

Supporting Information for

Highly efficient selective hydrogenation of cinnamaldehyde to cinnamyl alcohol over CoRe/TiO₂ catalyst

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Table S1. Hydrogenation of CAL over different Co-based catalysts.

Entry	Catalyst	Conv. (%)	Sel. (%)			
			COL	HCAL	HCOL	Others
1	Co ₁ Mo ₁ /TiO ₂	38	75	12	10	3
2	Co ₁ Ce ₁ /TiO ₂	41	84	6	10	/
3	Co ₁ Zr ₁ /TiO ₂	37	88	/	/	12
4	Co ₁ Re ₁ /TiO ₂	96	82	1	17	/
5	Co ₁ Re ₁ /SiO ₂	18	48	12	8	32
6	Co ₁ Re ₁ /ZrO ₂	24	13	17	3	67
7	Co ₁ Re ₁ /γ-Al ₂ O ₃	64	56	18	5	21
8	Co ₁ Re ₁ /ZSM-5	/	/	/	/	/

Reaction conditions: 3 mmol CAL, 10 mL isopropanol, 80 mg catalyst, 160 °C, 12 h. Others: allylbenzene, isopropenylbenzene, 1,1'-(1,5-hexadiene-1,6-diyl)bisbenzene and other unknown by-products.

Table S2. Co 2p and Re 4f dispersion on different catalysts.

Catalyst	Elemental species	Binding energy (eV)	Content
Re/TiO ₂	ReO 4f _{7/2}	41.9	65%
	ReO ₂ 4f _{7/2}	44.0	16%
	Re ₂ O ₅ 4f _{7/2}	46.0	19%
	ReO 4f _{5/2}	44.2	
	ReO ₂ 4f _{5/2}	46.3	
	Re ₂ O ₅ 4f _{5/2}	48.3	
Co/TiO ₂	Co 2p _{3/2}	778.2	17%
	CoO 2p _{3/2}	781.0	39%
	CoO 2p _{3/2} shakeup	796.1	44%
	Co 2p _{1/2}	793.4	
	CoO 2p _{1/2}	796.8	
	CoO 2p _{1/2} shakeup	802.5	
Co ₁ Re ₁ /TiO ₂	ReO 4f _{7/2}	41.7	71%
	ReO ₂ 4f _{7/2}	43.8	6%
	Re ₂ O ₅ 4f _{7/2}	45.8	23%
	ReO 4f _{5/2}	44.0	
	ReO ₂ 4f _{5/2}	46.1	
	Re ₂ O ₅ 4f _{5/2}	48.1	
	Co 2p _{3/2}	778.4	16%
	CoO 2p _{3/2}	781.2	39%
	CoO 2p _{3/2} shakeup	796.3	45%
	Co 2p _{1/2}	793.6	
	CoO 2p _{1/2}	797.0	
	CoO 2p _{1/2} shakeup	802.7	

Table S3. Hydrogenation of CAL to COL using different hydrogen donors.

Entry	Hydrogen donor	Reaction conditions	Conv. (%)	Sel. (%)			
				COL	HCAL	HCOL	Others
1 ^a	Isopropanol	160 °C, 12 h	96	82	1	17	/
2	Triethyl silicane	140 °C, 4 h	34	78	2	19	1
3	Ammonium formate	140 °C, 4 h	94	58	/	22	20
4 ^b	Formic acid	140 °C, 4 h	99	89	/	10	1

Reaction conditions: 3 mmol CAL, CAL:hydrogen donor = 1:2, 10 mL THF, 80 mg Co₁Re₁/TiO₂ catalyst. ^a10 mL isopropanol. ^bCAL:FA:NEt₃ = 1:2:2. Others: cinnamyl formate, allylbenzene, isopropenylbenzene, 1,1'-(1,5-hexadiene-1,6-diyl)bisbenzene and other unknown by-products.

Table S4. Hydrogenation of CAL to COL over various catalysts using formic acid as the hydrogen donor.

Entry	Catalyst	Conv. (%)	Sel. (%)			
			COL	HCAL	HCOL	Others
1	TiO ₂	/	/	/	/	/
2	Co/TiO ₂	26	93	2	5	/
3	Re/TiO ₂	98	74	/	8	18
4	Co ₁ Re ₁ /TiO ₂	99	89	/	10	1

Reaction conditions: 3 mmol CAL, CAL:FA:NEt₃ = 1:2:2, 10 mL THF, 80 mg catalyst, 140 °C, 4 h. Others: allylbenzene, isopropenylbenzene, 1,1'-(1,5-hexadiene-1,6-diyl)bisbenzene and other unknown by-products.

Table S5. Hydrogenation of CAL to COL over various catalytic systems.

Catalyst	Hydrogen donor	Temperature (°C)	Time (h)	Conv. (%)	Sel. (%)	Ref.
Pt/Co-Asp	H ₂ 2.0 MPa	60	2	89.7	89.3	[1]
Pt-Co/rGO	H ₂ 2.0 MPa	40	3	94.6	89.5	[2]
Pt-Co/SBA-15-0.6	H ₂ 1.0 MPa	80	2	71	91	[3]
Pt-Co/CNTs	H ₂ 1.5 MPa	60	1.5	77.7	93.6	[4]
Pt ₈ Co ₁ /ZSM-5-AT	H ₂ 2.0 MPa	100	2	>99	65	[5]
Fe _{0.5} Co@NC	H ₂ 2.0 MPa	80	2	95.1	91.7	[6]
CoB-F-EG	H ₂ 1.0 MPa	100	4	94.9	84.9	[7]
CoPt/Fe ₃ O ₄	H ₂ 3.0 MPa	160	4	95	84	[8]
Pt-Co/PCT	H ₂ 2.0 MPa	80	3	100	96	[9]
Co-Pt/MWCNTs	H ₂ 1.0 MPa	80	12	93.3	93.4	[10]
Pt ₃ -Co/rGO-MW	H ₂ 2.0 MPa	70	1.5	99.7	95.3	[11]
Pt-Co/N-CNT	H ₂ 2.0 MPa	70	1.5	99.7	87.9	[12]
Pt ₅₀ Re ₅₀ /rGO	H ₂ 2.0 MPa	120	4	94.1	88.7	[13]
Cu-MgO ^a	Isopropanol	180	7	11.6	100	[14]
Cu-MgO ^a	Cyclohexanol	100	7	97.2	100	[14]
UiO-66	Isopropanol	120	24	>99	94	[15]
Co@CN-900	<i>n</i> -Hexanol	80	48	>99	99	[16]
Co@CN-900	Isopropanol	80	48	97	90	[16]
Cu-Ru/MWCNT	NaBH ₄	RT	0.5	100	69	[17]
Cu-Ru/MWCNT	Formic acid	100	1	44	73	[17]
Cu-Ru/MWCNT	Acetic acid	100	1	15	63	[17]
AuNPore	Et ₃ SiH	70	24	73	99	[18]
AuNPore	Formic acid	90	22	97	100	[19]
Co ₁ Re ₁ /TiO ₂	Formic acid	140	4	99	89	This work

^a 1 MPa N₂.

Table S6. Metal contents in fresh and spent Co₁Re₁/TiO₂ catalyst measured by ICP-OES.

Catalyst	Co (wt%)	Re (wt%)
Fresh Co ₁ Re ₁ /TiO ₂	1.98	6.31
Spent Co ₁ Re ₁ /TiO ₂	1.90	6.22

Table S7. Labels and calculated metal contents of catalysts.

Catalyst Label	Co (wt%)	Re (wt%)	Co/Re (mol/mol)
Co/TiO ₂	2.0	0	N/A
Co ₂ Re ₁ /TiO ₂	2.0	3.2	2.0
Co ₁ Re ₁ /TiO ₂	2.0	6.3	1.0
Co ₁ Re ₂ /TiO ₂	2.0	12.6	0.5
Re/TiO ₂	0	2.0	0

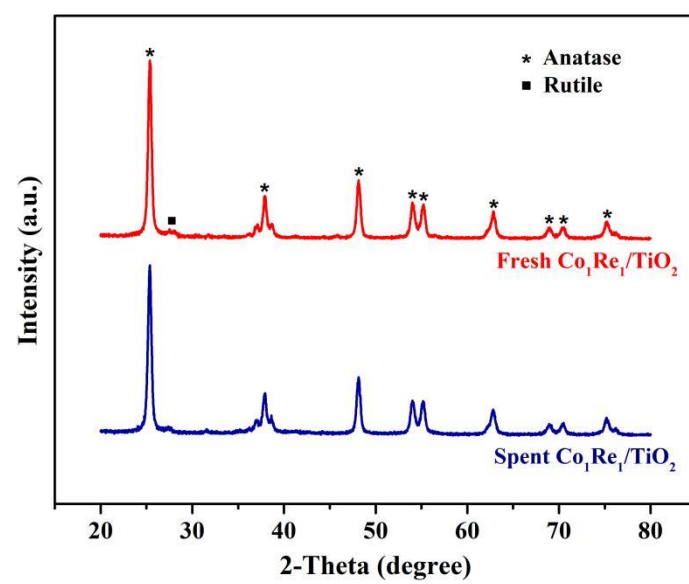


Figure S1. XRD patterns of fresh and spent Co₁Re₁/TiO₂.

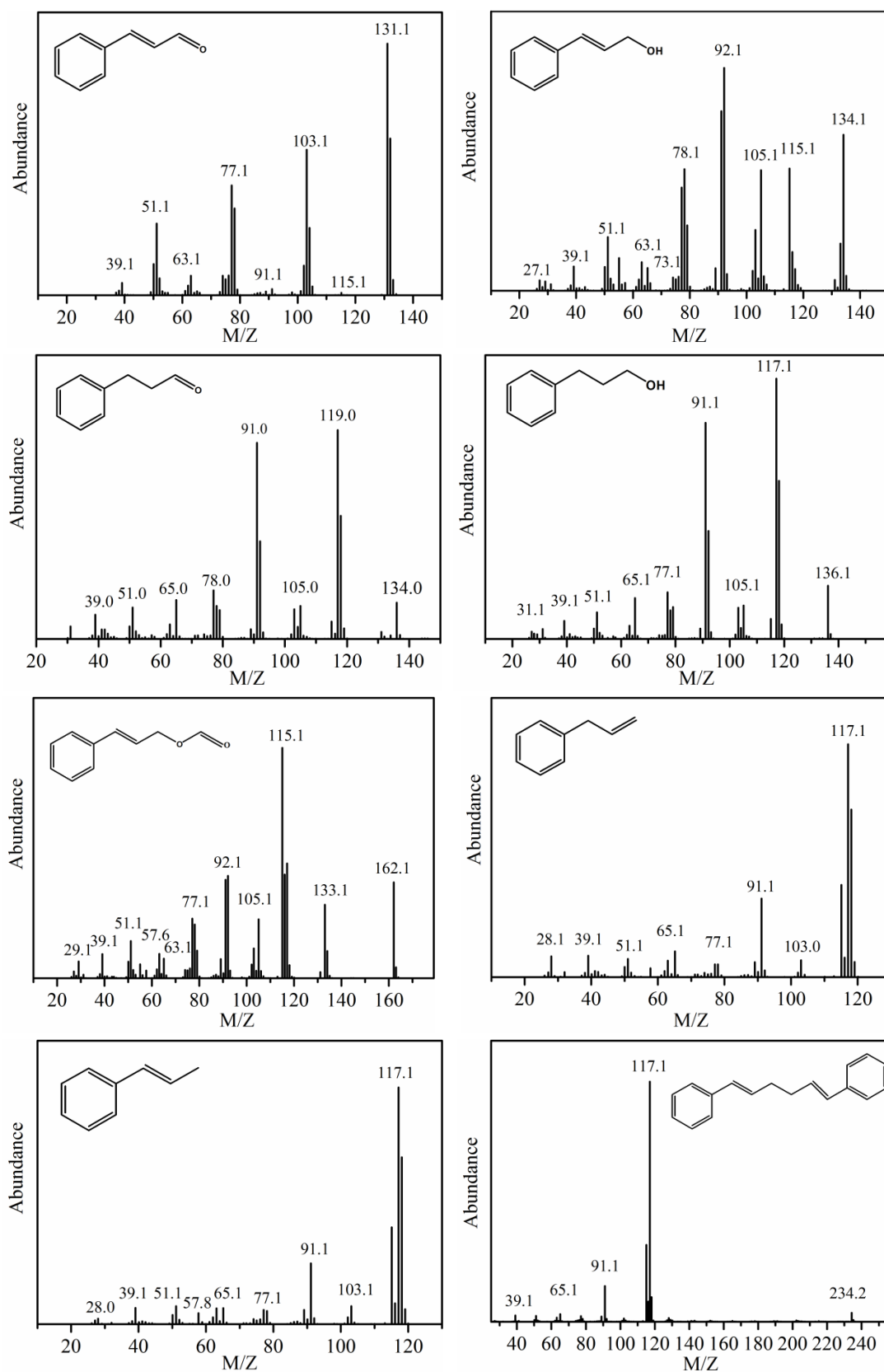


Figure S2. GC/MS spectra of substrate and products in the hydrogenation of COL.

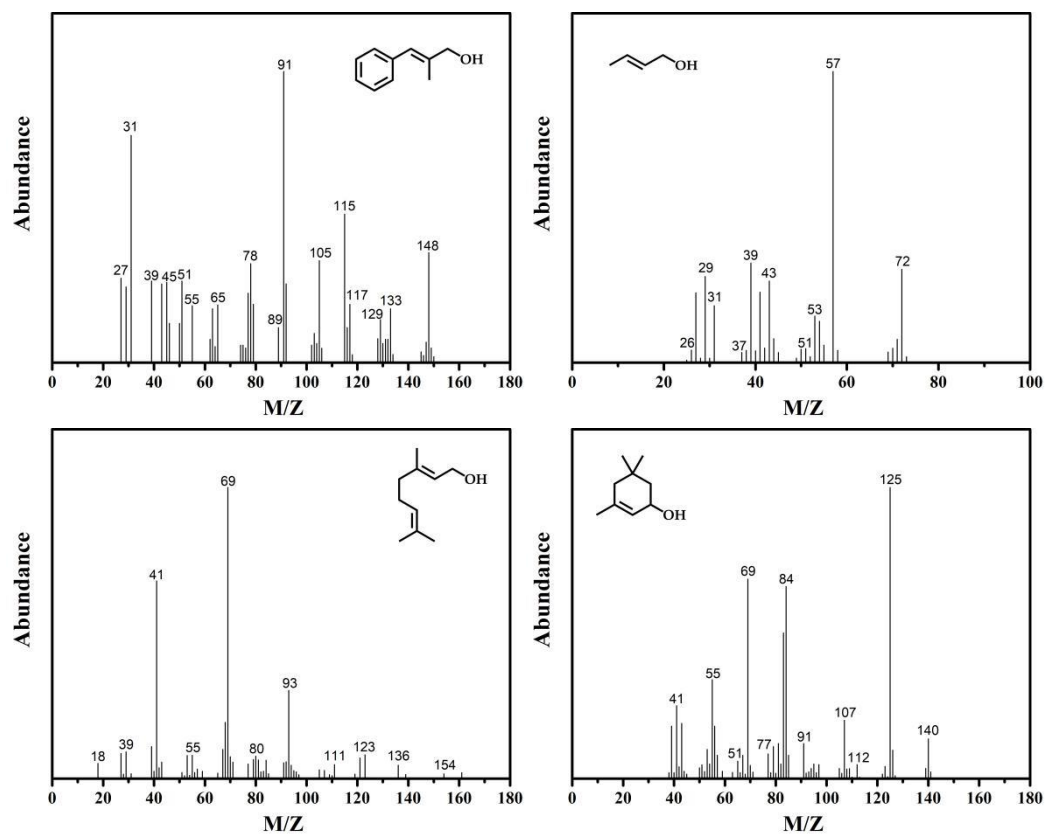


Figure S3. GC/MS spectra of the main products in the hydrogenation of other α,β -unsaturated aldehydes.

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