Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Aqueous-Phase Hydrogenation and Hydrodeoxygenation of Biomass-Derived Oxygenates with Bimetallic Catalysts

Jechan Lee, Yong Tae Kim, and George W. Huber*

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, Wisconsin 53706, USA

Table S1. Reaction time, conversion, and carbon balance for APH of propanal, xylose, and furfural over γ-Al_2O_3 supported monometallic and bimetallic catalysts. Reaction conditions: 373 K, 5.41 MPa, 5 wt% propanal, 5 wt% xylose, and 4.8 wt% furfural solutions as the feed.

Catalyst	propanal → 1-propanol			xylose → xylitol			furfural → furfuryl alcohol → THFA		
	Reaction time (min)	Conversion (%)	Carbon balance (%)	Reaction time (min)	Conversion (%)	Carbon balance (%)	Reaction time (min)	Conversion (%)	Carbon balance (%)
Pd_1Ni_1	35	6.8	91.3	35	15.4	96.8	75	15.2	94.0
Pd_1Ni_3	35	10.3	90.8	35	30.9	96.2	75	10.3	98.0
Pd_1Co_1	35	6.8	91.7	35	2.3	94.6	75	27.6	98.4
Pd_1Co_3	35	4.1	92.1	35	14.2	96.5	75	13.5	92.6
Pd_1Fe_1	35	6.8	93.2	35	2.3	95.6	75	54.0	98.1
Pd_1Fe_3	35	15.7	90.9	35	7.1	93.2	75	45.5	97.6
3 wt% Pd	120	12.9	90.4	180	10.3	90.4	75	30.1	97.4
Ru_1Ni_1	35	28.6	91.4	35	31.8	96.9	75	10.9	92.4
Ru_1Ni_3	35	30.6	93.5	35	32.3	96.5	75	15.2	93.5
Ru_1Co_1	35	25.6	94.1	35	29.6	97.1	75	23.5	94.1
Ru_1Co_3	35	23.3	95.0	35	28.5	95.6	75	21.3	91.4
Ru_1Fe_1	35	16.8	92.7	35	27.0	98.9	75	25.4	92.3
Ru_1Fe_3	35	16.2	91.6	35	27.0	95.6	75	21.2	95.6
3 wt% Ru	120	30.6	97.8	35	19.6	91.2	75	2.3	98.2
Pt_1Ni_1	35	38.3	93.1	35	24.5	95.9	75	5.9	91.4
Pt_1Ni_3	35	45.6	92.5	35	29.7	97.9	75	18.2	91.2
Pt_1Co_1	35	33.9	92.1	35	10.4	96.0	75	11.5	93.1
Pt_1Co_3	35	39.7	92.6	35	16.4	95.5	75	15.8	92.8
Pt_1Fe_1	35	40.5	92.7	35	9.5	95.4	75	17.6	94.6
Pt_1Fe_3	35	41.8	90.9	35	7.6	95.3	75	44.8	93.2
3 wt% Pt	120	26.7	90.6	180	24.9	93.3	180	10.6	90.7
20 wt% Ni	35	22.3	90.5	35	23.4	93.0	75	30.8	95.0
20 wt% Co	120	4.5	90.3	70	5.9	96.9	180	8.2	94.7
20 wt% Fe	120	0	98.2	180	0	99.8	180	0	98.9

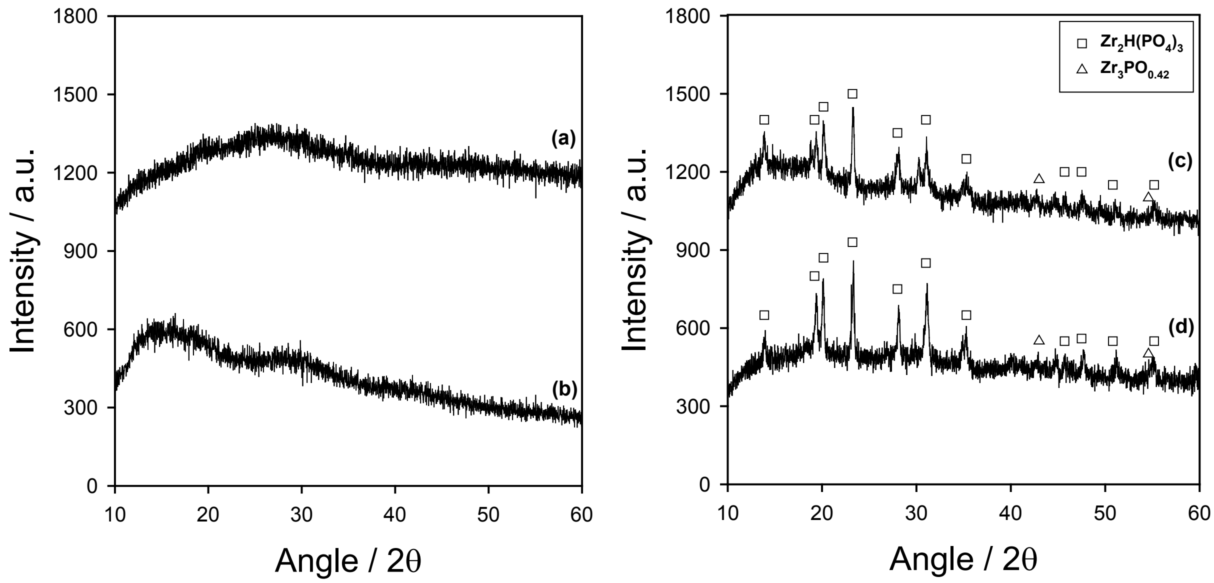
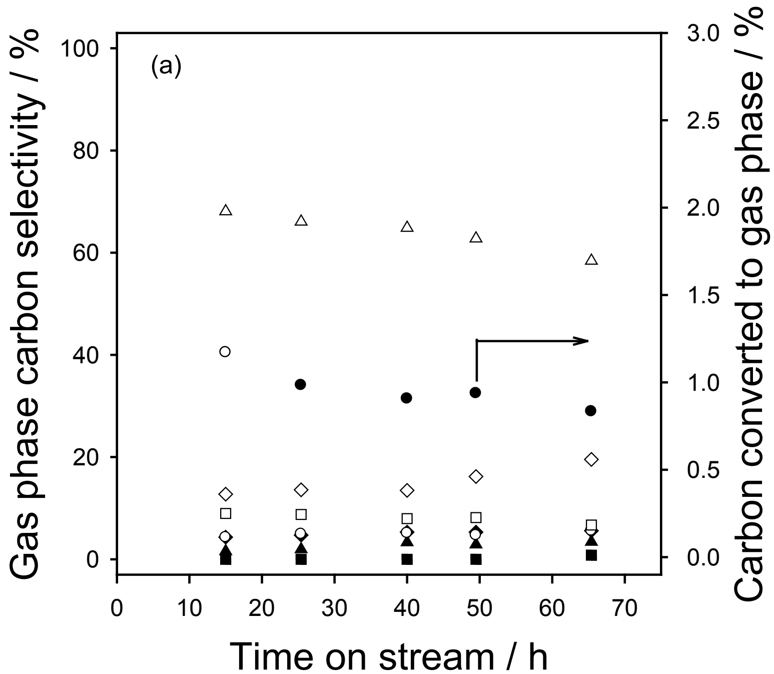


Figure S1. XRD patterns of (a) Pd/Zr-P before reaction, (b) Pd-Fe/Zr-P before reaction, (c) Pd/Zr-P after reaction, and (d) Pd-Fe/Zr-P after reaction. Reaction conditions: 518 K, 6.21 MPa, 20 wt% sorbitol solution as the feed, and flow rate of H_2 is 40 mL min^{-1}.



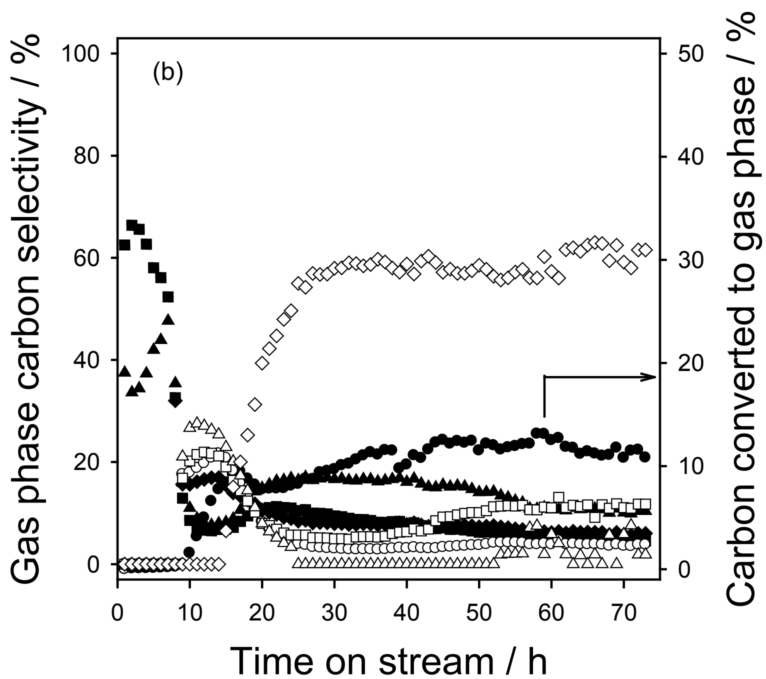


Figure S2. Carbon converted to gas phase (●) and gas phase carbon selectivity of C1 (■), C2 (▲), C3 (◆), C4 (○), C5 (□), C6 (△), and CO_2 (◇) as a function of time on stream over (a) 3 wt% Pd/Zr-P (WHSV = 0.73 h^{-1}) and (b) Pd_1Fe_3/Zr-P (WHSV = 0.16 h^{-1}). Reaction conditions: 518 K, 6.21 MPa, 20 wt% sorbitol solution as a feed, and flow rate of H_2 is 40 mL min^{-1}.

Table S2. Total molar carbon selectivity of products in gas- and liquid-phase as a function of WHSV over Pd/Zr-P and Pd-Fe/Zr-P for HDO of sorbitol. Reaction conditions: 518 K, 6.21 MPa, 20 wt% sorbitol solution as the feed, and flow rate of H_2 is 40 mL min^{-1}.

Catalyst	3 wt% Pd/Zr-P					Pd_1Fe_3/Zr-P	
WHSV (h^{-1})	0.16	0.38	0.73	1.27	2.92	0.16	2.92
Light gas yield (%)	2.4	1.2	0.5	0.3	0.1	10.1	0.8
C1-C4 light gas carbon selectivity (%)							
CO_2	51.9	69.2	72.5	76.0	76.9	68.0	99.5
Methane	1.9	1.2	1.4	1.5	1.4	6.2	0.3
Ethane	8.5	7.1	6.1	4.6	4.3	13.8	0.2
Propane	18.7	12.0	10.1	6.6	7.9	7.6	0
Butane	19.0	10.5	9.8	11.4	9.6	4.4	0
Gasoline-range products yield (%)	24.1	11.4	5.5	2.4	0.9	55.1	2.2
Gasoline-range products carbon selectivity (%)							
Pentane	1.0	0.8	1.0	0.5	0.5	2.3	0.1
Hexane	4.5	6.4	9.0	4.8	7.4	1.2	0.1
Ethanol	2.1	1.9	0.8	1.4	0	6.9	12.2
Propanol	11.4	12.1	4.0	6.4	2.0	21.2	2.5
Propanoic acid	1.1	0.7	0.7	0.4	0	0.8	0
Acetone	0.1	0.1	0	0	0	1.3	0
Butanol	1.8	1.2	0.3	1.1	0	3.4	0.1
Butanone	0.6	0.4	0	0.1	0	2.3	0
Butanal	0.2	0.4	1.6	5.6	2.2	0.1	8.4
Tetrahydrofuran	1.6	1.3	1.1	0.9	1.1	1.1	0
Hydroxy-tetrahydrofuran	0.4	0	0	0.7	0	1.5	0
Butanoic acid	0.3	0	0.1	0.8	0	0.4	0
Pentanol	1.1	1.4	0.8	1.4	0	2.8	0
Pentanone	4.3	3.4	4.2	2.5	2.9	2.6	8.1
Tetrahydropyran	2.9	1.8	1.5	0.6	0	2.0	0
Tetrahydro-4H-pyran-4-ol[a]	1.3	1.8	1.2	3.3	3.9	1.7	0.7
Methyl-tetrahydrofuran	1.2	1.0	1.5	0.8	1.6	1.3	0
Tetrahydro-furfuryl alcohol	3.4	3.6	2.6	7.1	5.6	4.9	14.3
Pentanoic acid	0.8	0.7	0.5	1.3	0	0.6	0.3
Hexanol	5.8	6.0	6.9	2.7	1.9	3.5	1.1
Hexanone	0.8	0.4	0.6	0.3	0	1.7	0
Dimethyl-tetrahydrofuran	10.1	11.2	18.8	14.8	27.3	3.0	12.2
Methyltetrahydrofuran-methanol[b]	5.8	9.2	10.2	12.7	13.1	5.8	4.8
Tetrahydro-methoxymethyl-furan[b]	2.8	3.5	3.4	8.5	5.8	4.0	6.9
Methyl-tetrahydropyran	13.6	14.1	19.5	10.7	16.1	5.0	18.0
Tetrahydropyran-methanol	20.3	14.4	7.4	7.8	5.2	17.3	1.2
Hexanoic acid	0.9	1.7	2.2	2.7	3.5	1.1	9.1
Estimated research octane number (RON)[b]	92.2	90.7	82.9	90.8	85.2	101.3	88.4

Aqueous phase product yield (%)	34.7	56.9	45.9	15.6	2.9	9.4	12.2
Aqueous cut carbon selectivity (%)							
Methanol	1.2	0.8	0.5	0.6	0.9	11.2	2.5
Ethylene glycol	3.1	1.3	0	1.4	2.2	3.5	26.0
Propanediol	0.3	0	0	1.3	1.3	11.5	32.4
Glycerol	0.5	0.4	0.1	1.5	0	3.4	2.3
Hydroxyacetone	0	0	0	0	0	1.8	10.5
Butanediol	0.3	0.6	0	0	0	17.8	4.7
Pentanediol	1.4	1.2	0.4	0.9	2.9	13.1	0.7
Hexanediol	0.3	0.9	0.5	0.8	2.0	9.4	0.3
Hexanetriol	0.4	0.4	0.2	0.4	0	0.2	0.9
Mannitol	8.4	10.7	13.6	0	0	0	0
Sorbitan	8.5	21.4	27.9	54.2	16.6	6.2	1.3
Isosorbide	75.6	62.5	56.7	38.9	74.0	21.8	18.4
Carbon identified (%)	63.5	89.6	94.1	93.1	98.8	75.9	99.7

[a] Tetrahydro-4H-pyran-4-ol (85%), 5-Methyltetrahydrofuran-2-methanol (88%), and Tetrahydro-2 methoxymethyl-furan (89%) is identified by GC-MS.
[b] Research octane number (RON) of the gasoline range products were estimated according to the method introduced in the literature.[1]

Reference

1. N. Li, G. A. Tompsett and G. W. Huber, *ChemSusChem*, 2010, **3**, 1154-1157.