu_y/BC catalyst.

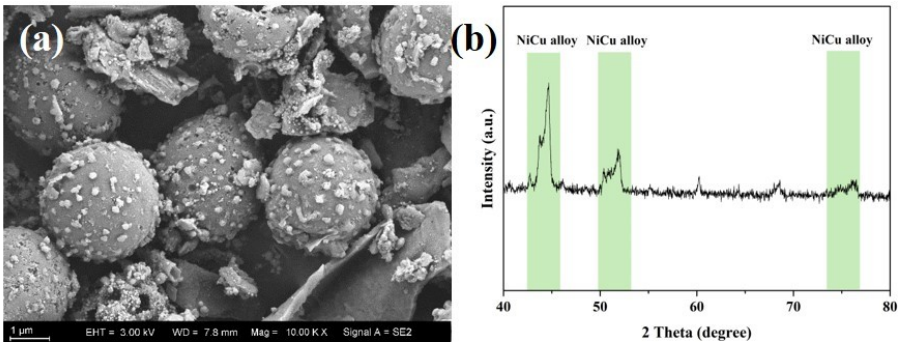


Fig. S3 (a-b) SEM images and XRD patterns of spent $Ni_{10}Cu_5$/BC catalyst.

Table S1 Conversion of VAN over different none-noble catalysts.

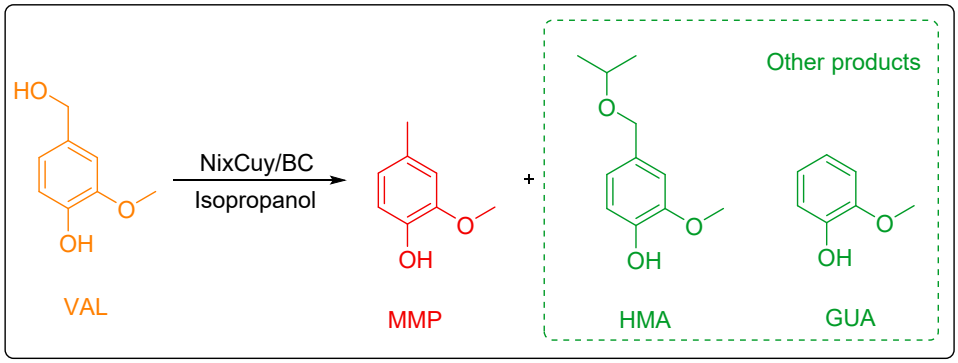
Catalysts	Solvents	Reaction conditions			Conv. (%)	Sel. (%)	Ref.
		H_2 (MPa)	T (°C)	*t* (h)			
Ni_2P/HY	ethanol	2	220	5	99	100	[1]
HD-Ni/N-CMS	H_2O	2	150	10	100	99	[2]
Cu-PMO	Methanol	4	180	18	100	90	[3]
Ni/SiO_2-ZrO_2	octane	5	300	16	100	54	[4]
Ni-MFC-700	methanol	2	200	10	100	96.5	[5]
Co@NP-700	H_2O	0.5	180	4	95.7	100	[6]
Ni/ZrP	isopropanol	2	220	0.5	97.25	88.39	[7]
CoNi/Al_2O_3	isopropanol	1	200	1	100	99.2	[8]
Ni/ZrP	isopropanol	0.5	180	1	100	87.8	[9]
Cu-Ni/CeO_2-SiO_2	H_2O	2.5	150	12	96	90.6	[10]
Ni/biochar	ethanol	3	170	2	79.3	80.4	[11]
Ni/T-Nb_2O_5	H_2O/ethanol	1	180	1	96.1	79.2	[12]
Cu-Ni/CZ-B	H_2O	2.5	160	12	96.0	90.2	[13]
$Ni_{10}Cu_5$/BC	isopropanol	/	240	4	~100	88.12	*This work*

Table S2 Metal content of $Ni_{10}Cu_5$/BC before and after VAN hydrodeoxygenation.

Catalysts	Metal content[a] (wt%)	
	Ni	Cu
Fresh $Ni_{10}Cu_5$/BC	9.8	5.12
Spent $Ni_{10}Cu_5$/BC	8.2	4.31

[a] Determined by ICP-OES.

Table S3 Control experiment with VAL as raw material.



Substrate	Conversion	HMA	MMP	GUA
VAL	~100%	3.15%	89.60%	7.25%

Reaction condition: 20mg $Ni_{10}Cu_5$/BC catalyst, 2.0 MPa N2, 4 h, 240 ℃, isopropanol.

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