Support information

Modulating the surface structure of nanodiamonds to enhance electronic metal-support interaction for efficient ruthenium catalyst in levulinic acid hydrogenation

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*Guojun Lan − Institute of Industrial Catalysis, Zhejiang University of Technology, Hangzhou 310032, PR China; Email: languojun@zjut.edu.cn
*Ying Li − Institute of Industrial Catalysis, Zhejiang University of Technology, Hangzhou 310032, PR China; Email: liying@zjut.edu.cn
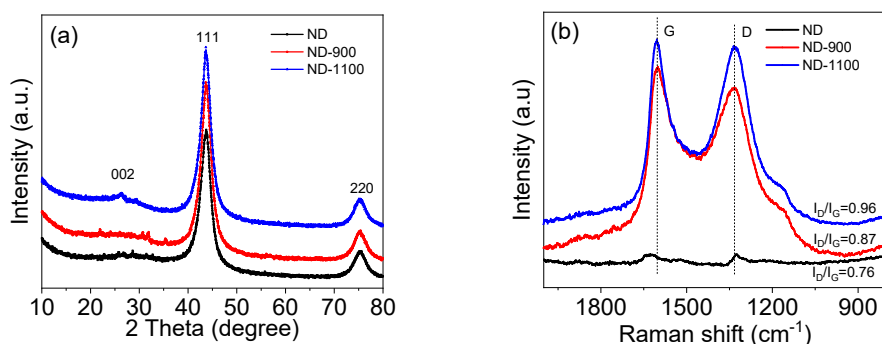
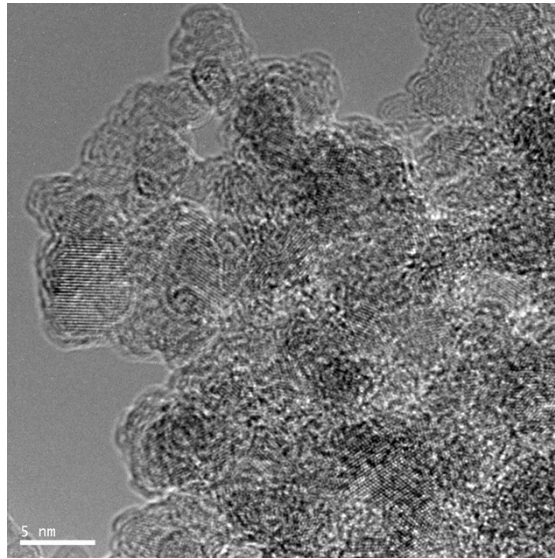Figure S1 (a) XRD patterns and (b) Raman spectra of ND-T support.

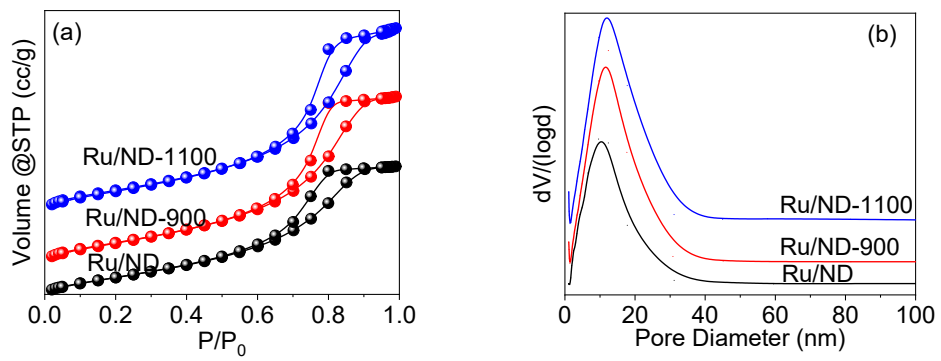Figure S2 Representative TEM image of ND-900.

Figure S3 Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of the Ru/ND, Ru/ND-900 and Ru/ND-1100.
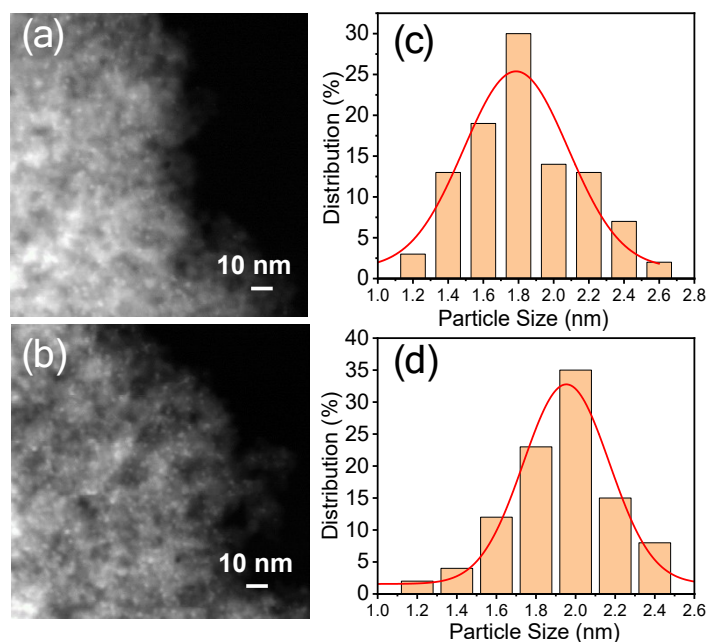
Figure S4 Representative TEM images and corresponding particle size distributions for Ru catalysts (a, c) 1wt%Ru/ND-900 and (b, d) 4wt%Ru/ND-900
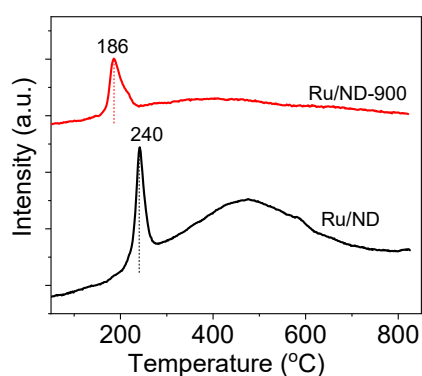

Figure S5 Temperature-programmed reduction curves of the Ru/ND and Ru/ND-900.

Table S1 Texture properties and elemental composition of ND, ND-900 and ND-1100.

Samples	S. A. (m²/g)	P. V. (cm³/g)	P. D. (nm)	I_D/I_G
ND	307	0.56	10.6	0.76
ND-900	351	0.74	11.4	0.87
ND-1100	345	0.78	11.7	0.96

Table S2 The comparison of the Ru/ND-900 catalyst and various carbons supported Ru catalysts for hydrogenation of levulinic acid toward GVL

samples	Conversion of LA	Selectivity of GVL

	(%)	(%)
1%Ru/ND-900	35.1	>99
2%Ru/ND-900	38.9	>99
4%Ru/ND-900	34.2	>99
2%Ru/AC	23.8	>99
2%Ru/CB	31.5	>99

Reaction condition: LA (1 g), water (10 mL), LA /Ru (mol ratio) = 5000, (molar ratio), 70 °C, 4 MPa H_2, 1000 rpm, and 1 h.

Table S3 The activation energy of hydrogenation of levulinic acid toward GVL for the Ru/ND-900 catalyst and the various Ru catalysts reported in reference.

Samples	Reaction temperature (°C)	H_2 Pressure (MPa)	Ea (kJ/mol)	Reference
Ru/C	90	0.1	26	[1]
Ru/C	30	0.1	48	[1]
Ru@C-Al_2O_3	25	0.1	34	[2]
Ru/BPhDS	120	4.0	53.3	[3]
Ru/ND-900	70	4.0	33.1	This work

Table S4. The binding energy shift of the Ru0 in the Ru/ND-T.

Catalysts	B.E. (eV)	B.E. shift (eV)
Ru/ND	461.3	-0.6
Ru/ND-700	461.1	-0.8
Ru/ND-900	460.8	-1.1
Ru/ND-1100	461.2	-0.7
Ru/ND-1300	461.5	-0.4
Ru/C*	461.9	none

* The Ru/C catalyst prepared by incipient-wetness impregnation method reported in the literature [Y. Li et al., Catalysis Today 2011, 174, 97 105]

[1] O.A. Abdelrahman, A. Heyden, J.Q. Bond, Analysis of Kinetics and Reaction Pathways in the Aqueous-Phase Hydrogenation of Levulinic Acid to Form γ-Valerolactone over Ru/C, ACS Catalysis, 4 (2014) 1171-1181.

[2] C. Van Nguyen, B.M. Matsagar, J.-Y. Yeh, W.-H. Chiang, K.C.W. Wu, MIL-53-NH_2-derived carbon-Al_2O_3 composites supported Ru catalyst for effective hydrogenation of levulinic acid to γ-valerolactone under ambient conditions, Molecular Catalysis, 475 (2019) 110478.

[3] C. Moustani, E. Anagnostopoulou, K. Krommyda, C. Panopoulou, K.G. Koukoulakis, E.B. Bakeas, G. Papadogianakis, Novel aqueous-phase hydrogenation reaction of the key biorefinery platform chemical levulinic acid into γ-valerolactone employing highly active, selective, and stable water-soluble ruthenium catalysts modified with nitrogen-containing ligands, Applied Catalysis B: Environmental, 238 (2018) 82-92.