Electronic supplementary information

HYBRID MAGNETICALLY SEPARABLE CATALYST FOR THE HYDROGENATION OF LEVULINIC ACID TO γ-VALEROLACTONE

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Figure S1. Synthesis of the hybrid organic-inorganic catalyst SiO₂-Fe₃O₄-HPP-Ru



Figure S2. Liquid nitrogen adsorption-desorption isotherms of the SiO₂-Fe₃O₄-HPP-Ru



Figure S3. XRD pattern of the SiO₂–Fe₃O₄–HPP–Ru sample

	Pos.	FWHM	% Area
Ru 3d _{5/2} (Ru(OH) ₃)	281.30	1.31	2.50
Ru 3d _{3/2} (Ru(OH) ₃)	285.47	1.57	1.64
Ru 3d _{5/2} (Ru(OH) ₃) Satellite	283.20	1.31	1.19
Ru 3d _{3/2} (Ru(OH) ₃) Satellite	287.57	1.57	0.80
$C 1s (C-C (sp^2))$	284.72	1.13	49.99
C 1s (C-N)	285.39	1.25	16.71
C 1s C-O-C	286.20	1.76	8.01
С 1s (С (л-л))	291.85	2.50	5.44
C 1s -COOH	289.59	2.50	2.14
Ru 3d _{5/2} (RuCl ₃)	282.36	1.34	4.66
Ru 3d _{3/2} (RuCl ₃)	286.53	1.60	3.14
Ru 3d _{5/2} (RuCl ₃) Satellite	284.26	1.34	2.27
Ru 3d _{3/2} (RuCl ₃) Satellite	288.63	1.60	1.51

Table S1. Deconvolution parameters of the Ru 3d and C 1s XPS spectra

Table S2. Activity of different catalysts in the hydrogenation of LA

Catalyst	Solvent	Reaction conditions	LA conv. (%)	GVL yield (%)	Ref.
5%Ru/TiO ₂ –SiO ₂	ethanol	130 °C, H_2 3 MPa, 0.1 g of the catalyst, 6 h	96	84	[1]
RuCl ₃	ethanol	100 °C, H ₂ 2 MPa, 0.5 mol % of the catalyst, 6 h	61	2	[1]
RuCl ₃ /PPh ₃	ethanol	100 °C, H ₂ 2 MPa, 0.5 mol % of the catalyst, 6 h	89	17	[1]
5%Ru/C	dioxane	265 °C, H ₂ 1 bar, 1 g of the catalyst, 50 h	100	98.6	[2]
1%Ru/TiO ₂	H_2O	70 °C, H_2 5 MPa, 0.3 g of the catalyst, 1 h	99	95	[3]
$Fe-Re(1:2)/TiO_2$,	H_2O	180 °C, H ₂ 4 MPa, 0.023 g of the catalyst, 4 h	100	95	[4]
1%Ru/TiO ₂	H_2O	150 °C, H ₂ 3.2 MPa, 0.4 mol % of the catalyst, 5 h	100	93	[5]
5% Ru/Zr/Al-SBA-15	-	400 °C, H ₂ 0.1 MPa, 0.5 g of the catalyst, 6h	90	15	[6]
0.5%Ru/SiO ₂	H_2O	130 °C, H_2 4 MPa, 0.1 g of the catalyst, 3 h	80	79	[7]
Ru-PVA	H_2O	140 °C, H ₂ 5 MPa, 0.03 mol % catalyst, 1 h	71	69.2	[8]
Ru/SiO ₂	H_2O	90 °C, H ₂ 4.5 MPa, 0.4 mol % catalyst, 6 h	26	14	[9]
Ru ₄₀ -DENs	H_2O	150 °C, H ₂ 1 MPa, 0.5 mol % Ru, 5 h	100	99	[10]
5%Ru/ZrO ₂	H_2O	130 °C, 2 MPa, 0.025 g of the catalyst, 2 h	100	99.5	[11]
1%Ru/zeolite-β	2-ethyl- hexanoic acid	200 °C, H ₂ 4 MPa, 0.3 g of the catalyst, 4 h	100	88	[12]
1%Ru/ZSM-5	2-ethyl- hexanoic acid	200 °C, H ₂ 4 MPa, 0.3 g of the catalyst, 4 h	100	90	[12]
5%Ru/ZrO ₂	H_2O	70 °C, H ₂ 0.5 MPa, 0.5 mol % Ru, 4 h	69	67	[13]
5%Ru/MCM-41	H_2O	70 °C, H ₂ 0.5 MPa, 0.5 mol % Ru, 4 h	89	84	[13]

1%Ru/OMC/H ₃ PO ₄	H ₂ O	70 °C, H ₂ 0.7 MPa, 0.1 mol % Ru, 6 h	98	92	[14]
1%Ru/OMC/H ₃ PO ₄	H_2O	200 °C, H ₂ 4 MPa, 0.1 mol % Ru, 6 h	99	67	[14]
3.5%G2-dendr-SiO ₂ -Ru	H_2O	120 °C, H ₂ 3 MPa, 2 h	84	78	[15]
SiO ₂ –Fe ₃ O ₄ –PPP–3%Ru	H_2O	130 °C, 2 MPa, 0.01 g of the catalyst, 4 h	100	99.5	this work

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References

- 1. L. D. Almeida, A. L. A. Rocha, T. S. Rodrigues, P. A. Robles-Azocar, *Catal. Today*, **2020**, *344*, 158–165. DOI: 10.1016/j.cattod.2018.12.022
- 2. P. P. Upare, J.-M. Lee, D. W. Hwang, S. B. Halligudi, Y. K. Hwang, J.-S. Chang, J. Ind. Eng. Chem., 2011, 17, 287–292. DOI: 10.1016/j.jiec.2011.02.025
- 3. A. M. Ruppert, J. Grams, M. Jędrzejczyk, J. Matras-Michalska, N. Keller, K. Ostojska, P. Sautet, *ChemSusChem*, **2015**, *8*, 1538–1547. DOI: 10.1002/cssc.201403332
- X. Huang, K. Liu, W. L. Vrijburg, X. Ouyang, A. I. Dugulan, Y. Liu, M. W. G. M. T. Verhoeven, N. A. Kosinov, E. A. Pidko, E. J. M. Hensen, *Appl. Catal.*, *B*, **2020**, 278, 119314. DOI: 10.1016/j.apcatb.2020.119314
- 5. A. Primo, P. Concepción, A. Corma, *Chem. Commun.*, **2011**, *47*, 3613–3615. DOI: 10.1039/c0cc05206j
- S. Kumaravel, S. Thiripuranthagan, E. Erusappan, M. Durai, T. Vembuli, M. Durai, *Microporous Mesoporous Mater.*, 2020, 305, 110298. DOI: 10.1016/j.micromeso.2020.110298
- J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, Y. Li, *ChemCatChem*, 2015, 7, 508–512. DOI: 10.1002/cctc.201402834
- E. Anagnostopoulou, P. Lilas, P. Diamantopoulou, C. Fakas, I. Krithinakis, E. Patatsi, E. Gabrielatou, A. P. van Muyden, P. J. Dyson, G. Papadogianakis, *Renewable Energy*, 2022, 192, 35–45. DOI: 10.1016/j.renene.2022.04.081
- 9. A. S. Piskun, J. E. de Haan, E. Wilbers, H. H. van de Bovenkamp, Z. Tang, H. J. Heeres, ACS Sustainable Chem. Eng., 2016, 4, 2939–2950. DOI: 10.1021/acssuschemeng.5b00774
- 10. M. Nemanashi, J.-H. Noh, R. Meijboom, *Appl. Catal.*, *A*, **2018**, 550, 77–89. DOI: 10.1016/j.apcata.2017.10.015
- B. Coşkuner Filiz, E. S. Gnanakumar, A. Martínez-Arias, R. Gengler, P. Rudolf, G. Rothenberg, N. R. Shiju, *Catal. Lett.*, **2017**, *147*, 1744–1753. DOI: 10.1007/s10562-017-2049-x
- W. Luo, U. Deka, A. M. Beale, E. R. H. van Eck, P. C. A. Bruijnincx, B. M. Weckhuysen, J. Catal., 2013, 301, 175–186. DOI: 10.1016/j.jcat.2013.02.003
- 13. Y. Kuwahara, Y. Magatani, H. Yamashita, *Catal. Today*, **2015**, 258, 262–269. DOI: 10.1016/j.cattod.2015.01.015
- 14. A. Villa, M. Schiavoni, C. E. Chan-Thaw, P. F. Fulvio, R. T. Mayes, S. Dai, K. L. More, G. M. Veith, L. Prati, *ChemSusChem*, **2015**, *8*, 2520–2528. DOI: 10.1002/cssc.201500331
- 15. A. L. Maximov, A. V. Zolotukhina, A. A. Mamedli, L. A. Kulikov, E. A. Karakhanov, *ChemCatChem*, **2018**, *10*, 222–233. DOI: 10.1002/cctc.201700691