

Electronic Supplementary Information

Catalytic aerobic oxidation of lignin-based vanillyl alcohol in
base-free condition over efficient and reusable LaFeO₃
perovskite for vanillin production

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S1 Bio-oil characterization

Gas chromatograph (GC) using flame ionization detector (FID) equipped with a DB-5 capillary column, which determines the yield of vanillin *via* an external standard method through injecting the corresponding authentic compound. The GC detection conditions: Helium (99.99%) was used as the carrier gas at a flow rate was 1.20 mL min⁻¹. The injector, detector and interface temperature were all set to 260°C. All the samples were filtered through a 0.45 µm syringe-driven filter before injection, and the injection volume was 1 µL. The sample injection was performed at a split ratio of 1:1, and the oven temperature was programmed from 60°C (kept for 2 min) to 260°C (kept for 2 min) with a 20°C min⁻¹ heating rate.

S2 Catalysts characterization method

The XRD patterns were recorded in the 2θ range of 10~80° with a scanning size of 4°/min and counting time on a PuXi XRD-3X using Cu Kα (λ=1.54056 Å) radiation under the operation of 40 kV and 30 mA. Crystal phases were identified by comparison with reference patterns from the JCPDS database. FTIR analysis by using a Spectrum Two transform infrared spectrometer (PerkinElmer). The sample and KBr was ground at a mass ratio of 1:100. Spectra was recorded in the wavenumber range of 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹, and each sample was performed for 16 scans. The appearance and internal structure of all samples was obtained using a scanning electron microscope (SEM). X-ray photoelectron spectrometer (XPS) spectra was obtained using a PerkinElmer PHI 1600 ESCA system with Mg Kα 1253.6 eV radiation as the excitation source. The spectra was collected at ambient temperature with an ultra-high vacuum. The binding energy of C1s (284.6 eV) was used as internal reference. The core levels of La 3d, O 1s, and Fe 2p species were recorded and their relative intensities were determined from the integration

of the Gaussian deconvolution signals by curve fitting. Raman scattering spectra was observed by using a microprobed Raman system with a back scattering configuration. The laser beam exited at 532 nm was focused to 2 μm in spot size on a sample surface. The scattered light was analyzed by a triple grating monochromator with a charge coupled detector. The temperature was controlled within 0.1 K. Thermogravimetric analysis under air atmosphere (air-TG) was performed using Perkin Elmer TGA-4000. In each experiment, the thermal stability and the amount of carbon deposited on surface of catalysts were determined by testing 3~5 mg sample in platinum crucible under air atmosphere (99.999%, flow rate of 19.8 mL min⁻¹) at a constant heating rate of 10°C min⁻¹, and first heated from room temperature to 105°C and remained for 15 min to remove absorbed moisture during operation. Afterwards, the sample was heated again from 105°C to 700°C at the same heating rate. The weight loss curves and differential curves were drawn automatically by the system software through the computer.

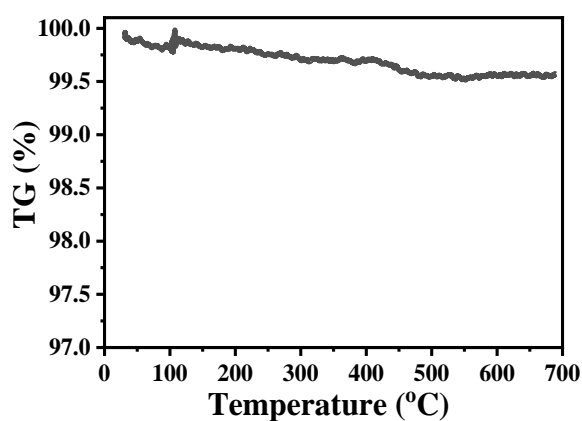


Fig. S1. Thermal stability of LaFeO₃ under air atmosphere.

Table S1 Main compounds (relative peak area-%) identified in bio-oil by GC–MS

Catalyst dosage (g)	Retention time (min)	Area (%)	Main compounds	Matching index
0	13.491	42.76	Vanillin	96
	14.846	48.19	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	76
	16.127	3.73	Vanillic acid	43
0.1	13.491	44.66	Vanillin	96
	14.843	42.73	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	70
	16.128	7.68	Vanillic acid	43
0.2	13.491	36.19	Vanillin	96
	14.845	46.47	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	64
	16.127	11.45	Vanillic acid	43
0.3	12.108	12.65	Vanillin	96
	13.555	84.43	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	58
	14.943	2.31	Vanillic acid	46
0.4	12.109	10.69	Vanillin	96
	13.556	86.24	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	52
	14.943	2.31	Vanillic acid	43
0.5	13.491	28.77	Vanillin	96
	14.847	59.05	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	76
	16.127	8.64	Vanillic acid	43

Table S2 Main compounds (relative peak area-%) identified in bio-oil by GC–MS

Oxygen pressure (MPa)	Retention time (min)	Area (%)	Main compounds	Matching index
0	14.144	31.66	4-Hydroxy-3-methoxybenzyl alcohol	98
	14.848	56.9	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	64
0.4	13.505	8.47	Vanillin	96
	14.854	86.57	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	49
	16.13	2.25	Vanillic acid	43
0.8	13.491	26.82	Vanillin	96
	14.849	64.19	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	52
	16.128	7.57	Vanillic acid	43
1.0	13.491	44.66	Vanillin	96
	14.843	42.73	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	70
	16.128	7.68	Vanillic acid	43
1.2	13.49	35.71	Vanillin	96
	14.848	52.54	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	64
	16.127	7.74	Vanillic acid	43
1.6	13.49	45.97	Vanillin	96
	14.843	6.53	4-Hydroxy-3-methoxybenzyl alcohol, di(propyl) ether	46
	16.127	13.14	Vanillic acid	43

Table S3 Comparison of our work and previous studies (mostly) in recent 10 years for the preparation of vanillin from vanillyl alcohol

Catalysts	Solvents	Conditions	Conv. (%)	Yield (%)	Refs.	Year
TiO ₂ P25 Degussa (ca. 80% anatase and 20% rutile)	H ₂ O	Oxygen, 27°C, 30 min, three external 15W/10 Philips fluorescent lamps	40	4	1	2012
TiO ₂ Merck (100% anatase)		Air, 27°C, 1 h, three external 15W/10 Philips fluorescent lamps	19	3		
Manganese-doped cobalt mixed oxide	Acetonitrile	Air, 140°C, 2 h	62	51	2	2013
Co ₃ O ₄ nanoparticles	NaOH, Isopropanol	Air, 80°C, 6 h.	80	78	3	2013
	Isopropanol		25	22		
nCo-MO	Acetonitrile	Air, 120°C, 2 h	7	0.4	4	2014
Mixed metal cobalt titanium oxide	NaOH	H ₂ O ₂ , 85°C, 5 h	99	67	5	2015
			94	57		
MnCl ₂	H ₂ O	H ₂ O ₂ , microwave irradiation, 80°C, 10 min	90	44	6	2015
CoCl ₂			48.1	16		
Pt/CuCIP	tert-Butanol	Air, 170, 10 h	32	25	7	2015
Mesoporous CuZrO ₃ nanoparticles	Acetonitrile	Air, 120°C, 2 h	91	69	8	2017
Cobalt-supported cobalt nanocomposite	Acetonitrile	85°C, H ₂ O ₂ , 1 h	-	50	9	2017
5.0%N-CNT/ZnO	H ₂ O	10 W UV-LED irradiation, Ar, 20°C, 20 min	46	11	10	2017
Co ₃ O ₄	H ₂ O	Air, 120°C, H ₂ O ₂ , 15 min	38	19	11	2017
Nitrogen-doped reduced graphene oxide/Mn ₃ O ₄	DMSO	Air, 120°C, 12 h	48	31	12	2017
	DMF		41	38		
Fe ₂ O ₃ /Al-SBA-15	Acetonitrile	50°C, H ₂ O ₂ , 2 h	99	87	13	2018
Al-SBA-15			10	9		
Cobalt nanoparticle-embedded carbon nanocomposite	Isopropanol	Air, 140°C,	94	46	14	2018
ZrO ₂	Acetonitrile	O ₂ , 140°C, 5 h	30	29	15	2019
CeO ₂			40	39		

CeO ₂ +ZrO ₂			55	53		
CuO/MgFe ₂ O ₄	Acetonitrile	H ₂ O ₂ , 90°C, 5 h	53	25	16	2019
Fe ₃ [Fe(CN) ₆] ₂	Isopropanol	O ₂ , 100°C, 2.5 h	70	31	17	2019
Au-Pd@HT-PO ₄ ³⁻	1,4-dioxane	Air, 30°C, 24 h, visible-light irradiation, 300 W Xe arc lamp	53	26	18	2019
Eugenol oxidase- agarose	Glycine- NaOH, acetone	H ₂ O ₂ , 30°C, 30 h	86	30	19	2019
TEMPO@SiO ₂ /CuBr	Isopropanol	O ₂ , 30°C, 30 min	96	93	20	2020
Pd/C	p-Xylene	O ₂ , 120°C, 24 h	72	72	21	2020
Nanopetal copper hydroxide nitrate	Isopropanol	Air, 120°C, 2,2,6,6- tetramethylpiperidin- oxyl (TEMPO), 2 h	99	99	22	2021
Pd/ZrO ₂	Isopropanol	O ₂ , 120°C, 4 h	69	60	23	2021
Nanostructured Bi ₂ WO ₆	1,4-dioxane	O ₂ , room temperature, 16 h, 300 W xenon light source ($\lambda > 420$ nm)	43	39	24	2021
Au/ZnO-MZ			85	85		
Au/ZnO-NH ₃			34	34		
Au/ZnO-NaOH	p-Xylene	O ₂ , 120°C, 24 h	22	22	25	2022
ZnO			0	0		
	Water		40	38		
	Acetonitrile		35	32		
NNS amine ligand (Schiff base ligand) with copper(II) chloride mononuclear complex	MeOH		32	31		
	EtOH	Air, TEMPO, 40°C, 6 h	32	30	26	2022
	THF		32	30		
	EtOAc		20	17		
	Acetone		16	14		
LaFeO ₃	EtOAc	O ₂ , 180°C, 2 h	100	33	This work	2022

Table S4 The proportion (%) of La valence states of fresh, spent and regenerated LaFeO₃ determined by La 3d spectra

Catalyst	<i>BE/eV</i>	<i>BE/eV</i>	<i>BE/eV</i>	<i>BE/eV</i>
Fresh	834.3 (31.9%)	837.9 (25.1%)	851.0 (27.7%)	854.9 (15.3%)
First run	834.8 (32.6%)	838.5 (25.2%)	851.2 (25.9%)	855.1 (16.3%)
Fourth run	834.6 (32.4%)	838.6 (26.6%)	852.5 (22.5%)	856.4 (18.5%)
Regenerated	833.9 (33.7%)	837.6 (25.3%)	850.5 (23.4%)	854.4 (17.6%)

Table S5 The proportion (%) of Fe valence states of fresh, spent and regenerated LaFeO₃ determined

by Fe 2p spectra

Catalyst	<i>BE/eV</i>	<i>BE/eV</i>	<i>BE/eV</i>	<i>BE/eV</i>
Fresh	710.0 (33.7%)	711.4 (32.2%)	723.4 (17.4%)	725.2 (16.7%)
First run	710.4 (34.5%)	712.1 (30.6%)	724.1 (19.1%)	724.9 (15.8%)
Fourth run	-	-	-	-
Regenerated	710.0 (25.2%)	711.0 (36.5%)	723.4 (17.7%)	724.4 (20.6%)

Table S6 The proportion (%) of oxygen species of fresh, spent and regenerated LaFeO₃ determined by O 1s spectra

Catalyst	O _H	O _{ads}	O _{latt}
	BE/eV	BE/eV	BE/eV
Fresh	-	531.1 (54.2%)	529.1 (45.8%)
First run	533.0 (74.8%)	531.5 (14.8%)	529.7 (10.4%)
Fourth run	533.1 (82.6%)	531.4 (13.2%)	530.0 (4.2%)
Regenerated	-	531.1 (48.1%)	528.9 (51.9%)

Supplementary references

1. V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, F. Parrino and M. A. Puma, *Applied Catalysis B: Environmental*, 2012, **111-112**, 555-561.
2. A. Jha, K. R. Patil and C. V. Rode, *ChemPlusChem*, 2013, **78**, 1384-1392.
3. A. Jha and C. V. Rode, *New Journal of Chemistry*, 2013, **37**, 2669-2674.
4. A. Jha, D. Mhamane, A. Suryawanshi, S. M. Joshi, P. Shaikh, N. Biradar, S. Ogale and C. V. Rode, *Catalysis Science & Technology*, 2014, **4**, 1771-1778.
5. M. Shilpy, M. A. Ehsan, T. H. Ali, S. B. Abd Hamid and M. E. Ali, *RSC Advances*, 2015, **5**, 79644-79653.
6. J. Pan, J. Fu and X. Lu, *Energy and Fuels*, 2015, **29**, 4503-4509.
7. C. S. Hinde, D. Ansovini, P. P. Wells, G. Collins, S. V. Aswegen, J. D. Holmes, T. S. A. Hor and R. Raja, *ACS Catalysis*, 2015, **5**, 3807-3816.
8. S. Saha and S. B. A. Hamid, *RSC Advances*, 2017, **7**, 9914-9925.
9. K.-Y. A. Lin, H.-K. Lai and Z.-Y. Chen, *Journal of the Taiwan Institute of Chemical Engineers*, 2017, **78**, 337-343.

10. M. J. Sampaio, A. Benyounes, P. Serp, J. L. Faria and C. G. Silva, *Applied Catalysis A: General*, 2018, **551**, 71-78.
11. R. Behling, G. Chatel and S. Valange, *Ultrasonics Sonochemistry*, 2017, **36**, 27-35.
12. Z. Yuan, S. Chen and B. Liu, *Journal of Materials Science*, 2017, **52**, 164-172.
13. F. Saberi, D. Rodríguez-Padrón, E. Doustkhah, S. Ostovar, A. Franco, H. R. Shaterian and R. Luque, *Catalysis Communications*, 2019, **118**, 65-69.
14. H.-K. Lai, Y.-Z. Chou, M.-H. Lee and K.-Y. A. Lin, *Chemical Engineering Journal*, 2018, **332**, 717-726.
15. P. R. G. N. Reddy, B. G. Rao, T. V. Rao and B. M. Reddy, *Catalysis Letters*, 2019, **149**, 533-543.
16. B. Rahmanivahid, M. Pinilla-de Dios, M. Haghghi and R. Luque, *Molecules*, 2019, **24**, 2597.
17. M.-W. Zheng, H.-K. Lai and K.-Y. A. Lin, *Waste and Biomass Valorization*, 2019, **10**, 2933-2942.
18. M. Wu, J.-H. Pang, P.-P. Song, J.-J. Peng, F. Xu, Q. Li and X.-M. Zhang, *New Journal of Chemistry*, 2019, **43**, 1964-1971.
19. M. García-Bofill, P. W. Sutton, M. Guillén and G. Álvaro, *Applied Catalysis A: General*, 2019, **582**, 117117.
20. M.-W. Zheng, K.-Y. A. Lin and C.-H. Lin, *Waste and Biomass Valorization*, 2020, **11**, 6917-6928.
21. W. Sun, S. Wu, Y. Lu, Y. Wang, Q. Cao and W. Fang, *ACS Catalysis*, 2020, **10**, 7699-7709.
22. B.-C. Li, N. N. Huy, J.-Y. Lin, S. Phattarapattamawong, G. Lisak, H. Wang and K.-Y. A.

- Lin, *Journal of Environmental Chemical Engineering*, 2021, **9**, 106092.
23. W. Sun, P. Lin, Q. Tang, F. Jing, Q. Cao and W. Fang, *Catalysis Science & Technology*, 2021, **11**, 7268-7277.
24. A. Kumar and R. Srivastava, *ACS Applied Nano Materials*, 2021, **4**, 9080-9093.
25. P. Lin, R. Shang, Q. Zhang, B. Gu, Q. Tang, F. Jing, Q. Cao and W. Fang, *Catalysis Science & Technology*, 2022, **12**, 4613-4623.
26. N. C. Jana, S. Sethi, R. Saha and B. Bagh, *Green Chemistry*, 2022, **24**, 2542-2556.