Supplementary Materials

Synergistic promotion of ultra-small Pt nanoparticles and oxygen vacancy in MOF catalyst for ethyl levulinate to valerolactone at room temperature

Wei Yan¹, Ying Wang^{1,*}, Xu Zhao², Siyi Pu¹, Chunyan Yang¹, Zirui Dao¹, Changfu Zhuang¹, Chungang Min^{3,*}, Xiao-Jun Zhao^{4,*}, Xiaoqin Zou^{2,*}

¹Key Laboratory of Forest Resources Conservation and Utilization in the Southwest Mountains of China Forestry and Grassland Administration, Southwest Forestry University, Kunming 650051, Yunnan, China.

²Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, China. ³Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming 650093, Yunnan, China.

⁴Key Laboratory of Advanced Materials of Tropical Island Resources, Ministry of Education, School of Chemistry and Chemical Engineering, Hainan University, Haikou 570228, Hainan, China.

*Correspondence to: Prof. Ying Wang, Key Laboratory of Forest Resources Conservation and Utilization in the Southwest Mountains of China Forestry and Grassland Administration, Southwest Forestry University, No. 300, Bailong Temple, Qingyun Street, Kunming 650051, Yunnan, China. E-mail: yingwang@swfu.edu.cn; Prof. Chungang Min, Research Center for Analysis and Measurement, Kunming University of Science and Technology, No. 68 Xuefu Road, Kunming 650093, Yunnan, China. E-mail: minchungang@163.com; Dr. Xiao-Jun Zhao, Key Laboratory of Advanced Materials of Tropical Island Resources, Ministry of Education, School of Chemistry and Chemical Engineering, Hainan University, No. 58 Renmin Avenue, Haikou 570228, Hainan, China. E-mail: xiaojunzhao2013@163.com; Prof. Xiaoqin Zou, Faculty of Chemistry, Northeast Normal University, No. 5268 Renmin Street, Changchun 130024, Jilin, China. E-mail: zouxq100@nenu.edu.cn

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Supplementary Table 2. Acid contents of different catalysts measured by NH₃-TPD.

Supplementary Table 3. Base contents of different catalysts measured by CO₂-TPD.



Supplementary Figure 1. XRD patterns of Pt₁/LaO_V-r and Pt₂/LaO_V-r.



Supplementary Figure 2. EPR spectra of Pt₁/LaO_V-r and Pt₂/LaO_V-r.



Supplementary Figure 3. H₂-TPD curves for Pt₁/LaO_V-r and Pt₂/LaO_V-r.



Supplementary Figure 4. H₂-TPR curves of Pt₁/LaO_V-r and Pt₂/LaO_V-r.



Supplementary Figure 5. NH₃-TPD curves of Pt₁/LaO_V-r and Pt₂/LaO_V-r.



Supplementary Figure 6. CO₂-TPD curves of Pt₁/LaO_V-r and Pt₂/LaO_V-r.



Supplementary Figure 7. XPS spectra of O 1s in Pt₂/LaO_V-r after cycling.



Supplementary Figure 8. (A-C) EL adsorbed on La and Ov in LaOv-r, La in Pt₂/LaOv-r.



Supplementary Figure 9. (A-C) Intermediates adsorbed on La and O_V in LaO_V-r, Pt in Pt₂/LaQS.

Catalysts	Т	Р	t	Solvent	Subst	Prod	Con.	Select.	Ref.
Catalysts	(°C)	(MPa)	(h)		rate	uct	(%)	(%)	
Pt-TiO ₂ /a-Al ₂ O ₃	150	3	3	H ₂ O	EL	GVL	98	98	[1]
$Pt/Sn_{0.8}Mn_1O_y$	120	2	6	Dioxane	LA	GVL	99	>99	[2]
Pt _{0.7} -Ce _{0.5} /TS-1	180	2	6	H ₂ O	LA	GVL	99	>99	[3]
1.6Pt/mesoporou s ZrO ₂	240	2.5	24	H ₂ O	LA	GVL	90	90	[4]
Pt ₂ /LaO _V -r	80	2	4	2-PrOH	EL	GVL	>99	>99	This Work
Pt ₂ /LaO _V -r	25	2	36	2-PrOH	EL	GVL	>99	>99	This Work

Supplementary Table 1. the comparison results of the catalytic properties with the existing literature

Supplementary Table 2. Acid contents of different catalysts measured by NH₃-TPD

Entry	Catalyst	NH ₃ -TPD acid	Medium acid content		
		content (µmol/g)	(µmol/g)		
1	Pt ₂ /LaO _V -r	3375.6	1803.6		
2	Pt_1/LaO_V -r	2944.5	1561.5		
4	Pt ₂ /LaQS	3248.0	1417.4		
5	LaO _V -r	2047.8	376.6		
6	LaQS	1992.4	680.9		

Supplementary Table 3. Base contents of different catalysts measured by CO₂-TPD

Entry	Catalyst	CO ₂ -TPD base	Medium base content		
		content (µmol/g)	(µmol/g)		
1	Pt ₂ /LaO _V -r	2350.5	1554.6		
2	Pt_1/LaO_V -r	2022.3	1133.9		
4	Pt ₂ /LaQS	1707.3	812.1		
5	LaO _V -r	1189.4	459.4		
6	LaQS	387.6	322.3		

REFERENCES

[1] F. Meng, X. Yang, S. Zhao, Z. Li, G. Zhang, Y. Qi, S. Chu, G. Wang, J. Zhang, Y. Qin,
B. Zhang, Shifting reaction path for levulinic acid aqueous-phase hydrogenation by Pt-TiO₂ metal-support interaction, Applied Catalysis B: Environmental, 324 (2023).
https://doi.org/10.1016/j.apcatb.2022.122236

[2] Y. Lu, Y. Wang, Q. Tang, Q. Cao, W. Fang, Synergy in Sn-Mn oxide boosting the hydrogenation catalysis of supported Pt nanoparticles for selective conversion of levulinic acid, Applied Catalysis B: Environmental, 300 (2022) 120746. https://doi.org/10.1016/j.apcatb.2021.120746

[3] J. Li, D. Li, P. Yu, Y. Wang, J. Bao, X. Sheng, Y. Zhang, Y. Zhou, Appl Organomet Chem 2024, 38(5), e7447. https://doi.org/10.1002/aoc.7447

[4] H.-T. Vu, F. M. Harth, M. Goepel, N. Linares, J. GarcíaMartínez, R. Gläser,

Aqueous-Phase Hydrogenation of Levulinic Acid Using Formic Acid as a Sustainable

Reducing Agent Over Pt Catalysts Supported on Mesoporous Zirconia, Chem. Eng. J. 2022,

430, 132763. https://doi.org/10.1021/acssuschemeng.9b05546