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Supplementary Information

One-step catalytic upgrading of bio-based furfural to γ-valerolactone actuated by coordination organophosphate-Hf polymers

Jinyu Tan,[1,2] Yixuan Liu,[1] Mingrui Li,[1] Hu Li,[1,*] Song Yang [1,*]

[1] *State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, State Local Joint Engineering Laboratory for Comprehensive Utilization of Biomass, Center for R&D of Fine Chemicals, Guizhou University, Guiyang, China*

[2] *Institute of Crops Germplasm Resources, Guizhou Academy of Agricultural Sciences, Guiyang, China*

* Correspondence.

E-mails: hli13@gzu.edu.cn (HL); jhzx.msm@gmail.com (SY).

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Table S1 Overview of GVL yields from the conversion of furfural in the best-behaving catalytic system.

Entry	Catalyst	Catalyst synthesis process	Synthesis time/h	Ref.
1	HZ-ZrP	(1) HZSM-5 zeolite and $NH_4H_2PO_4$ were added into $ZrOCl_2.8H_2O$ with stirring and ultrasonic dispersion for 1 h, (2) The precipitation was filtered, washed and dried at 378 K for 12 h, (3) The catalyst was powdered and calcined at 673K for 4 h.	17	1
2	HPW/Zr-Beta	(1) Dealumination of H-Al-Beta at 353K for 24 h, (2) The solid was dried and calcined at 16 h, (3) Zr-Beta zeolite was prepared by the SSIE method for 6 h, (3) Zr-Beta through incipient wetness impregnation, (4) HPA loaded samples.	46	2
3	Hf-MOF-808+Al-Beta	(1) Synthesis of Hf-MOF-808 for 85 h, (2) Synthesis of UiO-66-NH_2 (Hf) for 60 h.	145	3
4	DUT-67(Hf)-0.06	(1) Synthesis of UiO-66(Hf) for 28 h, (2) Synthesis of DUT-67(Hf) for 60 h, (3) Post-synthetic modification of pristine DUT-67(Hf) for 68 h.	156	4
5	Zr-Al-Beta(Al/Zr =0.2)	(1) Dealumination of the commercial zeolite at 25 ℃ for 24 h, (2) The sample was washed, recovered, dried at 110 ℃ for 12h, (3) Zr incorporation, (4) The solid was dried and then calcined for 24 h.	60	5
6	Zr-KIT-5(10)	(1) Dissolving and mixing the desired solution for 24 h, (2) Transferred the solution into autoclave and treated at 100 ℃ for 24 h, (3) The solid were dried at 80 ℃ for 12 h, (4) Calcined at 450 ℃ for 6 h.	66	6
7	Zr-Al-SCM-1	(1) H-SCM-1 and H-MCM-22 zeolite were synthesized for 142 h, (2) Dealumination for 24 h, (3) The sample was washed and calcined 4 h, (4) Zr-containing samples were synthesized via solid-state metallation for 4 h, (5) 2 wt%ZrO_2/H-SCM-1 sample is prepared by incipient wetness impregnation method for 20 h.	194	7
8	Au/ZrO_2+ZSM-5	(1) Rod CeO_2 was synthesized by a modified Hummer's method for 40 h, (2) Au/ZrO_2 was synthesized ultrasound-assisted deposition method for 13 h, (3) HPA/ZrO_2 were prepared by an incipient wet impregnation method for 16h, (4) Al-exchanged HPW (AlPW) catalyst was synthesized by an ion-exchange method for 18h, (5) ZSM-5 and Hmordenite were synthesized by a hydrothermal method for 84 h.	171	8
9	Sn-Al-Beta	(1) For dealumination at 80 ℃ for 24 h, drying at 90 ℃ for 4 h then followed by 200 ℃ for 16 h, (2) For SSIE process, mixed with the metal precursors and dimethyltin dichloride and then calcined at 550 ℃ for 6 h, (3) For grafting process for 7 h, (4) The solid was recovered and dried at 60 ℃ for 12 h and calcined for 6 h at 550 ℃, (5) Sn-Beta was synthesized need for 15 days, (6) The product was filtered, washed, dried, calcined for 24 h.	459	9
10	ZrO_2-SBA-15(2)	(1) A conformal ZrO_2 monolayer encapsulating the SBA-15 surface for 16 h, (2) To obtain bilayer and trilayer zirconia coated SBA-15 for 16 h, (3) Samples were calcined at 550 ℃ for 3 h.	35	10
11	Meso-Zr-Al-beta	(1) Synthesis metal incorporating beta zeolites for 23 h, (2) To create mesopores by alkali treatment for 14 h, (3) Prepared Si-beta for 24 h, (4) Synthesis Zr-containing microporous/mesoporous beta via post-synthetic for 18 h.	79	11
12	Zr-Al-beta	(1) Dealumination for 21 h, (2) The sample was washed, recovered, dried at 110 ℃ 12 h, (3) Zirconium incorporation and obtain the Zr-Al-bate for 24 h.	57	12
13	VPA-Hf(1:1.5)-0.5	(1) Synthesis of VPA-$HfCl_4$ by solvothermal method at 110 ℃ for 24 h, (2) The solid were dried at 80℃ for 6 h.	30	This work

Table S2. The reduction potential ($\Delta H_o f$), steric hindrance, and boiling point of various reducing alcohols (hydrogen donors).[13, 14]

Entry	Reducing alcohol	$\Delta H_o f$[a], kJ/mol	Steric hindrance, kcal/mol	Boiling point/°C
1	methanol	130.1	—	65.4
2	ethanol	85.4	2.813	78.0
3	1-propanol	80.0	3.777	97.0
4	1-butanol	—	4.688	117.0
5	2-propanol	70.0	4.116	82.0
6	2-butanol	—	5.312	99.0
7	2-pentanol	67.9	—	119.0

[a] $\Delta H_o f$ is defined as the difference of the standard molar enthalpy of formation between the alcohol and the corresponding carbonyl compound.

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