Supporting Information

Porous LaFeO₃ prepared by an in-situ carbon templating method for

catalytic transfer hydrogenation reactions

Ping Xiao,^{†, §} Junjiang Zhu,^{*,‡, §} Dan Zhao, [§] Zhen Zhao, [§] Francisco Zaera,^{*,//} Yujun Zhu,^{*,†}

[†] Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, School of Chemistry and Materials, Heilongjiang University, Harbin 150080, P R China

[‡] Hubei Key Laboratory of Biomass Fibers and Eco-dyeing & Finishing, College of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan 430200, China

[§] Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, China.

[#] Department of Chemistry and UCR Center for Catalysis, University of California, Riverside, 900 University Avenue, Riverside, California 92521, United States

*E-mail: yujunzhu@hlju.edu.cn (YJ Zhu); *E-mail: ciaczjj@163.com (JJ Zhu); *E-mail: zaera@ucr.edu (F Zaera)

Table of Contents

Figure S1. (A) TGA-DSC profiles from $LaFeO_3$ prepared by a co-precipitation method; (B) TGA profiles from La+Fe precursor, La+Fe nitrates, and citric acid conducted in O_2 or N_2 atmospheres

Figure S2. TGA profile from LaFeO₃_NA prepared by our in-situ-produced carbon template method

Figure S3. Deconvoluted Fe 2p and O 1s XPS spectra from LaFeO₃_A, and from fresh, dried, and calcined LaFeO₃_NA

Figure S4. O₂-TPD profiles from LaFeO₃_NA and LaFeO₃_A

Figure S5. H₂-TPR profiles from LaFeO₃_NA and LaFeO₃_A

Figure S6. NH₃- (left) and CO₂-TPD (right) profiles from LaFeO₃_NA, LaFeO₃_A, La₂O₃, and Fe₂O₃

Figure S7. XRD patterns from the fresh, dried, and calcined LaFeO₃_NA

Table S1. The reaction conditions of varied catalysts for CTH of furfural

Table S2. Activity of LaFeO₃_NA for the CTH of furfural to FOL with varied ratio of furfural to catalyst

Table S3. Calculated energies for Fe₄LaO₅ and reagents

Figure S8. Mass spectra of products from CTH of various carbonyl compounds over LaFeO₃_NA



Figure S1. (A) TGA-DSC profiles from $LaFeO_3$ prepared by a co-precipitation method; (B) TGA profiles from La+Fe precursor, La+Fe nitrates, and citric acid conducted in O_2 or N_2 atmospheres



Figure S2. TGA profile from LaFeO₃_NA prepared by our in-situ-produced carbon template method



Figure S3. Deconvoluted Fe 2p and O 1s XPS spectra from LaFeO₃_A, and from fresh, dried, and calcined LaFeO₃_NA



Figure S4. O₂-TPD profiles from LaFeO₃_NA and LaFeO₃_A



Figure S5. H₂-TPR profiles from LaFeO₃_NA and LaFeO₃_A



Figure S6. NH₃-TPD (left) and CO₂-TPD (right) profiles from LaFeO₃_NA, LaFeO₃_A, La₂O₃ and Fe₂O₃



Figure S7. XRD patterns from the fresh, dried, and calcined $LaFeO_3_NA$

Table S1. The reaction conditions of varied catalysts for CTH of furfural.

Entry	Catalyst	Catalyst / mg	Furfural / mg	Mass ratio ^a	Solvent	Volume / mL	Pressure	Temp. / °C	Time / h	Product ^b	Ref.
1	5 wt.% Ru/C	100	188	1.88	2-propanol	24	2.04 MPa (N ₂)	180	5	MF	1
2	Ru/RuO ₂ /C	100	188	1.88	2-propanol	24	2.04 MPa (N ₂)	180	5	MF	2
3	2 wt% Pd/Fe ₂ O ₃	500	1500	3.00	2-propanol	40	1.5 MPa (N ₂)	180	7.5	FOL	3
4	Cu _x Al	90	115	1.28	methanol	15	1 MPa (N ₂)	240	1.5	FOL	4
5	Cu/AC-SO ₃ H	96	96	1.00	2-propanol	5	0.4 MPa (H ₂)	110	2	FOL	5
6	Cu/AC-SO ₃ H	96	96	1.00	2-propanol	5	4 MPa (N ₂)	150	5	FOL	5
7	Ni-Cu/Al ₂ O ₃	1000	4487	4.49	2-propanol	-	4.5 MPa (N ₂)	200	4	FOL	6
8	γ-Fe ₂ O ₃ @HAP	40	96	2.40	2-propanol	15	1 MPa (N ₂)	180	3	FOL	7
9	La_2O_3	49	106	2.16	2-propanol	3	0.8 MPa (N2)	180	17	FOL	8
10	LaFeO3_NA	50	40	0.80	2-propanol	15	1 MPa (N ₂)	180	3	FOL	this
			(98)	(1.96)							work

^a Mass ratio of furfural to catalyst.

^b 2-methylfuran (MF) and furfuryl alcohol (FOL).

Entry	Catalyst content /mg	Furfural content / mg	Reaction time / h	Conversion / %	FOL Selectivity /%
1	50	40	3	90	94
2	50	98	3	53	85
3	50	98	5	62	89
4	250	490	5	59	87
5	250	595	7	53	84
6	250	765	7	49	82
7	500	1530	7	50	86

Table S2. Activity of LaFeO₃_NA for the CTH of furfural to FOL under varied conditions^{*a*}

^a Reaction conditions: iso-propanol as hydrogen donor (15 mL for Entry 1-6, 60 mL for Entry 7), dodecane as internal standard, and the reaction was carried out at 180 $^{\circ}$ C and 1 MPa N₂.

Energy / hartree Fe₄LaO₅ -749.260 C₄H₃OCHO -343.346 CH₃CHOHCH₃ -194.351 RC -1287.096 PC -1287.105 RC formation energy -87.1 / kcal mol⁻¹ (PC-RC) / kcal mol-1 -5.7

Table S3. Calculated energies for Fe₄LaO₅ and reagents





Entry 2 Cinnamyl alcohol





Entry 3 Benzyl alcohol

Entry 4 Benzenemethanol, 2-bromo-



Entry 5. Styralyl alcohol



Figure S8. Mass spectra of products from CTH of various carbonyl compounds over LaFeO₃_NA

REFERENCES

(1) Panagiotopoulou, P.; Vlachos, D. G., Liquid phase catalytic transfer hydrogenation of furfural over a Ru/C catalyst. *Appl. Catal., A* **2014,** *480*, 17-24.

(2) Panagiotopoulou, P.; Martin, N.; Vlachos, D. G., Effect of hydrogen donor on liquid phase catalytic transfer hydrogenation of furfural over a Ru/RuO₂/C catalyst. *J. Mol. Catal. A: Chem.* **2014**, *392*, 223-228.

(3) Scholz, D.; Aellig, C.; Hermans, I., Catalytic Transfer Hydrogenation/Hydrogenolysis for Reductive Upgrading of Furfural and 5-(Hydroxymethyl)furfural. *ChemSusChem* **2014**, *7*, 268-275.

(4) Zhang, J.; Chen, J., Selective Transfer Hydrogenation of Biomass-Based Furfural and 5-Hydroxymethylfurfural over Hydrotalcite-Derived Copper Catalysts Using Methanol as a Hydrogen Donor. *ACS Sustain. Chem. Eng.* **2017**, *5*, 5982-5993.

(5) Gong, W.; Chen, C.; Zhang, Y.; Zhou, H.; Wang, H.; Zhang, H.; Zhang, Y.; Wang, G.; Zhao, H., Efficient Synthesis of Furfuryl Alcohol from H₂-Hydrogenation/Transfer Hydrogenation of Furfural Using Sulfonate Group Modified Cu Catalyst. *ACS Sustain. Chem. Eng.* **2017**, *5*, 2172-2180.

(6) Reddy Kannapu, H. P.; Mullen, C. A.; Elkasabi, Y.; Boateng, A. A., Catalytic transfer hydrogenation for stabilization of bio-oil oxygenates: Reduction of p-cresol and furfural over bimetallic Ni–Cu catalysts using isopropanol. *Fuel Process. Technol.* **2015**, *137*, 220-228.

(7) Wang, F.; Zhang, Z., Catalytic Transfer Hydrogenation of Furfural into Furfuryl Alcohol over Magnetic γ -Fe₂O₃@HAP Catalyst. *ACS Sustain. Chem. Eng.* **2017**, *5*, 942-947.

(8) Natsir, T. A.; Hara, T.; Ichikuni, N.; Shimazu, S., Highly Catalytic Performance of La₂O₃ in the Selective Transfer Hydrogenation of Biomass-derived Furfural. *Chem. Lett.* **2017**, *46*, 1580-1583.