

Electronic supplementary information:

**Hydrogenation of dicarboxylic acids to diols over Re-Pd
catalysts**

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Catalyst characterization

X-ray diffraction (XRD) patterns were recorded with a diffractometer (MiniFlex600; Rigaku). The XRD patterns were normalized by adjusting the area of raw SiO₂ signals of the catalysts ($2\theta = 8^\circ - 35^\circ$) to the relative SiO₂ amount of the catalysts. The particle size (d) on the catalysts was calculated by the Scherrer's equation [S1]. The dispersion (D) was calculated by the following method. In the spherical particle equivalent approximation, the D is related to the volume-area mean diameter \bar{d}_{VA} [nm] as $D = 6(V_M/a_M)/\bar{d}_{VA}$, where a_M and V_M are the effective average area occupied by a metal atom in the surface and the volume per metal atom in the bulk, respectively [S2]. The values of $6(V_M/a_M)$ were calculated from the data in the literature ($V_M = 1.47 \times 10^{-2}$ (Re and Pd) nm³, $a_M = 6.49 \times 10^{-2}$ (Re) or 7.87×10^{-2} (Pd) nm²) [S2]; 1.36 [nm] for Re and 1.12 [nm] for Pd. XRD patterns were fitted by some Gaussian functions [S3, S4] expressed by Eq. (5):

$$y = \sum_i A_i \exp(- (x-x_{0,i})^2 / 2\omega_i^2) + B \quad FWHM = 2\omega\sqrt{2\ln 2} \quad (5)$$

here, A , x , x_0 , ω , B and FWHM are height of peak, the 2θ value, the 2θ position of the peak, standard deviation, background and full width at half maximum, respectively. Subscript i represents metal species. The value of ω was fixed to the same value for peaks for the same metal phase. A_i ratio and $x_{0, \text{Re(HCP)}}$ was fixed (Table S8), as the values have been reported for Re(HCP) (ICDD 01-074-6603), Pd(FCC) (ICSD no. 41517) and Re(FCC) (ICDD 01-088-2340). The XRD patterns were fitted so as to minimize root mean square error (RMSE).

For EXAFS analysis, the oscillation was first extracted from the EXAFS data using a spline smoothing method [S5]. Fourier transformation of the k^3 -weighted EXAFS oscillation from the k space to the r space was performed to obtain a radial distribution function. The inversely Fourier

filtered data were analyzed using a usual curve fitting method [S6]. The empirical phase shift and amplitude functions for Re=O and Re-O bonds were extracted from the data of NH_4ReO_4 . The empirical phase shift and amplitude functions for Re-Re and Pd-Pd bonds were extracted from the data of Re powder and Pd foil, respectively. Analyses of EXAFS and X-ray adsorption near edge spectra (XANES) data were performed using a computer program (REX2000, ver. 2.6.0; Rigaku Corp.).

Regarding the XANES, the white line area of the Re L_3 -edge XANES was analyzed. It has been previously reported that the average valence of Re species can be estimated from the white line area in the L_3 -edge XANES [S7] on the basis of the linear relation between the white line area and the valence of the Re species. In this analysis, the data of ReO_2 , ReO_3 and Re_2O_7 were used as reference data. The relation between the valence and the white line area is shown in Figure S12.

Field emission scanning transmission electron microscope (FE-STEM) images and energy-dispersive X-ray (EDX) analysis were obtained on a Hitachi spherical aberration corrected STEM/SEM HD-2700 instrument operated at 200 kV. The catalysts after the reaction were used as samples for the TEM observation. The samples were dispersed in ethanol by supersonic wave. The samples were placed on Mo grids under air atmosphere.

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Table S1 List of substrates used in this study.

Substrate	Purity grade	Source
Succinic acid (SUC)	> 99.5%	Wako Pure Chemical Industries, Ltd.
Glutaric acid (GLU)	> 98.0%	Wako Pure Chemical Industries, Ltd.
Adipic acid (ADI)	> 99.5%	Wako Pure Chemical Industries, Ltd.
Suberic acid (SUB)	> 98.0%	Wako Pure Chemical Industries, Ltd.
γ -Butyrolactone (GBL)	> 99.0%	Wako Pure Chemical Industries, Ltd.
δ -Valerolactone (DVL)	> 98.0%	Tokyo Chemical Industry Co., Ltd.
2-Hydroxy butyric acid (2-HBA)	> 95.0%	Tokyo Chemical Industry Co., Ltd.
Dimethyl succinate (DMS)	> 98.0%	Wako Pure Chemical Industries, Ltd.
Hexanoic acid (HXA)	> 99.0%	Wako Pure Chemical Industries, Ltd.
Octanoic acid (OCA)	> 98.0%	Wako Pure Chemical Industries, Ltd.
Stearic acid (STA)	> 95.0%	Wako Pure Chemical Industries, Ltd.

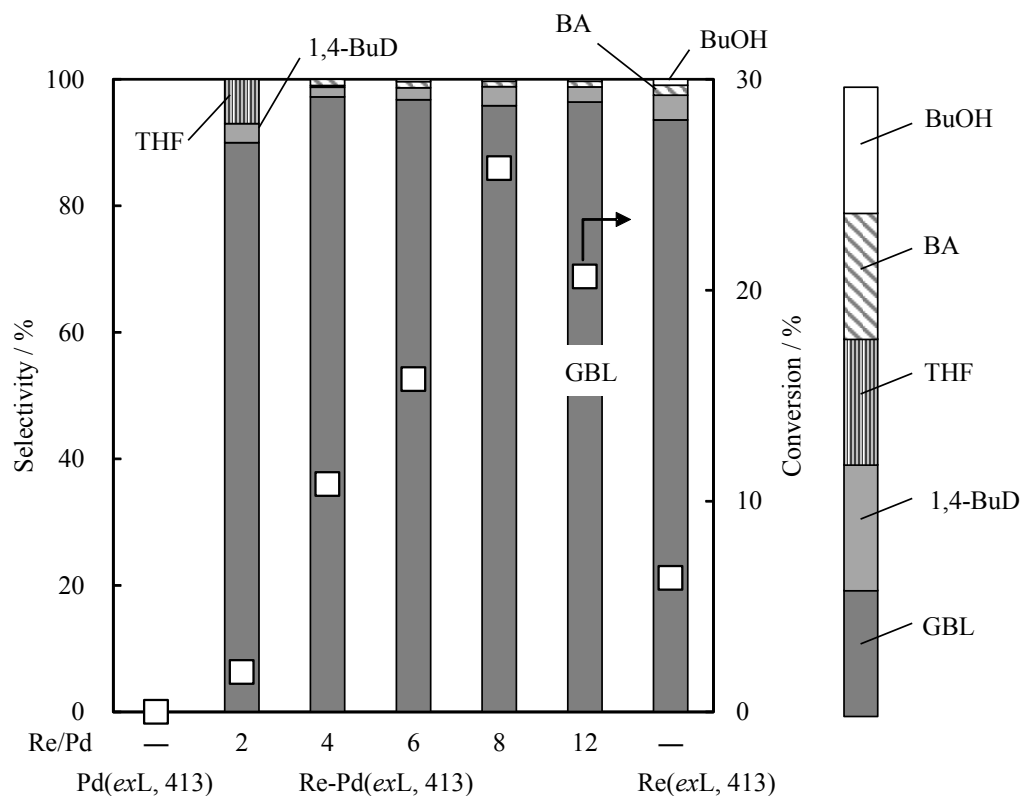


Figure S1. Effect of Re/Pd molar ratio on SUC hydrogenation over Pd(*exL*, 413), Re(*exL*, 413), and Re-Pd(*exL*, 413) catalysts.

Reaction conditions: 5 wt% SUC solution 20 g (SUC 1 g, 1,4-dioxane 19 g), Pd(*exL*, 413) (Pd = 1 wt%)

Re(*exL*, 413) (Re = 14 wt%) Re-Pd(*exL*, 413) (Re = 14 wt%, Re/Pd = 8) 0.1 g, reaction temperature 413 K, H₂ pressure 8.0 MPa, reaction time 4 h.

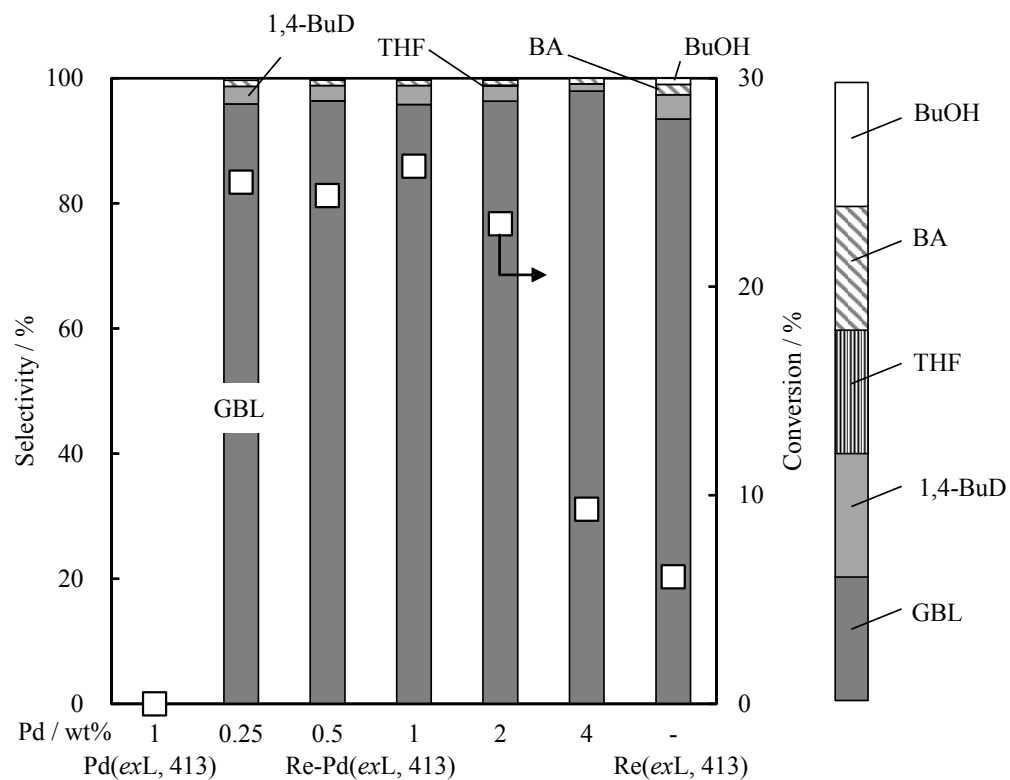


Figure S2. Effect of Re/Pd molar ratio on SUC hydrogenation over Re-Pd(*exL*, 413) catalysts.

Reaction conditions: 5 wt% SUC solution 20 g (SUC 1 g, 1,4-dioxane 19 g), Re-Pd(*exL*, 413) (Pd = 1 wt%) 0.1 g, reaction temperature 413 K, H₂ pressure 8.0 MPa, reaction time 4 h.

Table S2 Reaction time dependence on the hydrogenation of SUC, GLU and ADI over Re-Pd(*exL*, 413) (Re/Pd = 8) catalyst.

Entry	Substrate	Time / h	Conv. / %	Selectivity / %					Yield of diol / %
				Lactone	HCA	Diol	Monoalcohol	Others	
1	SUC	4	26	96	0.0	3.0	0.3	0.9	0.8
2		20	90	90	0.0	8.5	0.4	0.7	7.6
3		24	99	86	0.0	13	0.6	0.6	13
4		48	100	48	0.0	50	2.0	0.1	50
5		72	100	37	0.0	60	2.3	0.1	60
6		96	100	3.1	0.0	89	7.6	0.2	89
7		120	100	0.9	0.0	85	13	0.3	85
8	GLU	4	22	93	3.2	3.1	0.0	0.6	0.7
9		24	82	70	4.0	16	0.6	8.7	13
10		48	95	44	3.7	20	0.3	31	19
11		120	100	1.6	0.0	71	8.4	19	71
12	ADI	4	15	3.6	82	11	0.5	2.8	1.7
13		24	51	5.6	56	35	1.0	2.4	18
14		48	100	2.2	35	40	1.3	21	40
15		96	100	1.1	6.5	74	2.9	16	74
16		120	100	0.1	0.0	74	16	9.0	74

HCA, hydroxy carboxylic acid; Others, monocarboxylic acid, gas products and heavy products; SUC, succinic acid; GLU, glutaric acid; ADI, adipic acid.

Reaction conditions: substrate 1 g, 1,4-dioxane 19 g, Re-Pd(*exL*, 413) (Re/Pd = 8, Re = 14 wt%) 0.1 g, reaction temperature 413 K, H₂ pressure 8.0 MPa.

* The data corresponded to independent experiments at different reaction times.

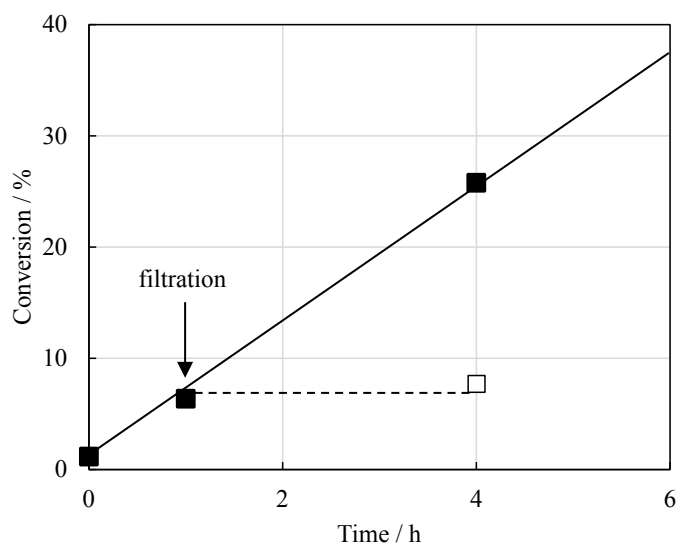


Figure S3. Activity tests of the SUC hydrogenation using Re-Pd(*exL*,413) (Re/Pd = 8, Re = 14 wt%) catalyst without or with the removal of the catalyst by filtration^a.

Reaction conditions: 5 wt% SUC solution 20 g (STA 1 g, 1,4-dioxane 19 g), catalyst amount 0.1 g, reaction temperature 413 K, H₂ pressure 8.0 MPa.

Solid line, ■: without filtration; broken line, □: after filtration.

^a The catalyst was removed after 1 h reaction time by filtration.

Table S3 Reusability test of Re-Pd(*exL*, 413) (Re/Pd=8) catalyst in the hydrogenation of SUC.

Number of uses	Catalyst amount / mg	SUC / g	1,4-dioxane / g	Conv. / %	Selectivity / %					ν^b / mmol h ⁻¹ g-Cat. ⁻¹
					GBL	BDO	THF	BA	BuOH	
1	100	1.0	19	12	97	2.3	0.0	1.0	0.2	5.0
2	(93) ^a	0.9	17	7.7	97	1.9	0.0	0.9	0.0	3.1
3	(85) ^a	0.8	15	6.6	97	1.9	0.0	0.9	0.0	2.5
4	(78) ^a	0.7	13	5.0	98	1.8	0.0	0.0	0.0	1.9

SUC, succinic acid; GBL, γ -butyrolactone; 1,4-BuD, 1,4-butanediol; THF, tetrahydrofuran; BA, butyric acid; BuOH, 1-butanol.

Reaction conditions: 5 wt% SUC solution, solvent: 1,4-dioxane, Re-Pd(*exL*, 413) (Re/Pd = 8, Re = 14 wt%), reaction temperature 413 K, H₂ pressure 8.0 MPa, reaction time 2 h.

^a The catalyst amount was calculated from the catalyst amount after 4th time reaction (70.4 mg) by assuming that the recovery ratio of the catalyst is constant for each recovery treatment.

^b Averaged conversion rate.

Method for reusability test: After the reaction, the autoclave was opened under N₂ atmosphere, and the catalyst was separated by decantation. The collected wet catalyst was added to an autoclave reactor under N₂ for the next test without exposure to air. The precise amount of the collected catalyst cannot be determined, and the catalyst amount in each number of uses was calculated from that after 4th time reaction test, assuming the ratio of the loss amount of the catalyst to the introduced catalyst amount is constant.

Table S4 Effect of dicarboxylic acid (SUC, GLU and ADI) concentration on the hydrogenation of dicarboxylic acids over Re-Pd(*exL*, 413) and Re(*exL*, 413) catalysts.

Entry	Substrate	Amount Catalyst	Concentration				Conv. / %	Selectivity / %					v^a / mmol · g-cat ⁻¹ · h
			Substrate / g	1,4-dioxane / g	Concentration / %	Lactone		HCA	Diol	monoalcohol	others		
1	SUC	Re-Pd(<i>exL</i> , 413)	0.060	0.60	19	3	22	96	-	2.3	0.6	1.5	4.5
2		Re/Pd = 8	0.10	1.0	19	5	26	96	-	3.0	0.3	0.9	5.4
3			0.10	1.0	13	7	20	97	-	1.1	0.3	1.2	4.3
4			0.10	1.0	9.0	10	21	98	-	0.8	0.0	1.2	4.4
5			0.10	1.0	5.7	15	23	98	-	0.4	0.0	1.4	4.9
6			0.10	1.0	2.3	30	28	98	-	0.7	0.0	1.0	6.0
7	GLU	Re-Pd(<i>exL</i> , 413)	0.060	0.60	19	3	24	92	3.7	3.4	0.0	0.7	4.4
8		Re/Pd = 8	0.10	1.0	19	5	22	93	3.2	3.1	0.0	0.6	4.1
9			0.10	1.0	13	7	22	94	2.8	3.0	0.0	0.6	4.2
10			0.10	1.0	9.0	10	19	94	3.2	2.5	0.0	0.6	3.6
11			0.10	1.0	5.7	15	21	93	4.8	1.6	0.0	0.6	4.0
12			0.10	1.0	2.3	30	18	88	10	0.9	0.0	1.0	3.4
13	ADI	Re-Pd(<i>exL</i> , 413)	0.060	0.60	19	3	20	1.5	91	5.1	0.0	2.1	3.4
14		Re/Pd = 8	0.10	1.0	19	5	15	3.6	82	11	0.5	2.8	2.6
15			0.10	1.0	13	7	13	5.4	82	10	0.0	2.8	2.3
16			0.10	1.0	9.0	10	11	7.9	82	7.7	0.0	2.6	1.9
17			0.10	1.0	5.7	15	10	8.8	81	7.7	0.0	2.9	1.7
18			0.10	1.0	2.3	30	5.7	9.3	78	3.8	0.0	9.1	1.0
19	SUC	Re(<i>exL</i> , 413)	0.060	0.60	19	3	5.8	88	-	5.1	2.1	5.0	1.2
20			0.10	1.0	19	5	7.0	94	-	3.9	0.9	1.6	1.5
21			0.10	1.0	9.0	10	9.2	94	-	4.2	0.6	1.5	2.0
22			0.10	1.0	5.7	15	11	98	-	0.8	0.0	1.4	2.2

HCA, hydroxy carboxylic acid; Others, monocarboxylic acid, gas products and heavy products; SUC, succinic acid; GLU, glutaric acid; ADI, adipic acid. Reaction conditions: 3~30 wt% dicarboxylic acid solution, 1,4-dioxane solvent 5.7-20 g, dicarboxylic acid 0.60-1.0 g, catalyst (Re = 14 wt%) 0.060-0.10 g, reaction temperature 413 K, H₂ pressure 8.0 MPa, reaction time 4 h.

^a Averaged conversion rate.

Table S5 Effect of H₂ pressure on the hydrogenation of dicarboxylic acids (SUC, GLU and ADI) over Re-Pd(*exL*, 413) and Re(*exL*, 413) catalysts.

Entry	Substrate	Catalyst	H ₂ pressure / MPa	Time Conv.		Selectivity / %					v ^a / mmol · g-cat ⁻¹ · h ⁻¹
				/ h	/ %	Lactone	HCA	Diol	Monoalcohol	Others	
1	SUC	Re-Pd(<i>exL</i> , 413)	2	4	5.9	95	-	4.1	0.0	1.0	1.3
2		Re/Pd = 8	4	4	8.7	95	-	3.0	0.5	1.0	1.9
3			6	4	13	97	-	1.7	0.4	0.9	2.8
4			8	4	26	96	-	3.0	0.3	0.9	5.4
5	GLU	Re-Pd(<i>exL</i> , 413)	2	4	4.8	98	2.1	0.0	0.0	0.0	0.9
6		Re/Pd = 8	4	4	11	96	2.2	1.5	0.0	0.7	2.2
7			6	4	17	95	2.6	1.9	0.0	0.7	3.2
8			8	4	22	93	3.2	3.1	0.0	0.6	4.1
9	ADI	Re-Pd(<i>exL</i> , 413)	2	4	2.9	5.1	88	3.2	0.0	4.1	0.5
10		Re/Pd = 8	4	4	5.5	4.3	87	5.2	0.0	3.6	0.9
11			6	4	9.3	4.0	85	7.0	0.0	4.2	1.6
12			8	4	15	3.6	82	11	0.5	2.8	2.6
13	SUC	Re(<i>exL</i> , 413)	2	16	3.2	96	-	1.1	0.0	2.6	0.2
14			4	16	6.8	96	-	1.6	0.4	1.8	0.4
15			6	16	10	94	-	3.5	1.0	1.6	0.5
16			8	16	13	96	-	2.1	0.6	1.5	0.7

HCA, hydroxy carboxylic acid; Others, monocarboxylic acid, gas products and heavy products; SUC, succinic acid; GLU, glutaric acid; ADI, adipic acid.

Reaction conditions: 5 wt% dicarboxylic acid solution 20 g (dicarboxylic acid 1 g, 1,4-dioxane 19 g), catalyst amount (Re = 14 wt%) 0.1 g, reaction temperature 413 K.

^a Averaged conversion rate.

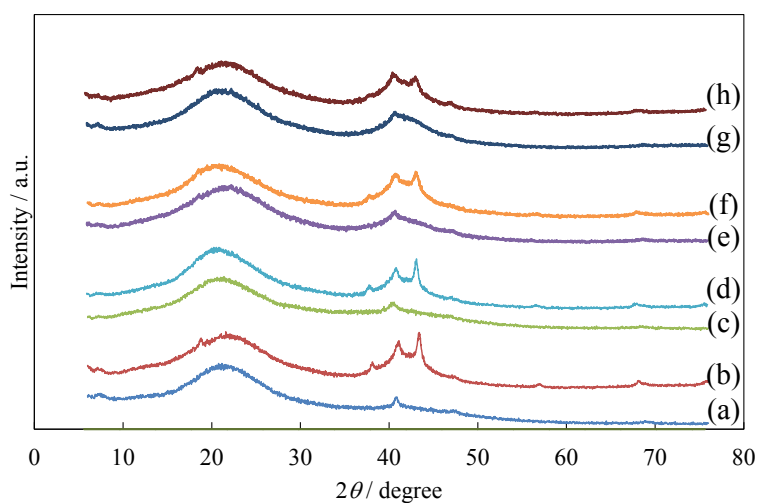


Figure S4. XRD patterns of Re-Pd catalysts after the reaction.

After SUC hydrogenation (a) Re-Pd(*inL*, 413, Reaction), (b) Re-Pd(*exL*, 473, Reaction); after ADI hydrogenation (c) Re-Pd(*inL*, 413, Reaction), (d) Re-Pd(*exL*, 473, Reaction); after HXA hydrogenation (e) Re-Pd(*inL*, 413, Reaction), (f) Re-Pd(*exL*, 473, Reaction); after STA hydrogenation [S3] (g) Re-Pd(*inL*, 413, Reaction), (h) Re-Pd(*exL*, 473, Reaction).

Reaction conditions are described in Table 3.

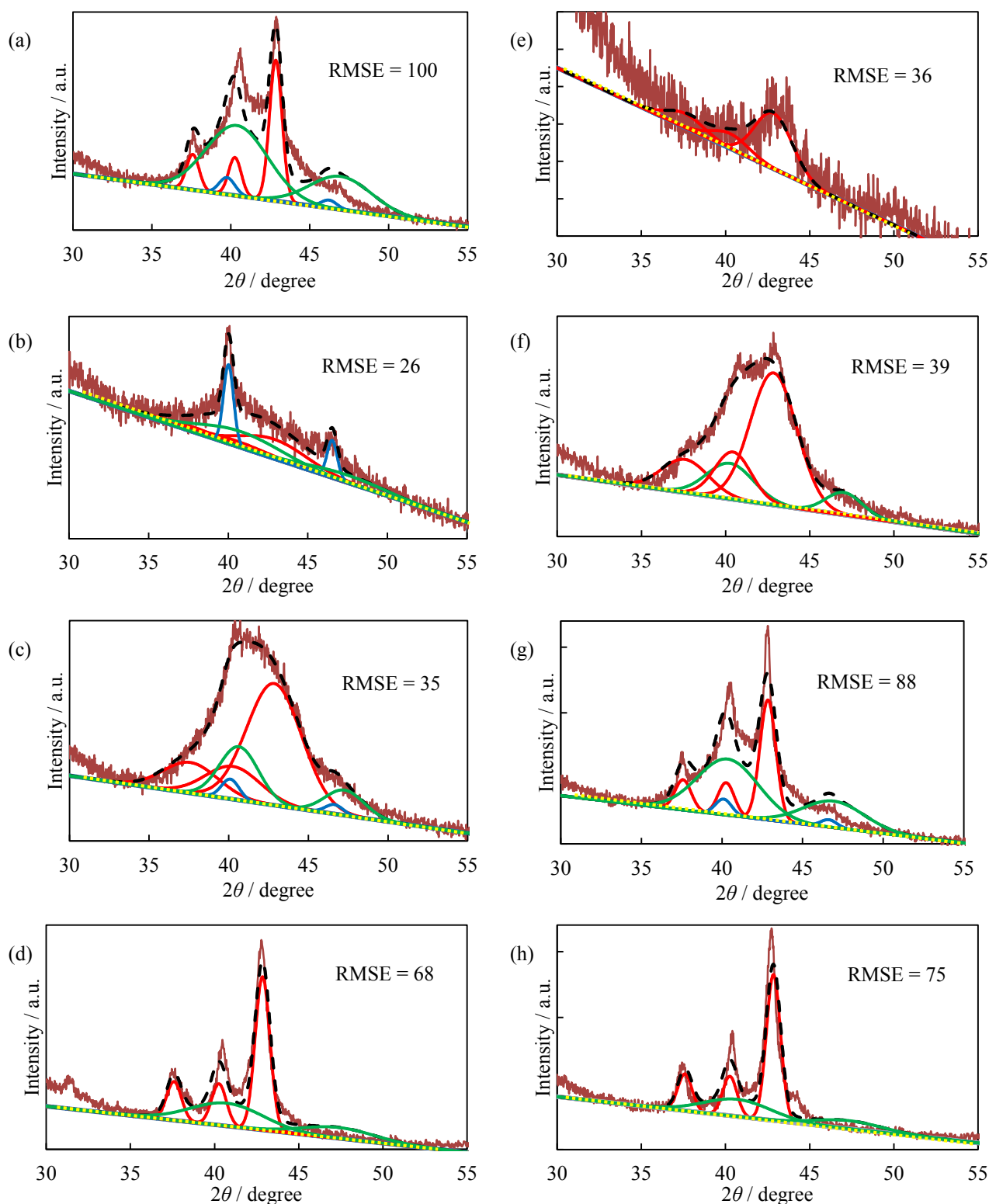


Figure S5. The fitting results of XRD peaks of Re and Re-Pd catalysts using Re(HCP), Re(FCC) and Pd metal species.

Brown line: raw data (Figure 4), yellow dotted line: background, red line: Re(HCP), blue line: Pd, green line: Re(FCC), black dotted line: the result of curve fitting. Fitting range: $2\theta = 35 - 55^\circ$.

((a) Re-Pd(*exL*, 413, Reaction), (b) Re-Pd(*inL*, 413, Reaction), (c) Re-Pd(G, 473, Reaction), (d) Re(*exL*, 413, Reaction), (e) Re (*inL*, 413, Reaction), (f) Re (G, 473, Reaction), (g) Re-Pd(*exL*, 413), (h) Re(*exL*, 413).

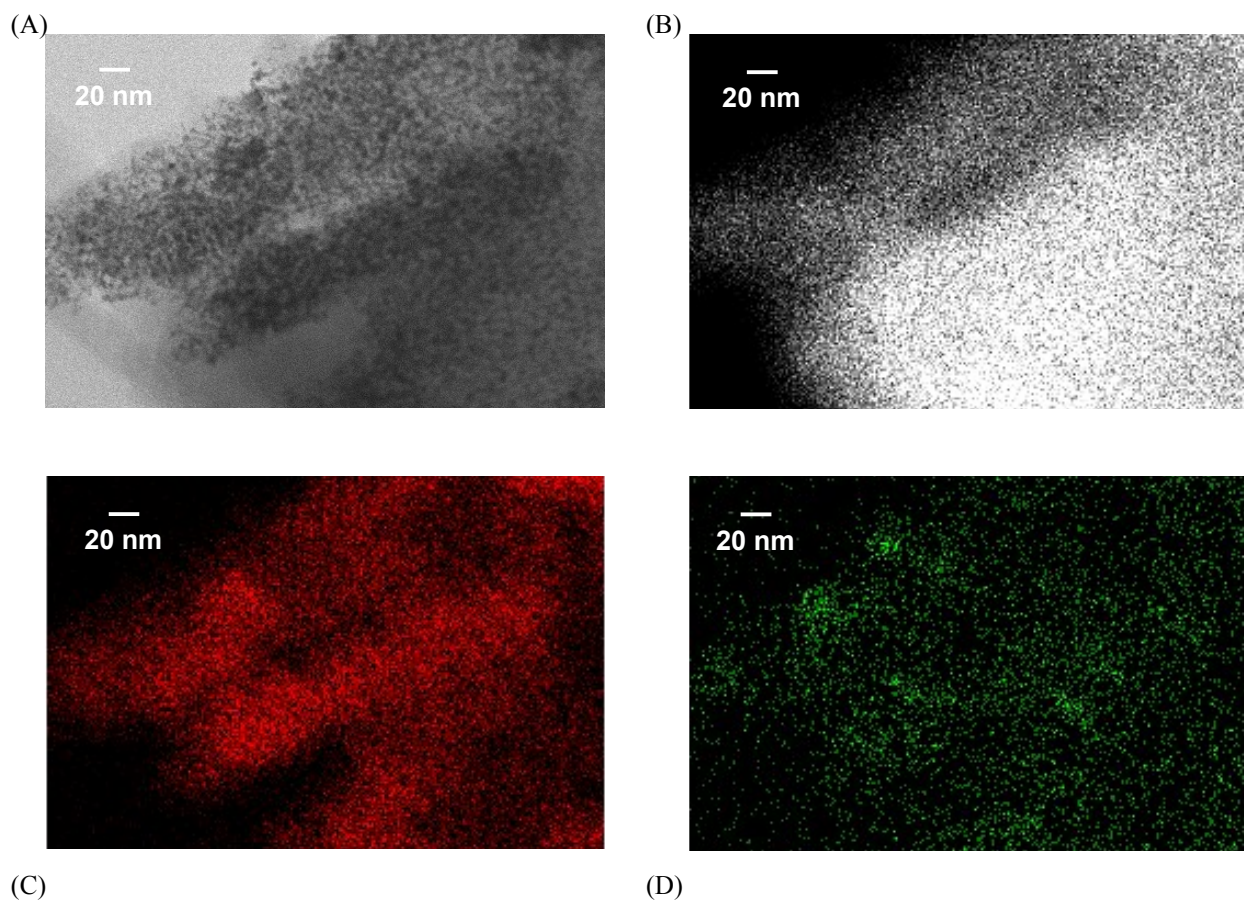


Figure S6. TEM image and elemental mappings by STEM-EDX of Re-Pd(*exL*, 413, Reaction) (Re/Pd = 8). (A) TEM images, (B) Si elemental mapping, (C) Re elemental mapping, (D) Pd elemental mapping.

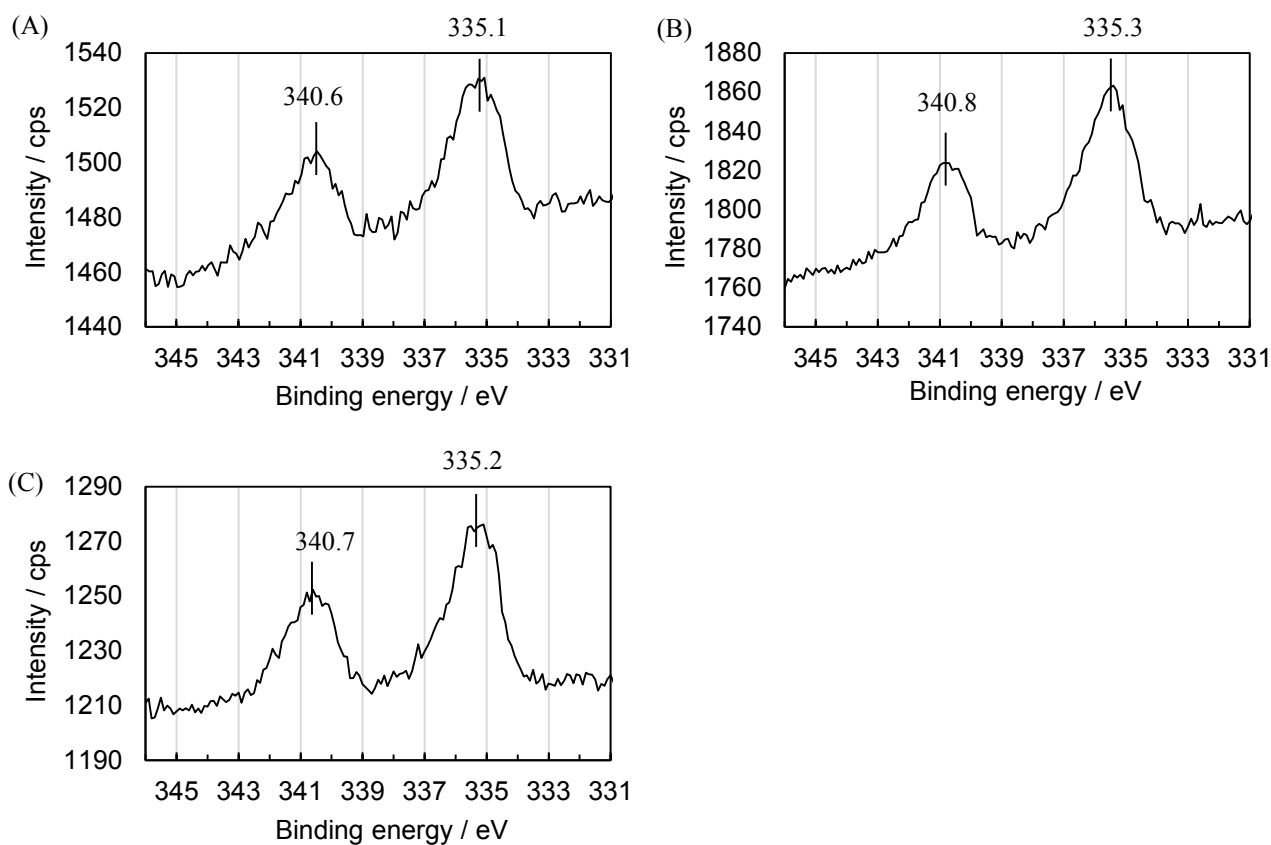


Figure S7. XPS for Pd 3d of (A) Re-Pd(*inL*, 413, Reaction), (B) Re-Pd(*exL*, 413) (Re/Pd = 8) and (C) Re-Pd(*exL*, 413, Reaction) (Re/Pd = 8) catalysts.

Reaction conditions: 5 wt% SUC solution 20 g (SUC 1 g, 1,4-dioxane 19 g), catalyst amount 0.1 g, reaction temperature 413 K, H₂ pressure 8.0 MPa, reaction time 4 h.

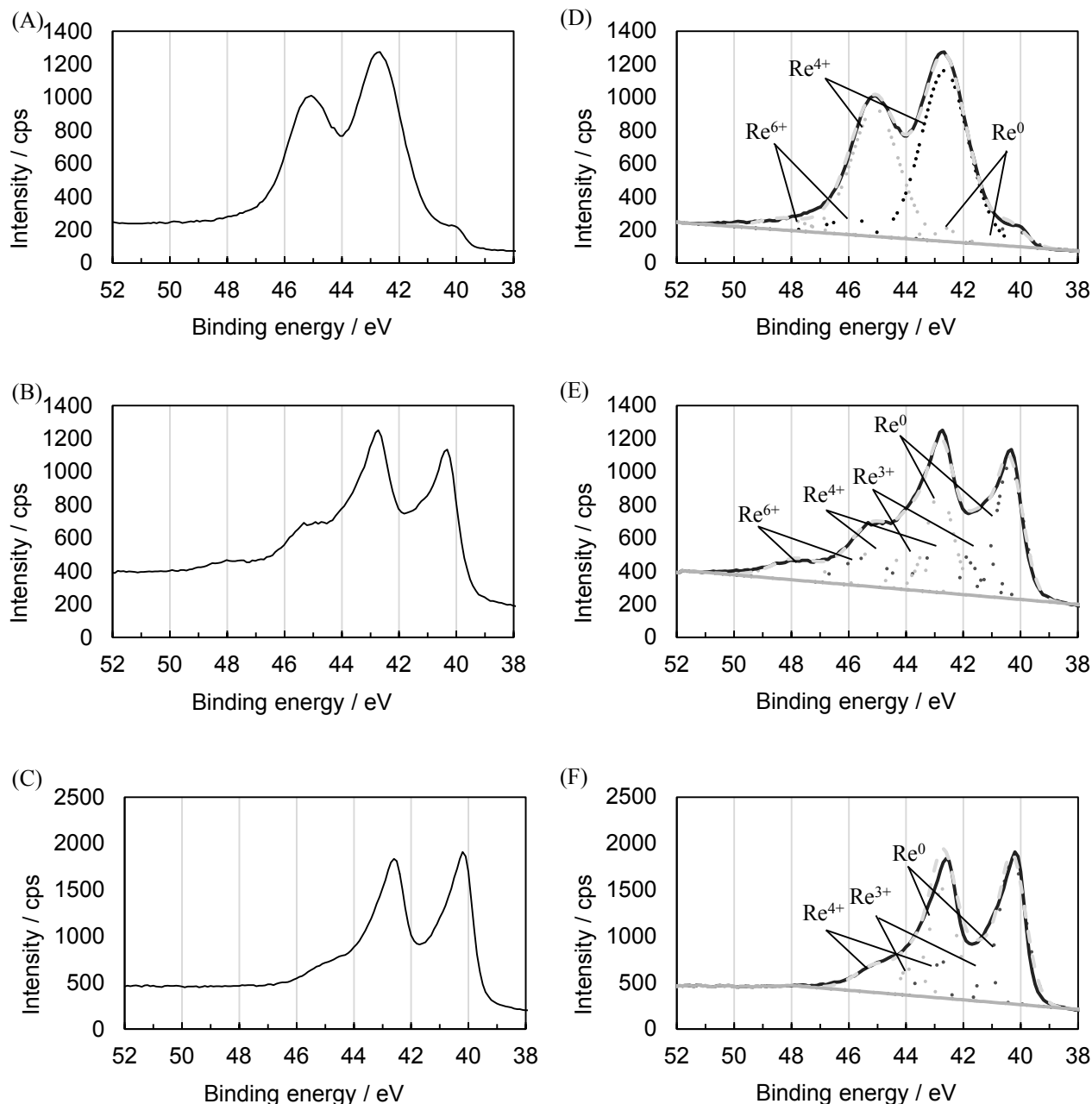


Figure S8. XPS for Re 4f of Re catalysts ((A, D) Re(*inL*, 413, Reaction), (B, E) Re(*exL*, 413), (C, F) Re(*exL*, 413, Reaction)). (A, B, C): Raw data, (D, E, F): analysis results.

Reaction conditions: 5 wt% SUC solution 20 g (SUC 1 g, 1,4-dioxane 19 g), catalyst amount 0.1 g, reaction temperature 413 K, H_2 pressure 8.0 MPa, reaction time 4 h.

Black line: raw spectra; black dotted line: $4f_{7/2}$ for Re^0 , Re^{3+} , Re^{4+} and Re^{6+} ; gray dotted line: $4f_{5/2}$ for Re^0 , Re^{3+} , Re^{4+} and Re^{6+} ; gray broken line: the result of fitting; gray line: background.

The fitted values are shown in Table 6.

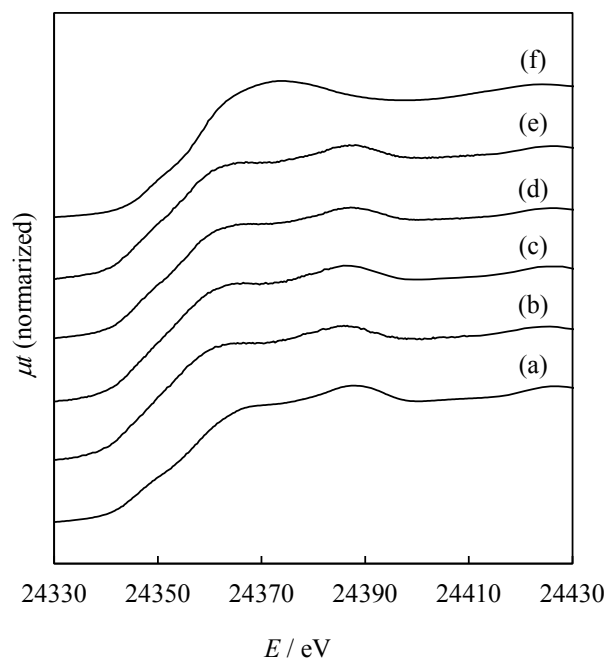


Figure S9. Pd *K*-edge XANES of Pd and Re-Pd catalysts after the reduction and SUC hydrogenation. (a) Pd foil, (b) Re-Pd(*inL*, 413, Reaction) (Re/Pd = 8), (c) Re-Pd(*exL*, 413) (Re/Pd = 8), (d) Re-Pd(*exL*, 413, Reaction) (Re/Pd = 8), (e) Re-Pd(*G*, 473, Reaction) (Re/Pd = 8), (f) PdO.

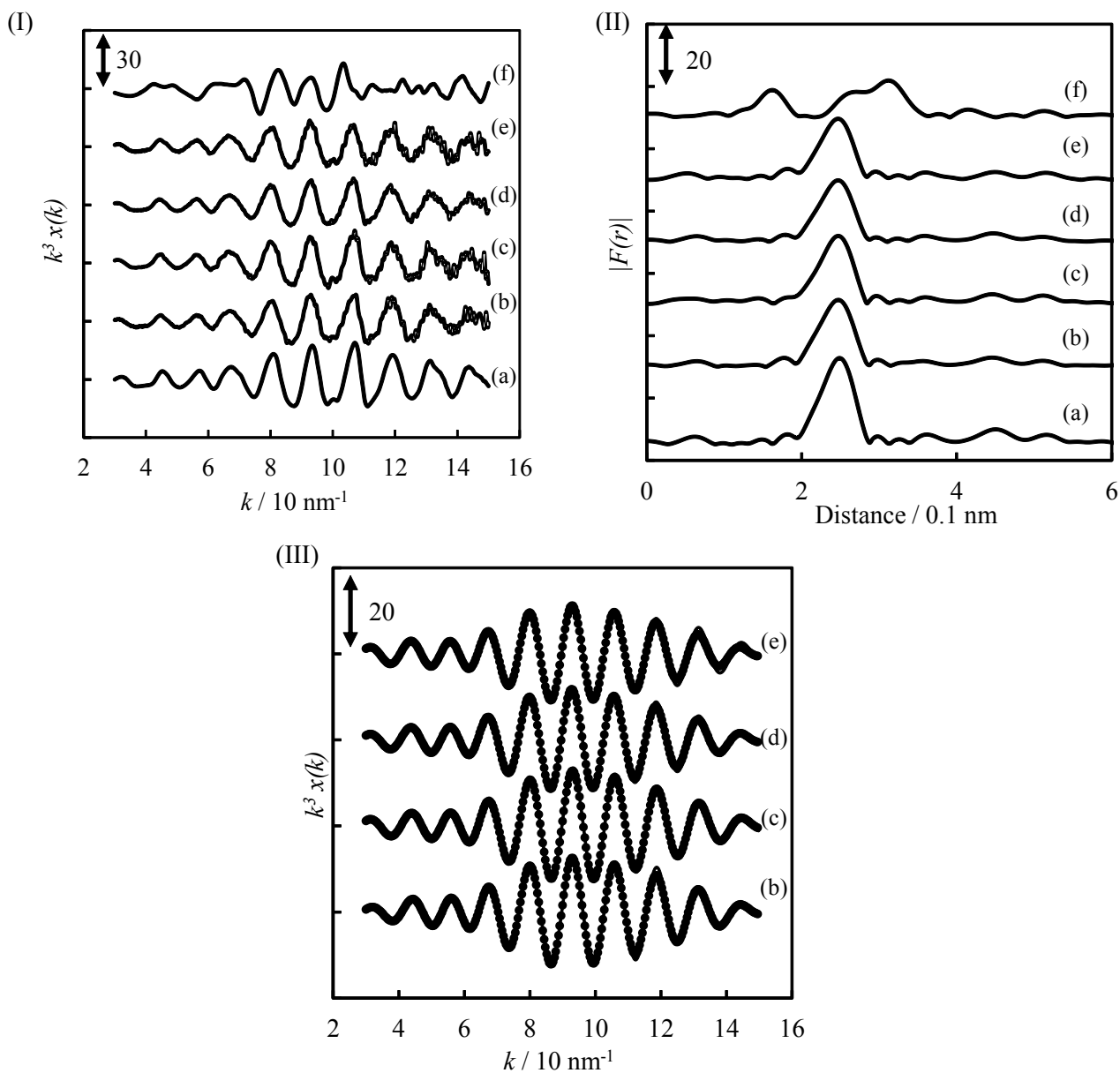


Figure S10. Results of Pd *K*-edge EXAFS analysis of Pd and Re-Pd (Re/Pd = 8) catalysts the reduction and SUC reaction

(I) k^3 -Weighted EXAFS oscillations. (II) Fourier transform of k^3 -weighted Pd *K*-edge EXAFS, FT range: 30–140 nm^{-1} . (III) Fourier filtered EXAFS data (solid line) and calculated data (dotted line), Fourier filtering range: 0.115–0.334 nm. (a) Pd foil, (b) Re-Pd(*inL*, 413, Reaction) (Re/Pd = 8), (c) Re-Pd(*exL*, 413) (Re/Pd = 8), (d) Re-Pd(*exL*, 413, Reaction) (Re/Pd = 8), (e) Re-Pd(*G*, 473, Reaction) (Re/Pd = 8), (f) PdO.

Table S6. Curve fitting results for the Pd *K*-edge EXAFS analysis of Pd and Re-Pd (Re = 14 wt%, Re/Pd = 8) catalysts after the reduction and SUC reaction^a.

Entry	Catalyst	Shells	CN ^b	R^c / 10 ⁻¹ nm	Σ^d / 10 ⁻¹ nm	ΔE_0^e / eV	R_f^f / %
1	Re-Pd(<i>in</i> L, 413, Reaction) ^g Re/Pd = 8	Pd-Pd	11.8	2.75	0.070	0.9	1.7
2	Re-Pd(<i>ex</i> L, 413) ^h Re/Pd = 8	Pd-Pd	11.6	2.74	0.069	0.1	0.5
3	Re-Pd(<i>ex</i> L, 413, Reaction) ^g Re/Pd = 8	Pd-Pd	11.6	2.75	0.072	0.1	1.1
4	Re-Pd(G, 473, Reaction) ^g Re/Pd = 8	Pd-Pd	11.7	2.75	0.074	0.6	1.6
	PdO	Pd-O	4	2.02	0.060	0.0	
	Pd foil	Pd-Pd	12	2.75	0.060	0.0	

^a Fourier filtering range: 0.115–0.334 nm.

^b Coordination number.

^c Bond distance.

^d Debye–Waller factor.

^e Difference in the origin of photoelectron energy between the reference and the sample.

^f Residual factor.

^g Reaction conditions: 5 wt% STA solution 20 g (STA 1 g, 1,4-dioxane 19 g), Cat. 200 mg, 413 K, 8 MPa, 2 h.

^h The catalysts were only reduced by *ex-situ* liquid-phase reduction method.

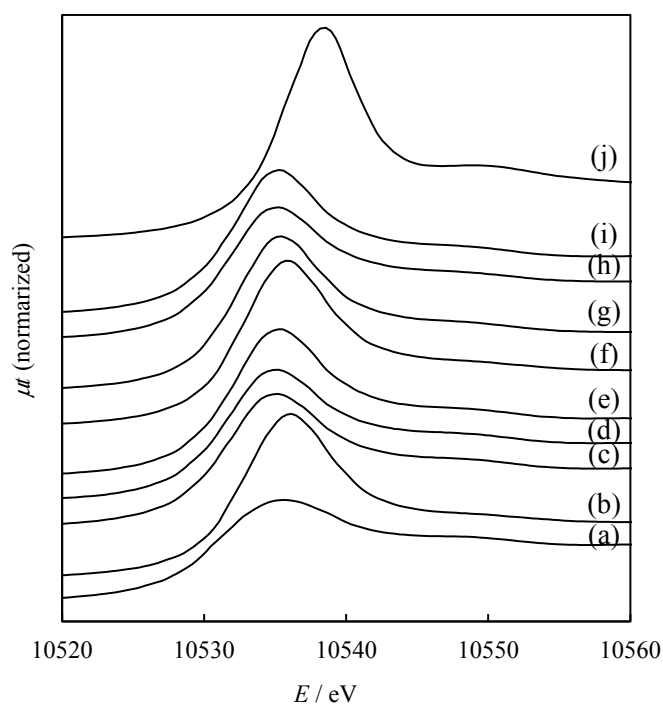


Figure S11. Re L_3 -edge XANES of Re-Pd (Re/Pd = 8) and Re (Re = 14 wt%) catalysts after the reduction and the SUC hydrogenation.

(a) Re powder, (b) Re(*inL*, 413, Reaction), (c) Re(*exL*, 413), (d) Re(*exL*, 413, Reaction), (e) Re(G, 473, Reaction), (f) Re-Pd(*inL*, 413, Reaction), (g) Re-Pd (*exL*, 413), (h) Re-Pd(*exL*, 413, Reaction), (i) Re-Pd(G, 473, Reaction), (j) Re_2O_7 .

Table S7. Estimation of the molar ratio of various Re species based on the characterization results.

Catalyst	Valence of Re (XANES) ^a	Molar ratio of (XPS) ^b			Molar ratio ^c				Molar ratio	Molar ratio ^e	CN _{Re-Re} Calculated ^g	EXAFS Fitting ^a
		Re ³⁺	Re ⁴⁺	Re ⁶⁺	Re ⁰ :Re ³⁺ :Re ⁴⁺ :Re ⁶⁺				Re ⁰ (HCP):Re ⁰ (FCC)	Re ⁰ (HCP) _S :Re ⁰ (FCC) _S		
					Re ⁰	Re ³⁺	Re ⁴⁺	Re ⁶⁺	(XRD area ratio) ^d	(XRD area ratio × Re dispersion) ^f		
Re-Pd(<i>inL</i> , 413, Reaction)	3.7	0.0	0.95	0.049	0.11	0.0	0.85	0.04	0.053:0.053	0.043:0.052	1.0	1.4
Re-Pd(<i>exL</i> , 413)	1.6	0.27	0.37	0.36	0.64	0.10	0.13	0.13	0.23:0.41	0.036:0.30	6.7	7.2
Re-Pd(<i>exL</i> , 413, Reaction)	1.2	0.67	0.33	0.0	0.63	0.25	0.12	0.0	0.18:0.45	0.028:0.34	6.5	6.2
Re-Pd(G, 473, Reaction)	1.3	0.25	0.34	0.4	0.71	0.072	0.10	0.12	0.54:0.17	0.35:0.080	7.3	7.4
Re(<i>inL</i> , 413, Reaction)	3.8	0.0	0.91	0.085	0.080	0.0	0.84	0.078	0.084:0.0	0.036:0.0	0.9	1.3
Re(<i>exL</i> , 413)	1.6	0.27	0.46	0.085	0.63	0.10	0.17	0.10	0.40:0.22	0.064:0.17	6.9	7.4
Re(<i>exL</i> , 413, Reaction)	1.1	0.37	0.63	0.0	0.69	0.11	0.19	0.0	0.40:0.30	0.068:0.24	7.5	8.0
Re(G, 473, Reaction)	1.4	0.52	0.31	0.16	0.64	0.19	0.11	0.059	0.50:0.14	0.26:0.058	6.7	7.3
Re-Pd(<i>inL</i> , 413, Reaction) ^h	2.0	0.38	0.62	0.0	0.45	0.21	0.34	0.0	0.28:0.17	0.17:0.085	4.6	4.7

^a Table 7.^b Table 6.^c The molar ratio of Re⁰:Re³⁺:Re⁴⁺:Re⁶⁺ is determined from using the following equations:

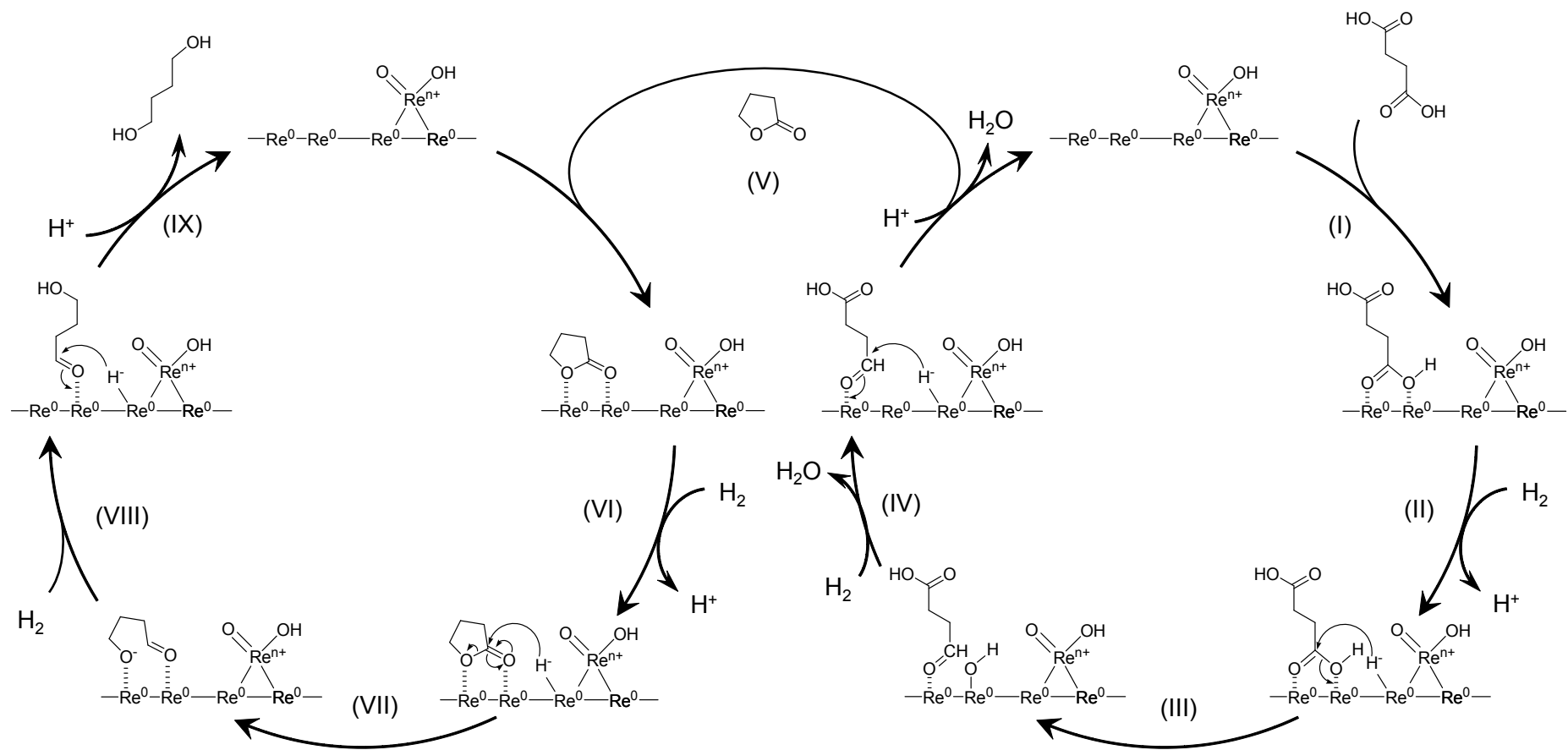
$$\text{Average valence of Re (XANES)} = M_{\text{Re}^0} \times 0 + M_{\text{Re}^{3+}} \times 3 + M_{\text{Re}^{4+}} \times 4 + M_{\text{Re}^{6+}} \times 6$$

$$(M_{\text{Re}^0} + M_{\text{Re}^{3+}} + M_{\text{Re}^{4+}} + M_{\text{Re}^{6+}} = 1)$$

^d $M_{\text{Re}^{n+}}$ means the molar ratio of Reⁿ⁺ to the total Re species, and $M_{\text{Re}^{3+}} : M_{\text{Re}^{4+}} : M_{\text{Re}^{6+}}$ can be determined from the XPS analysis.^e Table 5.^e The amount of surface Re metal atoms on Re⁰(HCP) and Re⁰(FCC) [Re⁰(HCP)_S and Re⁰(FCC)_S] is determined from using the relation between the dispersion (*D*) and the metal particle size (*d*).^f *D* was calculated from particle size of XRD (*d*_{XRD}, Table 5) by using the equation: $d_{\text{XRD}} [\text{nm}] = 1.36 (\text{Re}) / D$.^g Assuming that CN_{Re-Re} of the surface Re atoms on Re(HCP) and Re(FCC) is 9 and CN_{Re-Re} of the bulk Re atoms in Re(HCP) and Re(FCC) is 12.

$$\text{CN}_{\text{Re-Re}} (\text{calculated}) = M_{\text{Re}^0(\text{HCP})_S} \times D_{\text{Re}^0(\text{HCP})_S} \times 9 + M_{\text{Re}^0(\text{FCC})_S} \times D_{\text{Re}^0(\text{FCC})_S} \times 9 + M_{\text{Re}^0(\text{HCP})_B} \times (1 - D_{\text{Re}^0(\text{HCP})_S}) \times 12 + M_{\text{Re}^0(\text{FCC})_B} \times (1 - D_{\text{Re}^0(\text{FCC})_S}) \times 12$$

^h The results of the catalyst after STA hydrogenation [S3].



Scheme S1. Proposed reaction mechanism of SUC hydrogenation over Re-Pd(exL, 413), which is focusing on the role of Re⁰-Reⁿ⁺ interface and the role of Pd is not included.

Table S8. Parameters for XRD fitting

i	A_i ratio	$x_{0,i} / ^\circ$
Re(HCP)	0.25	37.52
	0.27	40.12
	1.00	42.74
Re(FCC)	1.00	(39.48)
	0.48	(45.92)
Pd(FCC)	1.00	(40.02)
	0.47	(46.66)

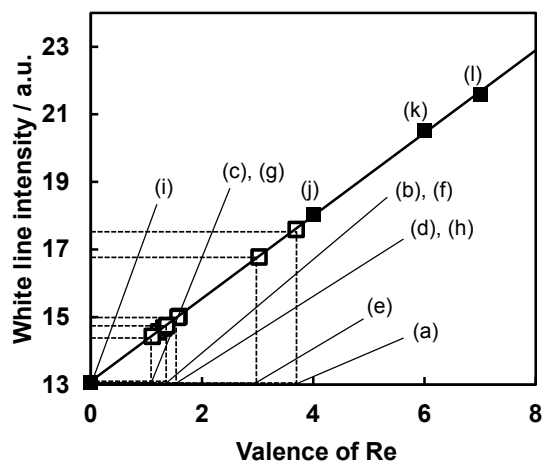


Figure S12. Relation between white line areas of Re L_3 -edge XANES and valence of Re.

(a) Re(*inL*, 413, Reaction) (Re = 14 wt%), (b) Re(*exL*, 413) (Re = 14 wt%), (c) Re(*exL*, 413, Reaction) (Re = 14 wt%), (d) Re(G, 473, Reaction) (Re = 14 wt%), (e) Re-Pd(*inL*, 413, Reaction) (Re = 14 wt%), (f) Re-Pd(*exL*, 413) (Re/Pd = 8), (g) Re-Pd(*exL*, 413, Reaction) (Re/Pd = 8), (h) Re-Pd(G, 473, Reaction), (i) Re powder, (j) ReO_2 , (k) ReO_3 , (l) Re_2O_7 .

(a)-(e): Re = 14 wt%; (f)-(h): Re = 14 wt%, Pd = 1 wt% (Re/Pd = 8).