Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Performance and characterization of rhenium-modified Rh-Ir alloy catalyst for one-pot conversion of furfural into 1,5-pentanediol

Sibao Liu, Yasushi Amada, Masazumi Tamura, Yoshinao Nakagawa* and Keiichi Tomishige*

Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

*****Corresponding authors: Keiichi Tomishige and Yoshinao Nakagawa

Department of Applied Chemistry, School of Engineering, Tohoku University

Tel + Fax : +81-22-795-7214

E-mail : tomi@erec.che.tohoku.ac.jp and yoshinao@erec.che.tohoku.ac.jp

Table S1. The effect of different preparation methods on conversion of furfural into 1,5-PeD.

Entry	Catalysts	T_1 / K	Time 1 / h	T_2 / K	Time 2 / h	Conversion / %	Yield / %									
							1,5-PeD	1,4-PeD	1,2-PeD	1-PeOH	2-PeOH	THFA	FFA	2-MTHF	1,2,5-PeT	Others
1	Rh(0.66)-Ir-ReO_x/SiO_2	313	8	373	24	>99.9	65.8	3.9	0.6	7.5	0.3	7.1	0.0	2.4	3.6	9.0
2	Sample-A	313	8	373	24	>99.9	0.9	11.6	0.0	0.4	0.1	20.0	0.2	3.3	6.1	57.4
3	Sample-B	313	8	373	24	>99.9	0.0	6.9	0.0	0.2	0.0	5.2	0.2	0.8	0.0	86.6

PeD: pentanediol; PeOH: pentanol; THFA: tetrahydrofurfuryl alcohol; FFA: furfuryl alcohol; 2-MTHF: 2-methyltetrahydrofuran; PeT: pentanetriol; Others: unidentified products.

Pretreatment: 473 K, H_2 (8 MPa), 1 h.

Reaction conditions: furfural (3 g), H_2O (3 g), catalyst (Re/Ir=2; 300 mg), initial H_2 (6 MPa).

Table S2. Conversion of furfural over Rh(0.66)-Ir-ReO_x/SiO_2

Entry	T_1 / K	Time 1 / h	T_2 / K	Time 2 / h	Conversion / %	Yield / %									
						1,5-PeD	1,4-PeD	1,2-PeD	1-PeOH	2-PeOH	THFA	FFA	2-MTHF	1,2,5-PeT	Others
1	313	1	-	-	92.2	0.1	0.1	0.0	0.0	0.0	2.2	84.3	0.4	0.0	5.2
2	313	2	-	-	>99.9	0.2	0.1	0.0	0.1	0.0	12.9	74.7	0.6	0.0	11.5
3	313	3	-	-	>99.9	0.2	0.1	0.2	0.1	0.0	21.4	63.8	0.7	0.0	13.6
4	313	4	-	-	>99.9	0.3	0.1	0.2	0.1	0.0	31.3	49.5	0.9	0.0	17.6
5	313	6	-	-	>99.9	0.4	0.4	0.0	0.2	0.0	50.0	27.0	1.2	0.0	20.8
6	313	8	-	-	>99.9	0.4	0.2	0.4	0.2	0.0	58.2	14.4	1.4	4.8	19.8
7[a]	313	8	373	0	>99.9	0.6	0.7	0.5	0.2	0.0	67.3	0.3	1.5	11.1	17.7
8	313	8	373	2	>99.9	10.6	3.6	0.6	0.6	0.1	61.3	0.1	2.0	17.0	4.1
9	313	8	373	4	>99.9	24.1	3.7	0.6	1.0	0.1	45.0	0.0	1.9	16.2	7.3
10	313	8	373	6	>99.9	33.3	3.8	0.6	1.4	0.1	38.9	0.0	2.1	15.2	4.4
11	313	8	373	8	>99.9	41.4	3.6	0.7	2.0	0.1	33.8	0.0	2.0	12.2	4.1
12	313	8	373	12	>99.9	48.1	3.8	0.7	3.0	0.2	25.1	0.0	2.3	9.3	7.5
13	313	8	373	18	>99.9	60.0	4.0	0.6	4.8	0.2	13.2	0.0	2.4	7.0	7.7
14	313	8	373	24	>99.9	65.8	3.9	0.6	7.5	0.3	7.1	0.0	2.4	3.6	9.0

PeD: pentanediol; PeOH: pentanol; THFA: tetrahydrofurfuryl alcohol; FFA: furfuryl alcohol; 2-MTHF: 2-methyltetrahydrofuran; PeT: pentanetriol; Others: unidentified products.

Pretreatment: 473 K, H_2 (8 MPa), 1 h.

Reaction conditions: furfural (3 g), H_2O (3 g), catalyst (Re/Ir=2; 300 mg), initial H_2 (6 MPa).

a: The reaction was stopped just after the temperature reached T_2.

Table S3. Conversion of furfural over Pd(0.66)-Ir-ReO_x/SiO_2

Entry	T_1 / K	Time 1 / h	T_2 / K	Time 2 / h	Conversion / %	Yield / %									
						1,5-PeD	1,4-PeD	1,2-PeD	1-PeOH	2-PeOH	THFA	FFA	2-MTHF	1,2,5-PeT	Others
1	313	1	-	-	92.2	0.0	0.0	0.0	0.0	0.0	12.3	71.0	0.9	0.0	15.7
2	313	2	-	-	>99.9	0.1	0.0	0.1	0.1	0.0	29.7	46.4	1.7	0.0	21.9
3	313	3	-	-	>99.9	0.1	0.1	0.2	0.1	0.0	42.8	25.8	2.6	0.0	28.2
4	313	4	-	-	>99.9	0.1	0.3	0.3	0.1	0.0	63.9	2.2	3.0	0.1	30.0
5	313	6	-	-	>99.9	0.2	0.9	0.0	0.1	0.0	65.4	0.0	3.3	5.0	25.1
6	313	8	-	-	>99.9	0.0	1.6	0.3	0.1	0.0	66.8	0.0	3.6	6.5	21.0
7[a]	313	8	373	0	>99.9	0.2	3.1	0.3	0.1	0.0	69.7	0.0	3.2	11.5	11.8
8	313	8	373	2	>99.9	3.2	6.7	0.4	0.4	0.0	64.8	0.0	4.4	10.2	9.9
9	313	8	373	4	>99.9	6.4	6.7	0.3	0.4	0.1	57.1	0.0	5.0	11.0	13.0
10	313	8	373	6	>99.9	13.9	6.9	0.4	0.6	0.1	51.5	0.0	4.5	8.4	13.8
11	313	8	373	8	>99.9	18.1	6.1	0.4	0.7	0.1	50.0	0.0	4.7	7.2	12.9
12	313	8	373	12	>99.9	28.4	6.9	0.4	1.2	0.1	39.0	0.0	4.3	6.5	13.2
13	313	8	373	18	>99.9	40.6	6.2	0.4	2.1	0.2	28.0	0.0	4.8	4.5	13.2
14	313	8	373	24	>99.9	44.5	6.1	0.5	3.3	0.3	20.9	0.0	3.7	4.6	16.0

PeD: pentanediol; PeOH: pentanol; THFA: tetrahydrofurfuryl alcohol; FFA: furfuryl alcohol; 2-MTHF: 2-methyltetrahydrofuran; PeT: pentanetriol; Others: unidentified products.

Pretreatment: 473 K, H_2 (8 MPa), 1 h.

Reaction conditions: furfural (3 g), H_2O (3 g), catalyst (Re/Ir=2; 300 mg), initial H_2 (6 MPa).

a: The reaction was stopped just after the temperature reached T_2.

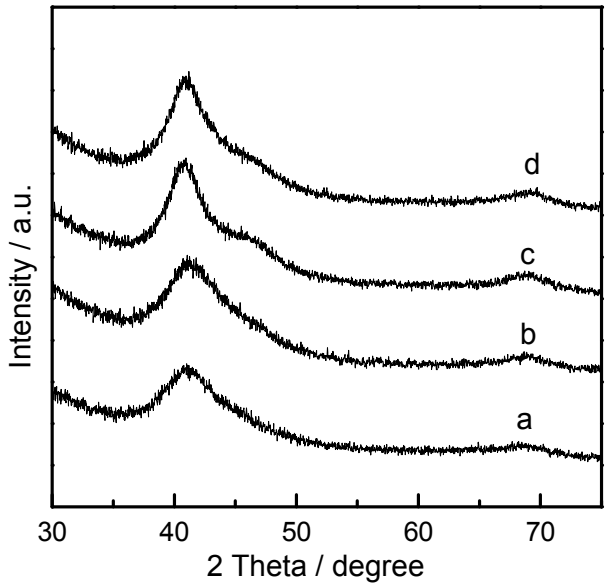

Fig. S1 XRD patterns of Rh(0.66)-Ir-ReO_x/SiO_2 catalysts. (a) after reduction, (b) after 1st reaction, (c) after 3rd reaction (calcined at 573 K for 3 h after 1st and 2nd reactions) and (d) after 3rd reaction (calcined at 773 K for 3 h after 1st and 2nd reactions).

Table S4 Curve fitting results without Ir-Rh shell of Ir L_3-edge EXAFS of Ir−ReO_x/SiO_2 and Rh−Ir−ReO_x/SiO_2 after the reduction.

Catalyst	Shells	CN[a]	R / 10^{-1} nm[b]	σ / 10^{-1} nm[c]	ΔE_0 / eV[d]	R_f / %[e]
Ir-ReO_x/SiO_2[f]	Ir-Ir (or -Re)	10.6 ± 0.9	2.76 ± 0.01	0.067 ± 0.004	−1.0 ± 1.2	0.9
Rh(0.66)-Ir-ReO_x/SiO_2	Ir-Ir (or -Re)	10.8	2.76	0.079	1.9	2.3
Rh(1)-Ir-ReO_x/SiO_2	Ir-Ir (or -Re)	10.9	2.77	0.080	3.6	4.2
Rh(2)-Ir-ReO_x/SiO_2	Ir-Ir (or -Re)	10.7	2.77	0.085	5.5	10.7
Ir powder	Ir-Ir	12	2.77	0.06	0	–

[a]Coordination number. [b]Bond distance. [c]Debye-Waller factor. [d]Difference in the origin of photoelectron energy between the reference and the sample. [e]Residual factor. [f]After glycerol hydrogenolysis[S1]. Fourier filtering range: 0.163-0.325 nm.

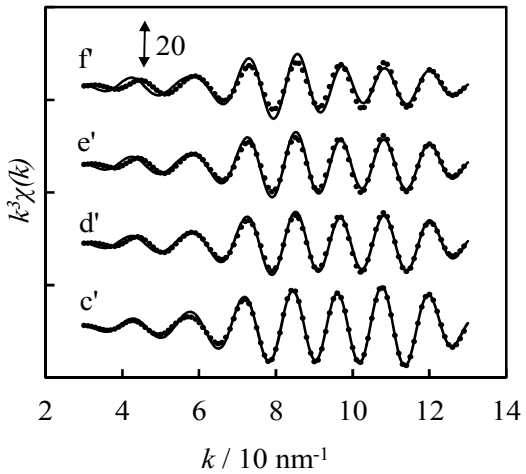

Fig. S2 Fourier filtered EXAFS data (solid line) and calculated data (dotted line) in Ir L_3-edge EXAFS analysis without Ir-Rh shell of Ir-ReO_x/SiO_2 and Rh-Ir-ReO_x/SiO_2 after the reduction. Fourier filtering range: 0.163-0.325 nm. (c') Ir-ReO_x/SiO_2 after glycerol hydrogenolysis[S1]. and (d'-f') Rh-Ir-ReO_x/SiO_2 after the reduction ((d') Rh = 0.66 wt%, (e') Rh =1 wt% and (f') Rh = 2 wt%).

Table S5 Curve fitting results without Re-Rh shell of Re L_3-edge EXAFS of Ir-ReO_x/SiO_2 and Rh-Ir-ReO_x/SiO_2 after the reduction.

Catalyst	Shells	CN[a]	R / 10^{-1} nm[b]	σ / 10^{-1} nm[c]	ΔE_0 / eV[d]	R_f / %[e]
Ir-ReO_x/SiO_2[f]	Re-O	1.7 ± 0.5	2.03 ± 0.03	0.080 ± 0.016	0.6 ± 5.0	2.5
	Re-Ir (or -Re)	6.1 ± 1.1	2.68 ± 0.01	0.082 ± 0.006	8.1 ± 1.8	
Rh(1)-Ir-ReO_x/SiO_2[f]	Re-O	1.0	2.04	0.084	−6.8	4.9
	Re-Ir (or -Re)	6.1	2.67	0.094	6.9	
Rh(2)-Ir-ReO_x/SiO_2[f]	Re-O	1.3	2.05	0.085	−4.8	17.3
	Re-Ir (or -Re)	6.0	2.66	0.097	10.0	
NH_4ReO_4	Re=O	4	1.73	0.06	0	–

[a]Coordination number. [b]Bond distance. [c]Debye-Waller factor. [d]Difference in the origin of photoelectron energy between the reference and the sample. [e]Residual factor. [f]After glycerol hydrogenolysis[S1]. Fourier filtering range: 0.138-0.325 nm.

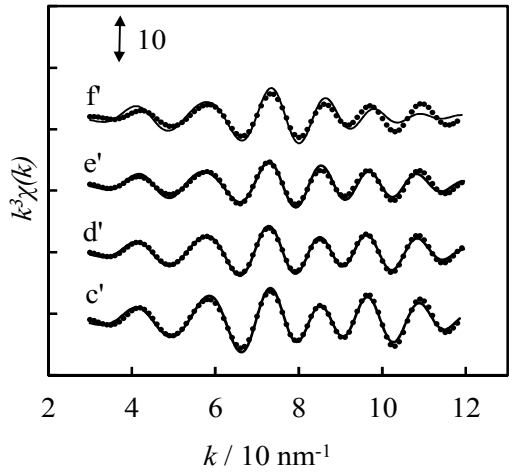

Fig. S3 Fourier filtered EXAFS data (solid line) and calculated data (dotted line) in Re L_3-edge EXAFS analysis without Re-Rh shell of Ir-ReO_x/SiO_2 and Rh-Ir-ReO_x/SiO_2 after the reduction. Fourier filtering range: 0.138–0.325 nm. (c') Ir-ReO_x/SiO_2 after glycerol hydrogenolysis[S1].and (d'-f') Rh-Ir-ReO_x/SiO_2 after the reduction ((d') Rh = 0.66 wt%, (e') Rh =1 wt% and (f') Rh = 2 wt%).

Table S6 Curve fitting results without Rh-Rh of Rh *K*-edge EXAFS of Rh-Ir-ReO_x/SiO_2 after the reduction.

Catalyst	Shells	CN[a]	R / 10^{-1} nm[b]	σ / 10^{-1} nm[c]	ΔE_0 / eV[d]	R_f / %[e]
Rh(0.66)-Ir-ReO_x/SiO_2	Rh-Ir (or -Re)	9.0	2.69	0.087	−2.3	3.1
Rh(1)-Ir-ReO_x/SiO_2	Rh-Ir (or -Re)	9.0	2.69	0.097	5.3	11.7
Rh(2)-Ir-ReO_x/SiO_2	Rh-Ir (or -Re)	9.1	2.69	0.107	15.8	56.0
Rh foil	Rh−Rh	12	2.68	0.06	0	–

[a]Coordination number. [b]Bond distance. [c]Debye-Waller factor. [d]Difference in the origin of photoelectron energy between the reference and the sample. [e]Residual factor. Fourier filtering range: 0.163-0.310 nm.

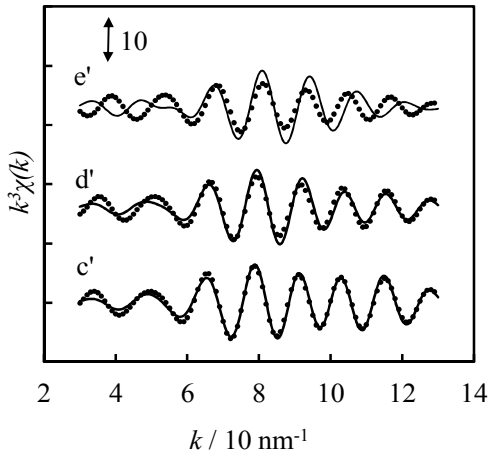

Fig. S4 Fourier filtered EXAFS data (solid line) and calculated data (dotted line) in Rh *K*-edge EXAFS analysis without Rh-Rh shell of Rh-Ir-ReO_x/SiO_2 after the reduction. Fourier filtering range: 0.163–0.310 nm. (c'-e') Rh-Ir-ReO_x/SiO_2 after the reduction ((c') Rh = 0.66 wt%, (d') Rh =1 wt% and (e') Rh = 2 wt%).

[S1] Y. Amada, Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B: Environ. 105 (2011) 117-127.