

Supplementary Material

Selective C=O hydrogenation of cinnamaldehyde over Ir-based catalysts and the comparison with C-O hydrogenolysis of polyols

Zhe Dong^a, Yoshinao Nakagawa^{a, b}, Ben Liu^a, Shogen Mihara^a, Mizuho Yabushita^{a, b}, Keiichi Tomishige^{a, b, c}

AUTHOR ADDRESS ^aDepartment of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan;

^bResearch Center for Rare Metal and Green Innovation, Tohoku University, 468-1, Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan;

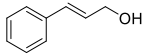
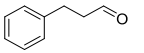
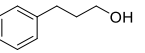
^cAdvanced Institute for Materials Research (WPI-AIMR), Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

Email: yoshinao@erec.che.tohoku.ac.jp (Y.N.); tomishige@tohoku.ac.jp (K.T.)

Table S1. The precursors, supports, and reagents used in this research

Precursors or reagents	Details of the chemicals
H ₂ IrCl ₆	Furuya Metals Co., Ltd.
SiO ₂	G6, Fuji Silysia, calcined at 973 K for 1 h, 485 m ² /g
Anatase TiO ₂	FUJIFILM Wako Pure Chemical Co., 13 m ² /g
Rutile TiO ₂	FUJIFILM Wako Pure Chemical Co., 6.8 m ² /g
P25 TiO ₂	Nippon Aerosil, 50 m ² /g
BN	FUJIFILM Wako Pure Chemical Co., 5.8 m ² /g
CeO ₂	Daiichi Kigenso Co., Ltd., HS, calcined at 873 K for 1 h, 84 m ² /g
TiC	FUJIFILM Wako Pure Chemical Co.
TiN	FUJIFILM Wako Pure Chemical Co.
MgO	FUJIFILM Wako Pure Chemical Co.
Co ₃ O ₄	FUJIFILM Wako Pure Chemical Co.
SnO ₂	FUJIFILM Wako Pure Chemical Co.
MnO ₂	FUJIFILM Wako Pure Chemical Co.
Fe(NO ₃) ₃ ·9H ₂ O	FUJIFILM Wako Pure Chemical Co.
Co(NO ₃) ₃ ·6H ₂ O	FUJIFILM Wako Pure Chemical Co.
NH ₄ ReO ₄	FUJIFILM Wako Pure Chemical Co.
Ni(NO ₃) ₂ ·6H ₂ O	FUJIFILM Wako Pure Chemical Co.
NbO(NO ₃) ₃	FUJIFILM Wako Pure Chemical Co.
(NH ₄) ₆ W ₇ O ₂₄ ·6H ₂ O	FUJIFILM Wako Pure Chemical Co.
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	FUJIFILM Wako Pure Chemical Co.
Pt(NH ₃) ₄ (NO ₃) ₂	FUJIFILM Wako Pure Chemical Co.
Pd(NO ₃) ₂	FUJIFILM Wako Pure Chemical Co.
RuNO(NO ₃) ₃	FUJIFILM Wako Pure Chemical Co.
RhCl ₃ ·3H ₂ O	FUJIFILM Wako Pure Chemical Co.
HAuCl ₄ ·4H ₂ O	FUJIFILM Wako Pure Chemical Co.
Cinnamaldehyde	Tokyo Chemical Industries, Ltd.
Crotonaldehyde	Tokyo Chemical Industries, Ltd.
1,4-dioxane	FUJIFILM Wako Pure Chemical Co.

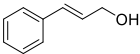
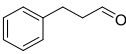
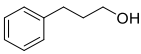
Table S2. Cinnamaldehyde hydrogenation over Ir/rutile with different Ir loading amounts

Entry	Loading amount (wt%)	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
						Others		
1	0.5	1	73 (0.7)	20	6	1	14	99
2	1	2	83 (1.7)	9	7	1	17	99
3	3	8	95 (7.6)	5	0	0	23	104
4	4	6	97 (5.8)	3	0	0	13	101
5	5	6	96 (5.7)	4	0	0	11	100
6	6	5	95 (4.8)	5	0	0	7	102
7	8	6	88 (5.3)	5	6	1	6	103

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

Table S3. Detailed data of cinnamaldehyde hydrogenation over Ir-MO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) (**Figure 1 (a)**)

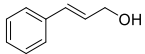
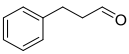
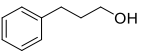
Entry	Additive metals	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
						Others		
1	None	8	95 (8)	5	0	0	23	104
2	Fe	41	98 (40)	1	1	0	153 ^b	98
3	Re	8	92 (7)	3	5	0	57	102
4	Mo	8	92 (7)	3	4	1	57	102
5	Ni	2	67 (1)	33	0	0	7.6	103
6	Co	21	77 (16)	18	4	1	123	95
7	W	22	97 (21)	2	1	0	169	100
8	Without catalyst	0.5	96 (0.48)	4	0	0	-	105

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

^bThe value of TOF was calculated by the data with 1 h reaction.

Table S4. The detail data of selective hydrogenation over Ir-M'O_x/rutile (Ir: 3 wt%, M' = Fe or Re, different molar ratio) (**Figure 1 (b)**)

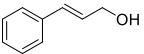
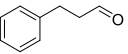
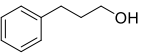
Entry	Catalyst	M/Ir ratio	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
							Others		
1	Ir-	0	8	95 (7.6)	5	0	0	23	104
2	FeO _x /rutile	0.01	5	95 (5)	0	5	1	16	102
3	(Ir: 3 wt%)	0.03	17	95 (16)	3	2	0	50	103
4		0.05	25	96 (24)	2	2	0	75	100
5		0.08	30	97 (29)	2	1	0	89	101
6		0.1	41	98 (40)	1	1	0	153 ^b	98
7		0.25	38	98 (37)	1	1	0	117	105
8		0.3	33	96 (32)	2	1	1	101	101
9		0.5	22	97 (21)	2	1	0	68	103
10		1	14	97 (14)	0	3	0	43	104
11	Ir-	0.1	8	91 (7)	3	5	1	23	102
12	ReO _x /rutile (Ir: 3 wt%)	0.25	35	97 (34)	1	2	0	108	102
13		0.5	28	96 (27)	2	2	0	86	105

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

^bThe value of TOF was calculated by the data with 1 h reaction.

Table S5. Detailed data of cinnamaldehyde hydrogenation over Ir-FeO_x/support (Ir: 3 wt%, Fe/Ir = 0.1) catalysts (**Figure 2**)

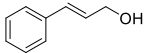
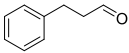
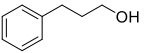
Entry	Support	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
						Others		
1	Rutile	41	98 (40)	1	1	0	153 ^b	98
2	Anatase	28	99 (28)	0	1	0	86	100
3	P25	22	96 (21)	4	0	0	65	103
4	SiO ₂	34	98 (33)	1	1	0	104	110
5	BN	20	98 (20)	1	1	0	61	103
6	MgO	0	0 (0)	0	0	0	-	100
7	TiN	2	99 (2)	1	0	0	6	104
8	TiC	0.4	95 (0.4)	4	1	0	1	102
9	Co ₃ O ₄	12	64 (8)	27	8	1	24	102
10	MnO ₂	0	0 (0)	0	0	0	-	100
11	SnO ₂	0	0 (0)	0	0	0	-	100
12	CeO ₂	27	97 (26)	1	2	0	81	99

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

^bThe value of TOF_m was calculated by the data with 1 h reaction.

Table S6. Cinnamaldehyde hydrogenation over M-FeO_x/rutile (M: 3 wt%, Fe/M = 0.1) catalysts

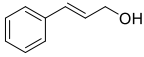
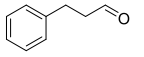
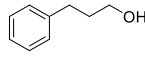
Entry	Host metal (M')	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
						Others		
1	Ir	41	98 (40)	1	1	0	153 ^b	98
2	Ru	1	73 (0.7)	27	0	0	2	102
3	Rh	14	12 (2)	83	4	1	36	100
4	Au	-	-(0)	-	-	-	-	100
5	Pt	27	83 (22)	12	4	1	68	98
6	Pd	56	1 (0.6)	57	41	1	-	91

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

^bThe value of TOF_m was calculated by the data with 1 h reaction.

Table S7. Detailed data of cinnamaldehyde hydrogenation over Ir-FeO_x/rutile (Ir: x wt%, Fe/Ir = 0.1) catalysts (**Figure 3**)

Entry	Ir loading amount (wt%)	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
						Others		
1	1	2	96 (2)	4	0	0	18	102
2	2	17	96 (16)	2	2	0	78	105
3	3	41	98 (40)	1	1	0	153 ^b	98
4	4	47	97 (46)	2	1	0	-	103
5	5	56	98 (55)	1	1	0	-	102
6	6	66	98 (65)	1	1	0	-	103
7	8	71	99 (70)	1	0	0	-	104
8	10	67	98 (66)	1	1	0	-	100

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

^bThe value of TOF_m was calculated by the data with 1 h reaction.

Table S8. Summary of D_{CO} of the catalysts with various Ir loading amount, Fe/Ir ratio and support.

Catalyst	Ir loading amount (wt%)	Fe/Ir ratio	D_{co} (%) ^a
Ir/rutile	3	0	20
Ir/rutile ^b	5	0	14
Ir-FeO _x /rutile	3	0.1	22
Ir-FeO _x /rutile	3	0.25	23
Ir-FeO _x /rutile	3	0.5	19
Ir-FeO _x /rutile ^b	5	0.25	13
Ir-FeO _x /anatase	3	0.1	12
Ir-FeO _x /P25	3	0.1	11
Ir-FeO _x /BN	3	0.1	10
Ir-FeO _x /SiO ₂	3	0.1	16
Ir-FeO _x /CeO ₂	3	0.1	48

^a D_{CO} was calculated by the CO adsorption. The fresh catalysts were prereduced at 573 K for 1 h in the gas phase.

^bRef S1.

Table S9. 1,2-Butanediol hydrogenolysis over various Ir/TiO₂ and Ir-FeO_x/TiO₂ catalysts.

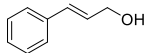
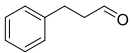
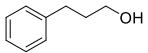
Catalyst	Ir loading amount (wt%)	Fe/Ir ratio	Conv. (%)	Selectivity (%)						C.B. (%)
				1- BuOH	2- BuOH	Butane	1- PrOH	Methane	Propane	
							+2- PrOH			
Ir-FeO _x /rutile	3	0.1	4.6	7.7	71.7	9.5	9.6	1.5	0	101
Ir-FeO _x /rutile ^a	5	0.25	17.1	15.0	64.2	13.6	4.6	2.1	0.5	102
Ir _{c-r} -FeO _x /rutile ^{a, b}	5	0.25	8.7	6.5	66.4	16.7	6.6	3.1	0.7	95
Ir-FeO _x /rutile	5	0.1	5.5	4.1	76.5	7.1	9.7	2.7	0.0	94
Ir/rutile	3	0	2.5	32.3	49.6	13.2	2.6	1.0	1.3	99
Ir/rutile ^a	5	0	7.5	27.5	53.0	14.4	2.1	1.3	1.5	99

^aRef S1.

^bThe catalyst prepared with the procedure involving calcination and reduction before loading of Fe.

Reaction conditions: catalyst = 200 mg substrate = 0.5 g; solvent: H₂O = 4 g; H₂ pressure = 8 MPa; reaction temperature = 453 K, Reaction time = 24 h; H₂ pressure = 8 MPa.

Table S10. Cinnamaldehyde hydrogenation over Ir-FeO_x/TiO₂ (Ir: 3 wt%) catalysts with different prerduction conditions (**Figure 4** square markers)

Reduction method	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
					Others		
No reduction	9	88 (8)	12	0	0	25	90
L 473 K	41	97 (40)	1	1	1	153 ^b	99
G 473 K	4	93 (4)	7	0	0	12	103
G 573 K	38	99 (38)	1	0	0	116	94
G 673 K	26	98 (25)	2	0	0	76	94
G 773 K	17	98 (17)	2	0	0	52	100
G 873 K	18	99 (18)	1	0	0	55	101
G 973 K	12	99 (12)	1	0	0	36	101

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with different reduction conditions: L: liquid phase reduction under 8 MPa for 1 h; G: gas phase reduction under flowing H₂ 30 mL/min (0.1 MPa) for 1 h.

^aYields (%) of cinnamyl alcohol are given in the parentheses.

^bThe value of TOF was calculated by the data with 1 h reaction.

Table S11. Detailed data of previous work of 1,2-Butanediol hydrogenolysis over Ir-FeO_x/TiO₂ (Ir: 5 wt%, Fe/Ir = 0.25) catalyst [S1] (**Figure 4** circle markers).

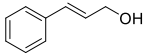
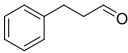
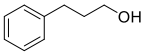
Catalyst	Reduction method	Conv. (%)	Selectivity (%)						C.B. (%)
			1-BuOH	2-BuOH	Butane	1-PrOH +2-PrOH	Methane	Propane	
Ir-FeO _x /rutile	No reduction ^b	17.1	15.0	64.2	13.6	4.6	2.1	0.0	102
	G, 473 K	17.7	12.3	66.3	14.4	4.5	2.1	0.0	103
	G, 573 K	14.6	13.0	65.0	15.9	3.8	1.8	0.5	102
	G, 673 K	19.3	15.9	63.4	16.0	3.0	1.3	0.4	102
	G, 773 K	13.1	9.2	63.3	19.0	5.5	2.5	0.4	103
Ir _{c-r} -FeO _x /rutile ^a	No reduction ^b	8.7	6.5	66.4	16.7	6.6	3.1	0.7	95

^aThe catalyst prepared with the procedure involving calcination and reduction before loading of Fe.

^bThe catalysts without reduction was shown as red marker in **Figure 4**

Reaction conditions: catalyst = 200 mg; substrate = 0.5 g; solvent: H₂O = 4 g; H₂ pressure = 8 MPa; reaction temperature = 453 K, Reaction time = 24 h. The catalysts were pretreated before the reaction with different reduction conditions: G: gas phase reduction under flowing H₂ 30 mL/min (0.1 MPa) for 1 h.

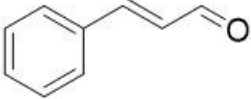
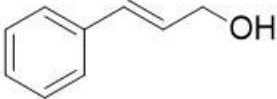
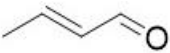

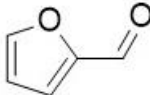
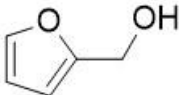
Table S12. Detailed data of time course of cinnamaldehyde hydrogenation over Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) catalyst (**Figure 5**)

Entry	Catalyst	Reaction Time (h)	Conv. (%)	Selectivity (%) ^a				C.B. (%)
							Others	
1	Ir-FeO _x /rutile (Ir: 3 wt%, Fe/Ir = 0.1)	0	4	97 (4)	3	0	0	100
2		0.3	9	97 (9)	3	0	0	100
3		0.5	18	97 (17)	2	1	0	100
4		1	20	97 (20)	2	1	0	104
5		2.5	41	97 (40)	1	1	1	99
6		6	78	98 (76)	2	1	1	90
7		8	88	98 (86)	2	0	0	96
8		12	91	97 (88)	2	1	0	100
9		16	96	98 (94)	2	0	0	100
10		24	97	88 (85)	1	10	1	102
11		48	98	86 (84)	1	12	1	99
12	Ir/rutile (Ir: 3 wt%)	0	1	84 (0.8)	15	0	1	99
13		1	3	92 (2)	7	0	1	100
14		2.5	8	95 (7.6)	5	0	0	104
15		4	12	94 (11)	5	1	1	105
16		8	15	95 (14)	4	1	0	99
17		18	24	95 (23)	3	1	1	99
18		24	38	94 (36)	4	1	1	98
19		48	52	95 (49)	4	1	0	99
20		72	71	95 (68)	3	1	1	95

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

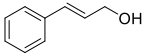
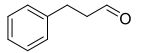
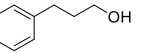
^aYields (%) of cinnamyl alcohol are given in the parentheses.

Table S13. Detail data of the time course of Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) catalyst for various substrate

Entry	Substrate	Product	Reaction time (h)	Conv. (%)	Yield (%)	Selectivity (%)
1			1	23	20	97
2			2.5	39	41	96
3			8	78	82	99
4			12	91	88	97
5			16	96	94	98
6			2.5	33	43	96
7			8	67	76	94
8			12	95	90	95
9			2.5	43	45	>99
10			8	95	93	>99
11			12	99	99	>99

Reaction conditions: catalyst = 50 mg; substrate = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h, H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

Table S14. Detail data of the reuse test of Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) catalyst for cinnamaldehyde hydrogenation (**Figure 6**)

Entry	Reuse times	Conv. (%)	Selectivity (%) ^a				TOF _m (h ⁻¹)	C.B. (%)
						Others		
1	Fresh	38	97 (37)	2	1	0	113	98
2	1	37	97 (36)	1	1	1	111	100
3	2	37	98 (36)	2	0	0	111	90
4	3	37	99 (37)	1	0	0	113	94
5	4	35	99 (35)	1	0	0	108	103

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

Reuse method: The catalyst after each run was separated from the reaction system by centrifugation, washed by H₂O and ethanol for 4 times respectively, dried at 383 K overnight, and directly used for the next run.

^aYields (%) of cinnamyl alcohol are given in the parentheses.

Table S15. Leached amount of Ir and Fe after the cinnamaldehyde hydrogenation from Ir-FeO_x/rutile (Ir= 3 wt%, Fe/Ir = 0.1) after reuse test, determined by ICP-OES

Reuse times	Leached amount (%)	
	Ir	Fe
0	< 0.1	0.4
1	< 0.1	0.3
2	< 0.1	0.3
3	< 0.1	0.3
4	< 0.1	0.2

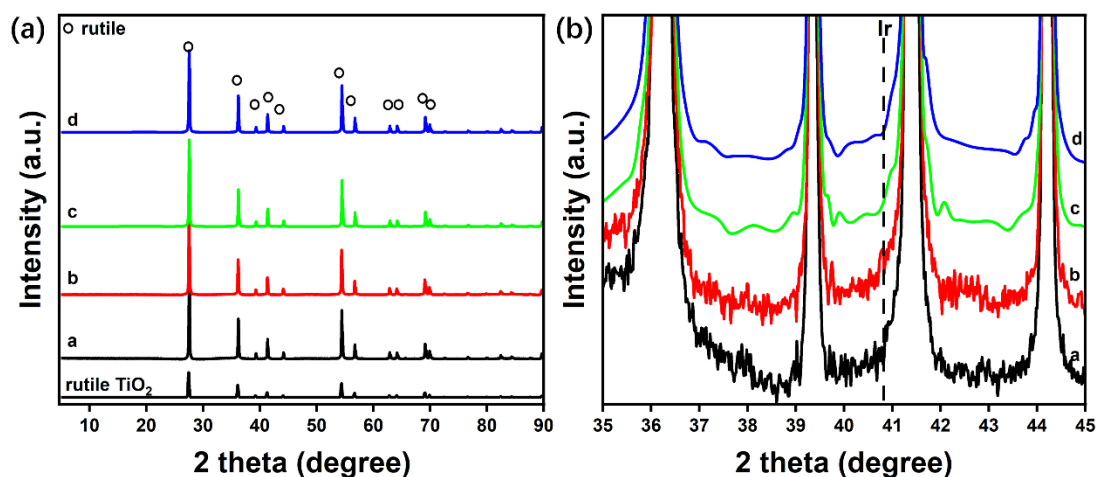


Figure S1. (a) XRD patterns (10° - 75°) for **a.** Ir/rutile (Ir: 3 wt%), **b.** Ir-FeO_x/ rutile (Ir: 3 wt%, Fe/Ir = 0.1), **c.** Ir-FeO_x/ rutile (Ir: 3 wt%, Fe/Ir = 0.25), **d.** Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.5), (b) enlarged part of XRD patterns (35° - 45°)

All samples were measured after reaction. Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h, H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

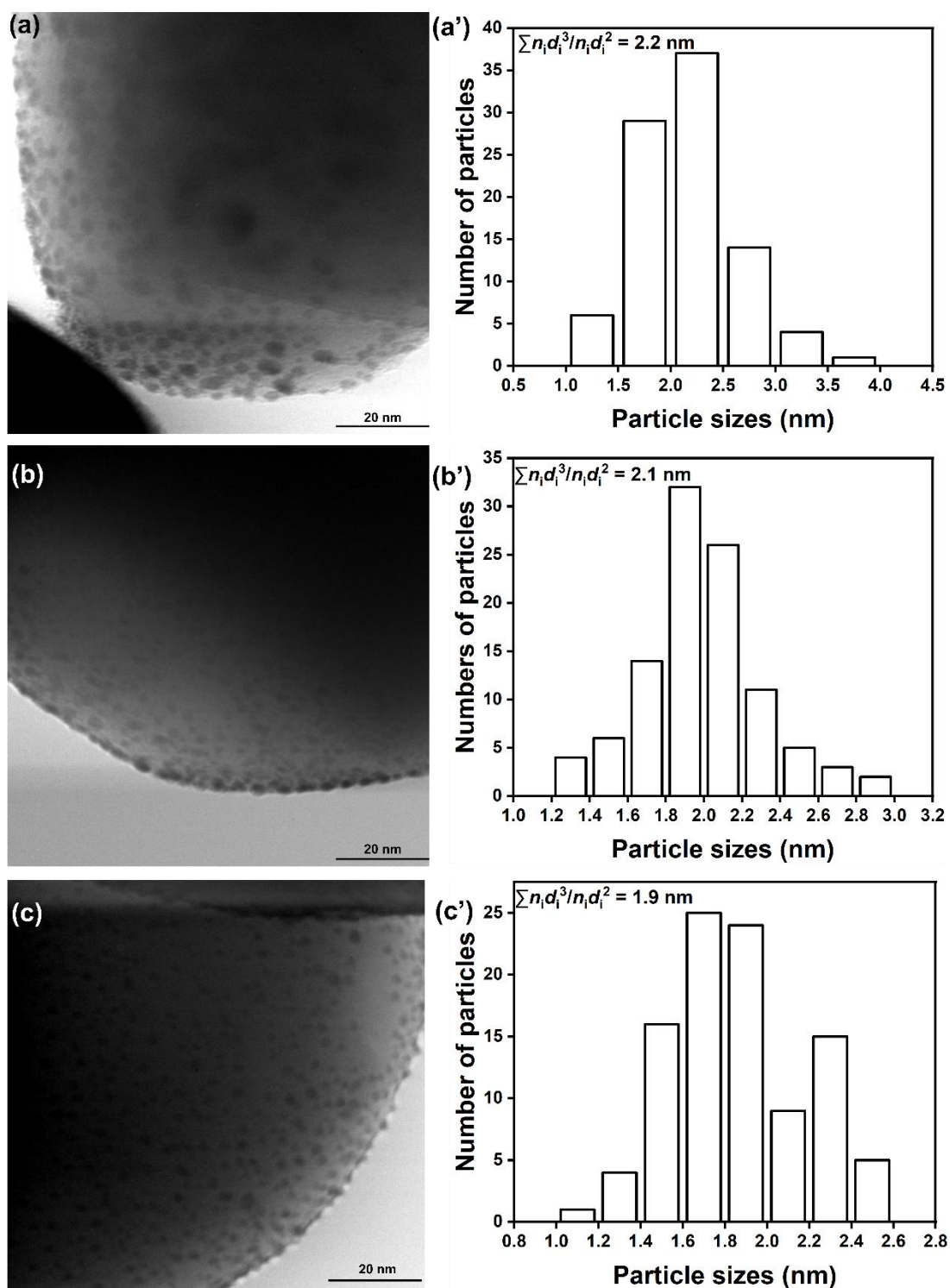


Figure S2 TEM images (a-c) and particle size distribution (a'-c') of Ir/rutile (Ir: 3 wt%) and Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) with gas phase reduction at different temperatures: (a), (a') G, 473 K; (b), (b') G, 573 K; (c), (c') G, 673 K

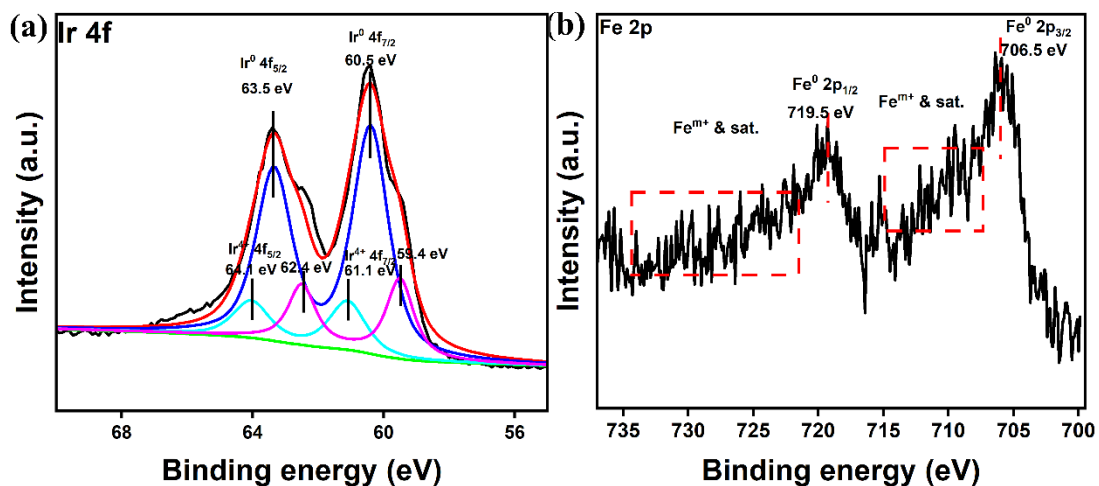


Figure S3. XPS of Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) catalyst: (a) Ir 4f spectrum;
(b) Fe 2p spectrum

Pretreatment method: The Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) catalyst was reduced at 473 K under 8 MPa H₂ in the autoclave (liquid phase reduction)

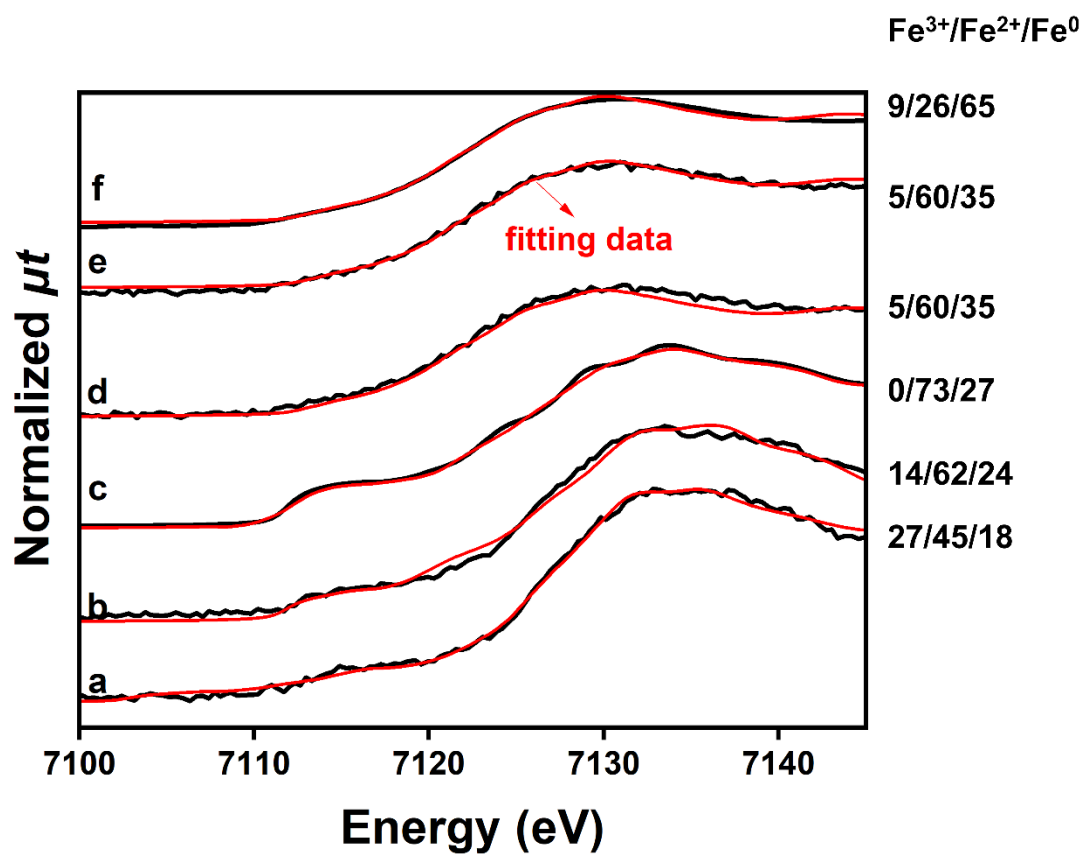
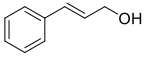
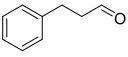
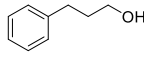


Figure S4. Fitting results of Fe K-edge XANES of Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) catalysts with different pre-reduction methods. (a) G, 473 K (b) G, 573 K (c) G, 673 K; (d) L, 473 K (e) L, 473 K after reaction; (f) Ir_{c-r}-FeO_x/rutile (Ir: 5 wt%, Fe/Ir = 0.25; after reaction for 1,2-butanediol hydrogenolysis) reported in our previous work [S1]

(f) was Reproduced from ref. [S1] with permission from the American Chemical Society, copyright 2022.

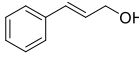
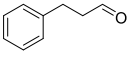
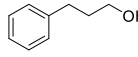
Table S16. Cinnamaldehyde hydrogenation over Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) with different stirring rate during reaction

Entry	Stirring rate (rpm)	Conv. (%)	Selectivity (%) ^a				C.B. (%)
						Others	
1	100	15	97 (15)	2	1	0	91
2	300	15	96 (14)	2	2	0	95
3	500	17	97 (16.5)	2	1	0	99
4	700	16	95 (15)	2	2	0	95
5	900	15	98 (15)	1	1	0	95

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5-20 g; reaction temperature = 303 K; reaction time = 0.5 h; H₂ pressure = 0.8 MPa; stirring rate is different. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

^aYields (%) of cinnamyl alcohol are given in the parentheses.

Table S17. Detailed data of concentration dependence of cinnamaldehyde hydrogenation over Ir /rutile (Ir: 3 wt%) and Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) (**Figure 11 (a)**)

Entry	Catalyst	Solvent amount (g)	Conv. (%)	Selectivity (%)				C.B. (%)
							Others	
1	Ir /rutile	5	3.4	86 (2.9)	11	0	0	102
2	(Ir: 3 wt%)	10	3.6	97 (3.3)	1	0	1	96
3		15	3.7	93 (3.4)	5	1	0	98
4		20	3.0	95 (2.9)	3	0	1	98
5	Ir-	5	14.0	96 (13.4)	4	3	0	97
6	FeO _x /rutile	10	14.2	96 (13.6)	3	2	0	97
7	(Ir: 3 wt%, Fe/Ir =	15	14.1	98 (13.9)	1	2	0	99
8	0.1)	20	15.0	98 (14.7)	1	1	1	101

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5-20 g; reaction temperature = 303 K; reaction time = 0.5 h for Ir-FeO_x/rutile, 1 h for Ir/rutile; H₂ pressure = 0.8 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

Table S18. Detailed data of H₂ pressure dependence of cinnamaldehyde hydrogenation over Ir /rutile (Ir: 3 wt%) and Ir-FeO_x/rutile (Ir: 3 wt%, Fe/Ir = 0.1) (**Figure 11 (b)**)

Entry	Catalyst	H ₂ pressure (MPa)	Reaction time (h)	Yield (%)	Product Selectivity (%)	C.B. (%)
1	Ir/rutile (Ir: 3 wt%)	0.8	1	3.1	96	94
2			3	20.8	96	99
3			4	27.7	97	99
4	Ir- FeO _x /rutile (Ir: 3 wt%, Fe/Ir = 0.1)	1	1	9.7	95	100
5			3	23.0	96	100
6			4	29.7	96	101
7			0.5	6.7	93	100
8			0.7	9.3	95	100
9			1	15.4	94	100
10	Ir- FeO _x /rutile (Ir: 3 wt%, Fe/Ir = 0.1)	4	0.5	7.8	94	100
11			0.7	13.5	94	100
12			1	23.5	95	100
13			0	0.5	96	99
14	Ir- FeO _x /rutile (Ir: 3 wt%, Fe/Ir = 0.1)	0.2	0.5	2.7	93	97
15			1	6.5	96	99
16			1.5	9.5	97	100
17			0	3.3	96	100
18	Ir- FeO _x /rutile (Ir: 3 wt%, Fe/Ir = 0.1)	0.8	0.3	9.0	97	100
19			0.5	16.9	97	99
20			0	3.8	98	96

21		0.3	10.5	96	99
22		0.5	20.4	96	95
23	2	0	7.4	96	100
24		0.3	20.0	98	100
25		0.5	36.6	96	100

Reaction conditions: catalyst = 50 mg; substrate: cinnamaldehyde = 6 mmol; solvent: H₂O = 5 g; reaction temperature = 303 K; reaction time = 2.5 h; H₂ pressure : 0.2-4 MPa. The catalysts were pretreated before the reaction with liquid phase reduction (8 MPa H₂, 473 K in the autoclave).

Reference

S1. B. Liu, Y. Nakagawa, C. Li, M. Yabushita and K. Tomishige, *ACS Catal.*, 2022, 12, 15431-15450.