Supporting Information

Selective hydrogenation of 2-pentenal using highly dispersed Pt catalysts supported on ZnSnAl mixed metal oxides derived from layered double hydroxides

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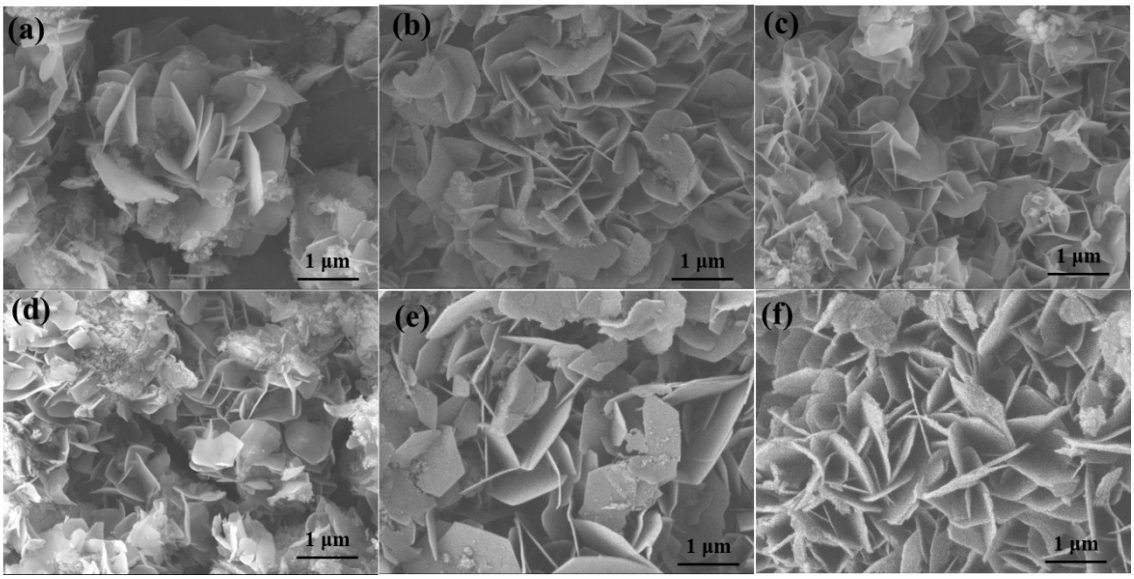

Figure S1. SEM images of (a)-(d) Zn(xSn)Al-LDH/Al_2O_3 (x = 1, 2, 4, 8), (e) ZnAl-LDH/Al_2O_3 and (f) MgSnAl-LDH/Al_2O_3.

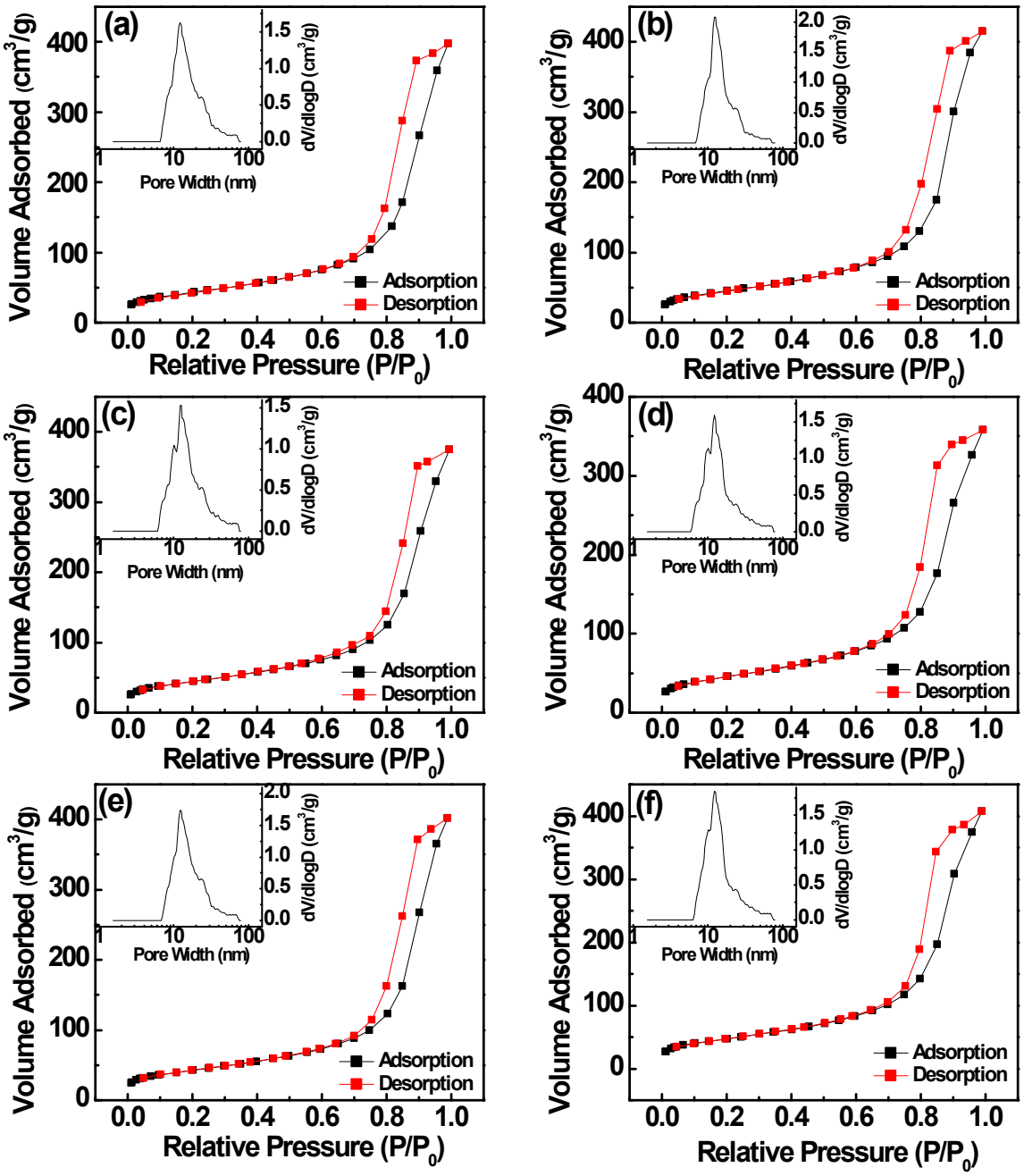

Figure S2. N_2 adsorption-desorption isotherms and (inserted) mesopore size distribution of (a)-(d) Zn(xSn)Al-LDH/Al_2O_3 (x=1, 2, 4 and 8), (e) ZnAl-LDH/Al_2O_3, and (f) MgSnAl-LDH/Al_2O_3.

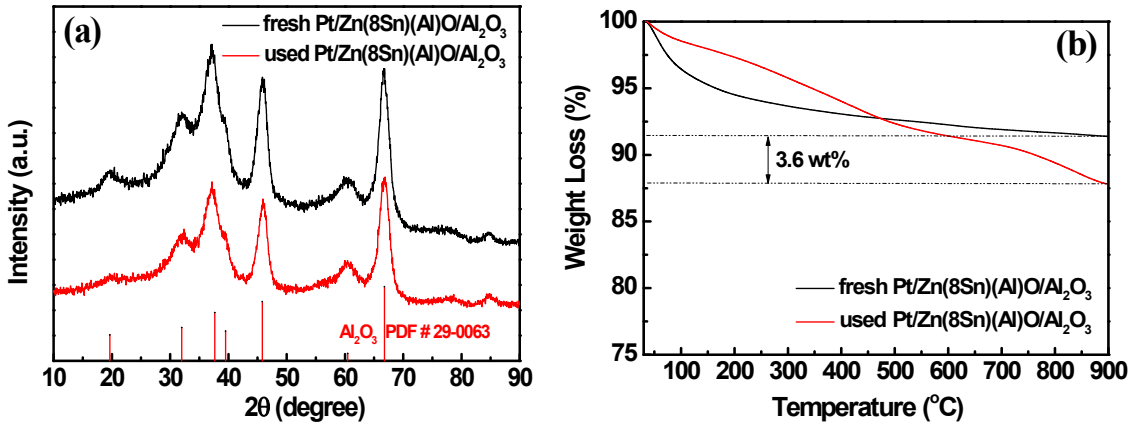

Figure S3. (a) XRD patterns and (b) TG profiles of fresh and used Pt/Zn(8Sn)(Al)O/Al_2O_3 catalysts.

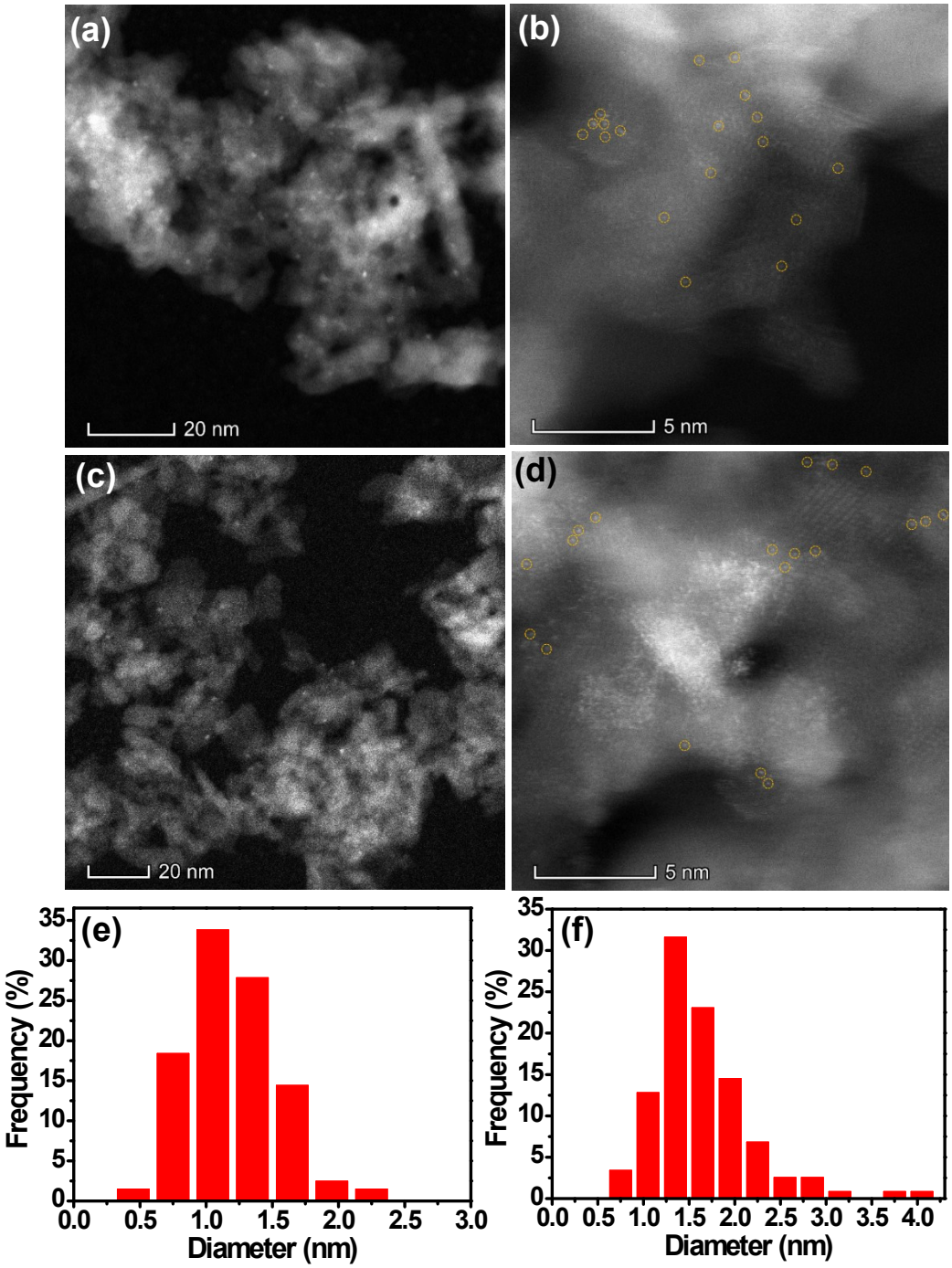

Figure S4. HAADF-STEM images of (a)-(b) and (e) fresh and (c)-(d) and (f) used Pt/Zn(8Sn)(Al)O/Al_2O_3 catalysts.

Table S1. ICP results of different catalysts.

Entry	Catalyst	Pt/wt%	Sn/wt%
1	Pt/Al_2O_3	0.09	0
2	$Pt\text{-}SnO_x/Al_2O_3$	0.12	0.19
3	$Pt/Mg(Sn)(Al)O/Al_2O_3$	0.12	0.26
4	$Pt\text{-}SnO_x/Zn(Al)O/Al_2O_3$	0.13	0.21
5	$Pt/Zn(1Sn)(Al)O/Al_2O_3$	0.11	0.24
6	$Pt/Zn(2Sn)(Al)O/Al_2O_3$	0.14	0.48
7	$Pt/Zn(4Sn)(Al)O/Al_2O_3$	0.12	1.08
8	$Pt/Zn(8Sn)(Al)O/Al_2O_3$	0.11	1.80

Table S2. H_2-TPR results of fresh catalysts.

Entry	Catalyst	Temperature of peak/^oC			Signal for H_2 consumption/a.u.·g-1 cat
1	PtO_2/Al_2O_3	259	447		12248
2	SnO_2/Al_2O_3	458			18323
3	$PtO_2\text{-}SnO_2/Al_2O_3$	281	402		22764
4	$PtO_2\text{-}SnO_2/Zn(Al)O/Al_2O_3$	401	453	535	25511
5	$PtO_2/Zn(1Sn)(Al)O/Al_2O_3$	387	450	515	28834
6	$PtO_2/Zn(2Sn)(Al)O/Al_2O_3$	443			37730
7	$PtO_2/Zn(4Sn)(Al)O/Al_2O_3$	459			49041
8	$PtO_2/Zn(8Sn)(Al)O/Al_2O_3$	470			96481
9	$PtO_2/Mg(Sn)(Al)O/Al_2O_3$	401	454		30373

Table S3. XPS results of different catalysts.

Catalysts	Zn (II)	Sn(IV)		Sn(II)		Sn^0	
	B.E. (eV)	B.E. (eV)	Content (%)	B.E. (eV)	Content (%)	B.E. (eV)	Content (%)
Pt-SnO_x/Al_2O_3	/	487.62	44.2	486.64	49.5	485.6	6.3
SnO_x/Al_2O_3	/	487.25	71.3	486.31	28.7	485.5	0.0
Pt-SnO_x/Zn(Al)O/Al_2O_3	498.14	486.7	33.1	485.99	41.0	485.32	25.9
SnO_x/Zn(Al)O/Al_2O_3	498.25	486.88	33.3	486.08	42.2	485.31	24.5
Pt/Zn(1Sn)(Al)O/Al_2O_3	498.88	487.44	47.2	486.45	44.8	485.5	8.0
Zn(1Sn)(Al)O/Al_2O_3	499.51	487.92	43.5	486.96	54.7	485.5	1.8

Table S4. Catalytic performance of different catalysts for 2-pentenal hydrogenation.

Entry	Catalyst	Reaction time/h	Conversion/%	Selectivity/%			Catalyst productivity*/h^{-1}
				n-pentanal	n-pentanol	2-pentenol	
1	Pt/Al_2O_3	1	42.7	74.2	21.4	4.4	798.9
2	Pt-SnO_x/Al_2O_3	8	39.9	66.3	18.4	15.3	192.3
3	Pt/Mg(Sn)(Al)O/Al_2O_3	3	48.6	44.7	28.6	26.7	345.0
4	Pt-SnO_x/Zn(Al)O/Al_2O_3	24	40.5	30.3	14	55.7	75.8
5	Pt/Zn(1Sn)(Al)O/Al_2O_3	6	43.7	22.5	17.7	59.8	206.6

Reaction conditions: 0.3 g 2-pentenal, 0.3 g catalyst, 50 mL cyclohexane, 80 ^oC, and 3.0 MPa H_2. *Catalyst productivity was calculated by dividing the moles of 2-pentenal converted per hour by total moles of Pt determined by ICP-OES, using the results after 2 h of reaction.

Table S5. Catalytic performances of Zn-based catalysts with different Sn content for 2-pentenal hydrogenation.

Entry	Catalyst	Reaction time/h	Conversion/%	Selectivity/%			Catalyst productivity/h^{-1}
				n-pentanal	n-pentanol	2-pentenol	
1	Pt/Zn(1Sn)(Al)O/Al_2O_3	2	19.6	25.2	15.6	59.2	206.6
2	Pt/Zn(2Sn)(Al)O/Al_2O_3	2	18.3	20.9	17.1	62	151.6
3	Pt/Zn(4Sn)(Al)O/Al_2O_3	8	25	20.6	7.3	72.1	91.8
4	Pt/Zn(8Sn)(Al)O/Al_2O_3	24	28.5	12.2	5.6	82.2	47.4

Reaction conditions are the same as in Table S2.

Table S6. Summary of different heterogeneous catalysts for selective hydrogenation of 2-pentenal to 2-pentenol in recent published works.

Catalysts	Metal loading/%	T/°C	P/MPa	t/h	Conversion/%	Selectivity/%	Catalyst productivity*/h^{-1}	Ref.
Ir-ReO_x/SiO_2	4.00	30	0.8	1	53.1	94.8	153	[1][a]
Pt/SiO_2	0.22	80	3.0	1	11.3	4.3	357.4	[2][b]
Pt-0.5SnO_x/SiO_2	0.22	80	3.0	1	10.1	21.4	319.4	
Pt-1.0SnO_x/SiO_2	0.25	80	3.0	2	10.4	40.8	144.7	
Pt-1.5SnO_x/SiO_2	0.25	80	3.0	2	13.7	61.5	63.5	
Pt@ZIF-8	0.58	80	3.0	3	11.9	31.0	47.6	
Pt-0.5SnO_x@ZIF-8	0.56	80	3.0	5	10.8	48.5	8.9	
Pt-1.0SnO_x@ZIF-8	0.54	80	3.0	7	11.6	62.0	7.1	
Pt-1.5SnO_x@ZIF-8	0.53	80	3.0	17	10.6	80.9	2.7	
$Pt/Zn(8Sn)(Al)O/Al_2O_3$	**0.11**	**80**	**3.0**	**24**	**28.5**	**82.2**	**47.4**	**this work[c]**

Reaction conditions: [a]3.0 mmol reactant, 50 mg catalyst, 3.0 g H_2O; [b]0.3 g reactant, 0.3 g catalyst, 30 mL cyclohexane; [c]0.3 g reactant, 0.3 g catalyst, 50 mL cyclohexane. *Catalyst productivity was calculated by dividing the moles of substrate converted per hour by total moles of metal.

Table S7. Summary of heterogeneous catalysts for selective hydrogenation of 3-methyl-2-butenal to prenol in recent works.

Catalysts	Metal loading/%	T/°C	P/MPa	t/h	Conversion/%	Selectivity/%	Catalyst productivity*/h^{-1}	Ref.
MIL-101(Cr)@Pt@MIL-101(Fe)$^{8.83}$	3.60	25	3.0	10	85.0	64.4	28.8	[3][a]
MIL-101(Fe)@Pt@MIL-101(Fe)$^{9.2}$	4.70	25	3.0	17	71.1	87.8	14.2	
MIL-101(Fe)@Pt@MIL-101(Fe)$^{22.0}$	4.20	25	3.0	24	59.9	92.5	8.5	
Pt-0.23/SiO_2	0.23	80	3.0	4	32.9	23.3	49.7	[4][b]
Pt-0.47/ZIF-8	0.47	80	3.0	8	30.3	58.3	4.7	[4][c]
Pt-1.16@ZIF-8	1.16	80	3.0	2	31.2	90	7.8	
Pt/Zn(1Sn)(Al)O/Al_2O_3	**0.11**	**80**	**3.0**	**36**	**29.2**	**79.5**	**26.0**	**this work[d]**

Reaction conditions: [a]0.4 mmol reactant, 0.23 mg Pt NPs, 2 mL isopropanol; [b]0.5 g reactant, 0.5 g catalyst, 100 mL cyclohexane; [c]0.3 g reactant, 1.2 g catalyst, 100 mL cyclohexane; [d]0.3 g reactant, 0.3 g catalyst, 50 mL cyclohexane. *Catalyst productivity was calculated by dividing the moles of substrate converted per hour by total moles of metal.

Table S8. Summary of heterogeneous catalysts for liquid-phase selective hydrogenation of crotonaldehyde to crotyl alcohol in recent works.

Catalysts	Metal loading/%	T/°C	P/MPa	t/h	Conversion/%	Selectivity/%	Catalyst productivity*/h^{-1}	Ref.
Pt/ZnO-175	5.0	50	0.34	/	10.6	95.0	7.2	[5][a]
CuH5	5.5	100	1.0	/	10	55.0	4.0	[6][b]
Cu/SiO_2	8.1	100	1.0	/	10	7.0	10.8	
Au5/$CeO_2$240	4.72	80	1.0	4	/	26	10.8	[7][c]
Ag/SBA-15	6.9	140	2.0	2.42	95	54	2.5	[8][d]
Ag–In/SBA-15	6.1/1.9			12.33	99	87	1.8	
Pt/ZrO_2-180	6.4	30	0.41	8	37	4	14.1	[9][e]
Pt/ZnO-175	5.1				1	75	0.5	
Pt/SnO_2-270	5				1	25	0.5	
Pt/Fe_2O_3-130	5.6				20	15	8.7	
Pt/Fe_3O_4-250	6.1				21	12	8.4	
Pt/TiO_2-400	4.5				16	6	8.7	
Au/Mg_2AlO	1.20	120	0.93	2	23.6	62.1	94.6	[10][f]
$Au_{5.0}In_{0.75}$/APTMS-SBA-15	4.90	120	2.0	5	94	75	9.2	[11][g]
Pt/Al_2O_3	5	25	2.0	9	86	16	89.9	[12][h]
Pt/SiO_2	3				73	18	127.5	
Pt/C	5				60	7	62.6	
Pt/MgO	2.5				70	20	146.9	
Pt/K-10	2.5				82	31	171.8	
Pt/BenH	3.2				84	43	137.4	
Pt/ZnO ex-nit	1.0	80	0.4	5	18	26	134.4	[13][i]

Pt/ZnO ex-cl	1.0				19	45	136.4	
Pd-Pb/α-Al_2O_3	0.2				3	4	205.8	
Pd-Zn/α-Al_2O_3	0.2				6	1	328.8	
Ir-ReO_x/SiO_2	4.0	30	0.8	1	43.3	95.0	125	[1][g]
Sn-modified SiO_2-coated Pt	3.9	100	2.0	20	4.1	100	0.5	[14][k]
SiO_2-encapsulated SnPt	7.3	100	0.1	20	41.1	66.7	5.9	[15][l]

Reaction conditions: [a] 100 mg catalyst, 20 mL water/dioxane solvent (1:1(v/v)), 0.5 M crotonaldehyde; [b] 200 mg catalyst, 0.1 M crotonaldehyde in isopropanol; [c] 200 mg catalyst, 0.04 M crotonaldehyde, 60 mL isopropanol; [d] 200 mg catalyst, 0.1 ml crotonaldehyde, 29 ml n-hexane; [e] 100 mg catalyst, 20 mL 1,4-dioxane, 0.5 M crotonaldehyde; [f] 0.5 g catalyst, 2 ml crotonaldehyde, 78 ml cyclohexane; [g] 1.0 g catalyst, 1.0 ml crotonaldehyde, 49.0 ml hexane; [h] 50 mg catalyst, 0.57 M crotonaldehyde, 20 mL 2-propanol; [i] 0.150 g catalyst, 0.07 M crotonaldehyde in isopropanol; [g] 50 mg catalyst, 3.0 mmol substrate, 3.0 g H_2O; [k] 50 mg catalyst, 0.2 mL crotonaldehyde, 4 mL 2-methyl-2-butanol; [l] 22.5 mg catalyst, 0.2 mL crotonaldehyde, 4 mL 2-methyl-2-butanol. *Catalyst productivity was calculated by dividing the moles of substrate converted per hour by total moles of metal.

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