

Supporting Information:

**Characterization of Re-Pd/SiO₂ catalysts for
hydrogenation of stearic acid**

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Table S1. The normalization data for XRD on the catalysts.

Entry	Spectra (Figure 1)	Catalyst	Re/Pd	Amount of SiO ₂ / wt%	SiO ₂ area (8 ° – 35 °) / 10 ⁴ degree•counts	
					raw	normalized
1	(a)	Pd(L, 413, Reaction)	—	99	55.2	55.2
2	(b)	Re-Pd(L, 413, Reaction)	2	96	76.1	53.0
3	(c)	Re-Pd(L, 413, Reaction)	4	92	60.4	51.3
4	(d)	Re-Pd(L, 413, Reaction)	6	89	59.6	49.1
5	(e)	Re-Pd(L, 413, Reaction)	8	85	52.5	47.5
6	(f)	Re-Pd(L, 413, Reaction)	12	78	48.6	43.6
7	(g)	Re(L, 413, Reaction)	—	86	57.5	48.0
8	(h)	Re-Pd(G, 473)	8	85	41.4	47.5
9	(i)	Re(G, 473)	—	86	43.3	48.0
10	(j)	Re(G, 773)	—	86	45.8	48.0

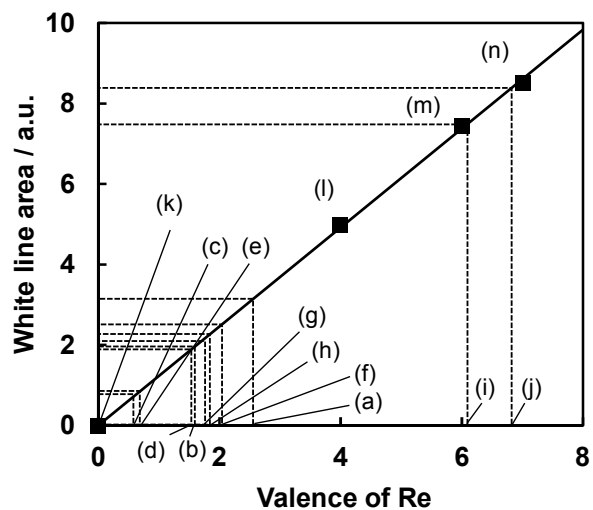


Figure S1. Relation between white line areas of Re L_3 -edge XANES spectra and valence of Re.

(a) Re(L, 413, Reaction) (Re = 14 wt%), (b) Re(G, 473) (Re = 14 wt%), (c) Re(G, 773) (Re = 14 wt%), (d) Re(G, 473, Reaction) (Re = 14 wt%), (e) Re(G, 773, Reaction) (Re = 14 wt%), (f) Re-Pd (L, 413, Reaction) (Re/Pd = 8), (g) Re-Pd(G, 473) (Re/Pd = 8), (h) Re-Pd(G, 473, Reaction) (Re/Pd = 8), (i) Re(Calcination), (j) Re-Pd(Calcination), (k) Re powder, (l) ReO_2 , (m) ReO_3 , (n) Re_2O_7 .

Table S2. The parameter of XRD fitting method

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)

Table S3. Effect of the reduction methods over Re-Pd catalysts reduced in liquid phase at 413 K in the STA hydrogenation.

Entry	Conversion / %	Selectivity / %				Conversion rate / mmol·g-Cat ⁻¹ ·h ⁻¹	TOF / h ⁻¹
		C ₁₈ H ₃₇ OH	C ₁₈ H ₃₈	C ₁₇ H ₃₆	Others		
1 ^a	54	96	2.8	0.5	0.3	4.5	6.2
2 ^b	46	97	2.5	0.2	0.3	3.9	5.3

Reaction conditions: 5 wt% STA solution 20 g (STA 1 g, 1,4-dioxane 19 g), Re-Pd(L, 413) (Re/Pd = 8) 100 mg, reaction temperature 413 K, H₂ pressure 8.0 MPa, reaction time 4 h, Others: CO₂, CH₄ and C₂H₆.

^a Standard procedure for Re-Pd(L, 413), and the catalyst was reduced during the reaction.

^b The catalyst was reduced in only the solvent (1,4-dioxane, 19 g) at 413 K. After cooling down to room temperature, the autoclave was opened in N₂ atmosphere and stearic acid (1 g) was added to the autoclave reactor, where all the procedures were carried out without exposure to air.

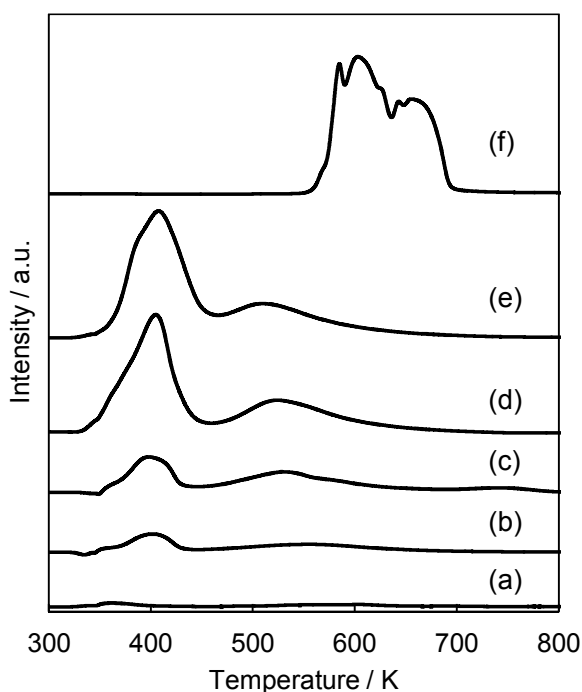


Figure S2. TPR profiles of the calcined Pd, Re and Re-Pd catalysts

(a) Pd(Calcination), (b) Re-Pd(Calcination) (Re/Pd = 2), (c) Re-Pd(Calcination) (Re/Pd = 4), (d) Re-Pd(Calcination) (Re/Pd = 8), (e) Re-Pd(Calcination) (Re/Pd = 12), (f) Re(Calcination).

Conditions: Catalyst 0.05 g, 5% H₂/Ar 30 mL/min, 10 K/min.

Experimental method for TPR

Temperature-programmed reduction (TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector using 5% H₂ diluted with Ar (30 mL/min). The amount of catalyst was 0.05 g, and the temperature was increased from room temperature to 1123 K at a heating rate of 10 K/min. Reduction degree of Re on Re-Pd catalyst was determined by using the consumed H₂ amount of Pd/SiO₂ catalyst (entry 1). In general, Pd metal species can be easily reduced at room temperature, and therefore the consumed amount of H₂ is lower than the total Pd amount.

Table S4. Results for TPR profiles of the calcined Pd, Re and Re-Pd catalysts.

Entry	Catalyst	Re/Pd	Loading amount		H ₂ consumption ^a		Reduction degree of Re ^b		Re valence ^c	
			/ mmol • g-Cat ⁻¹		/ mmol • g-Cat ⁻¹					
			Pd	Re	323-473 K	323-710 K	323-473 K	323-710 K	323-473 K	323-710 K
1	Pd(Calcination)	-	0.094	-	0.04 ^d	0.04 ^d	-	-	-	-
2	Re-Pd(Calcination)	2	0.094	0.19	0.19	0.38	0.26	0.54	5.2	3.2
3	Re-Pd(Calcination)	4	0.094	0.37	0.38	0.80	0.27	0.65	5.1	2.9
4	Re-Pd(Calcination)	8	0.094	0.75	1.2	1.9	0.46	0.69	3.8	2.1
5	Re-Pd(Calcination)	12	0.094	1.1	1.5	2.2	0.38	0.56	4.3	3.1
6	Re(Calcination)	-	0.094	0.75	0.0	2.3	0.0	0.86	7.0	1.0

^a H₂ consumption was estimated in the range of 323-473 or 323-710 K.

^b Reduction degree of Re = (H₂ consumption [mol] * 2 – H₂ consumption of Pd (entry 1) [mol]) / ((Re amount [mol]) * 7).

^c Re valence was calculated from H₂ consumption. Initial valence of Re before TPR is +7. Valence of Re after TPR is calculated by 7 – (H₂ consumption [mol] * 2) / (Re amount [mol]).

^d This amount is lower than the total amount of Pd, which is due to the reduction of Pd species at room temperature.

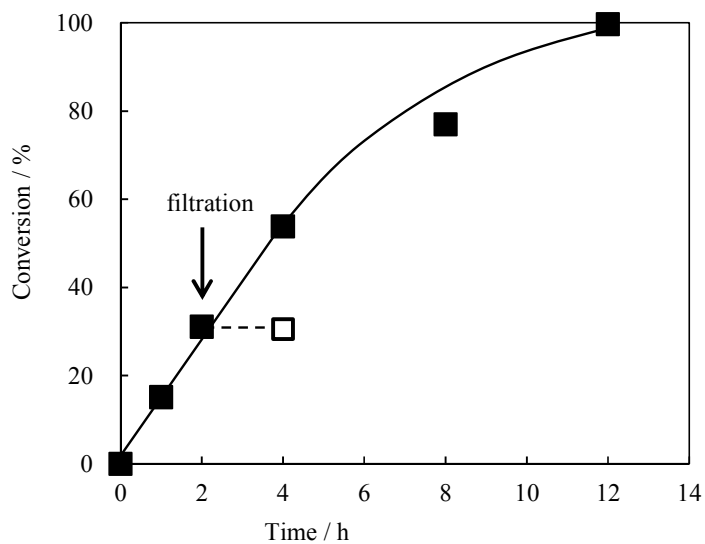
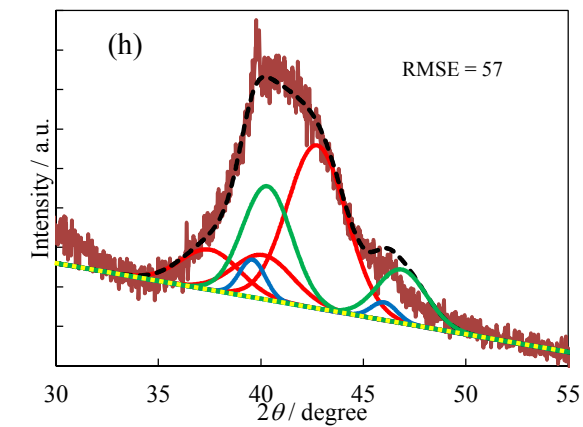
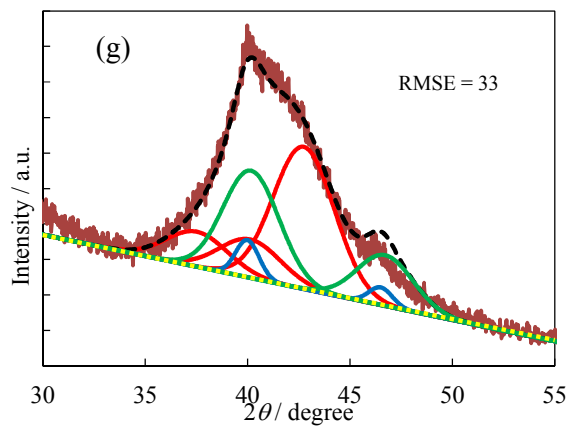
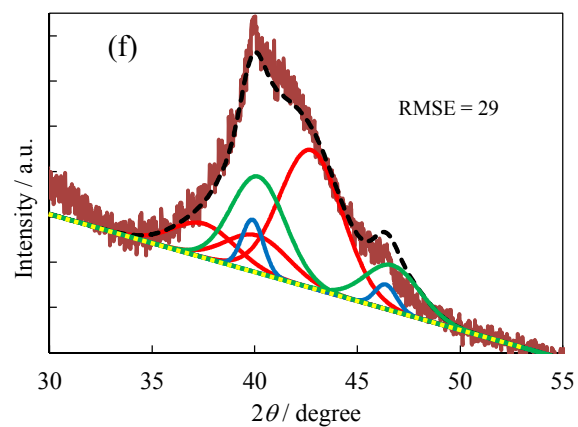
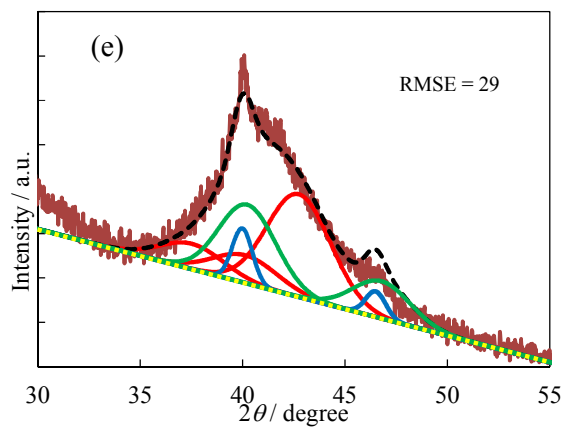
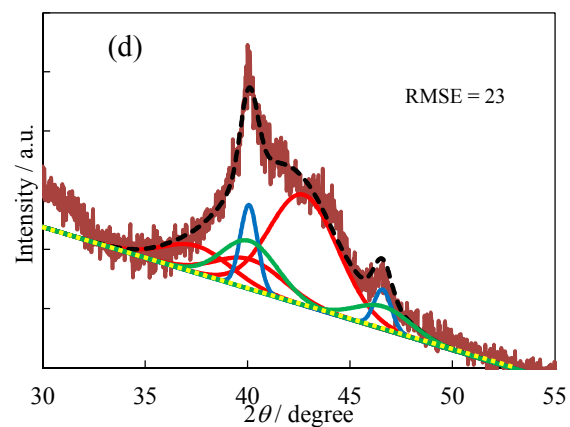
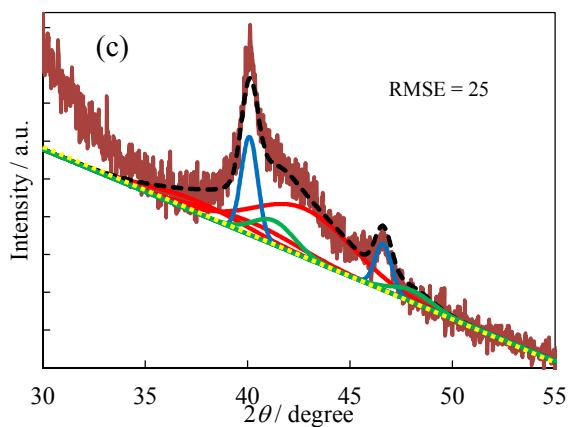
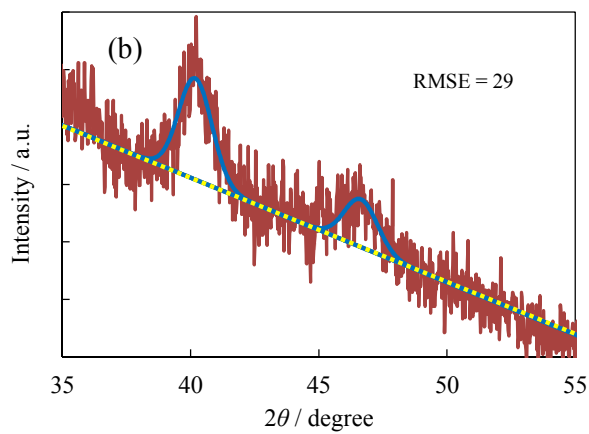
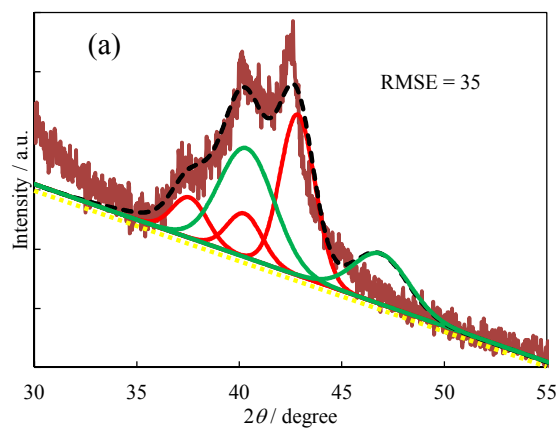


Figure S3. Activity tests of the STA hydrogenation using Re-Pd(L,413) (Re/Pd = 8) catalyst without or with the removal of the catalyst by filtration^a.

Reaction conditions: 5 wt% STA solution 20 g (STA 1 g, 1,4-dioxane 19 g), catalyst amount 100 mg, reaction temperature 413 K, H₂ pressure 8.0 MPa.

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

^a The catalyst was removed after 2 h reaction time by filtration



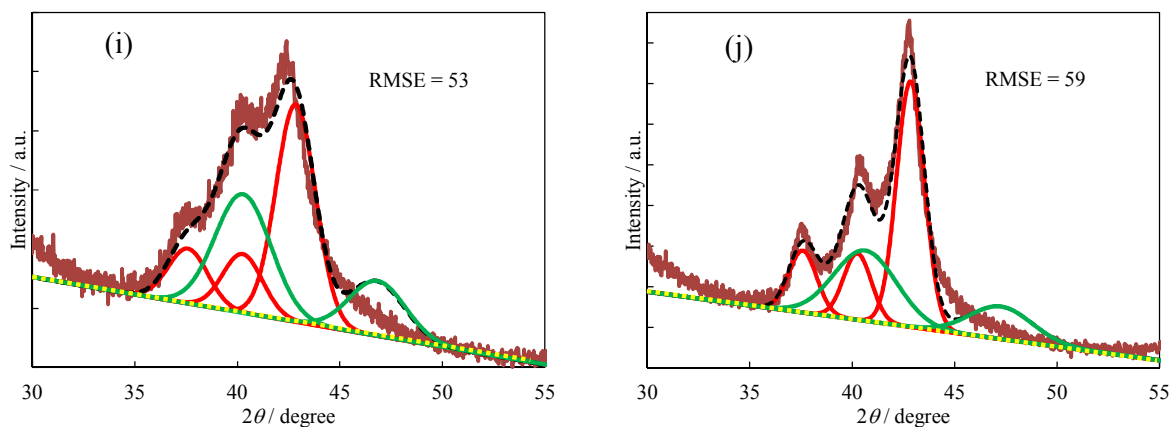


Figure S4. The fitting results of XRD peaks of Re, Pd and Re-Pd catalysts using Re(HCP), Re(FCC) and Pd metal species.

Brown line: raw data (Figure 1), 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(L, 413, Reaction) (Re = 14 wt%), (b) Pd(L, 413, Reaction) (Pd = 1 wt%), (c) Re-Pd (L, 413, Reaction) (Re/Pd = 2), (d) Re-Pd (L, 413, Reaction) (Re/Pd = 4), (e) Re-Pd (L, 413, Reaction) (Re/Pd = 6), (f) Re-Pd (L, 413, Reaction) (Re/Pd = 8), (g) Re-Pd (L, 413, Reaction) (Re/Pd = 12), (h) Re-Pd(G, 473) (Re/Pd = 8), (i) Re (G, 473) (Re = 14 wt%), (j) Re (G, 773) (Re = 14 wt%).

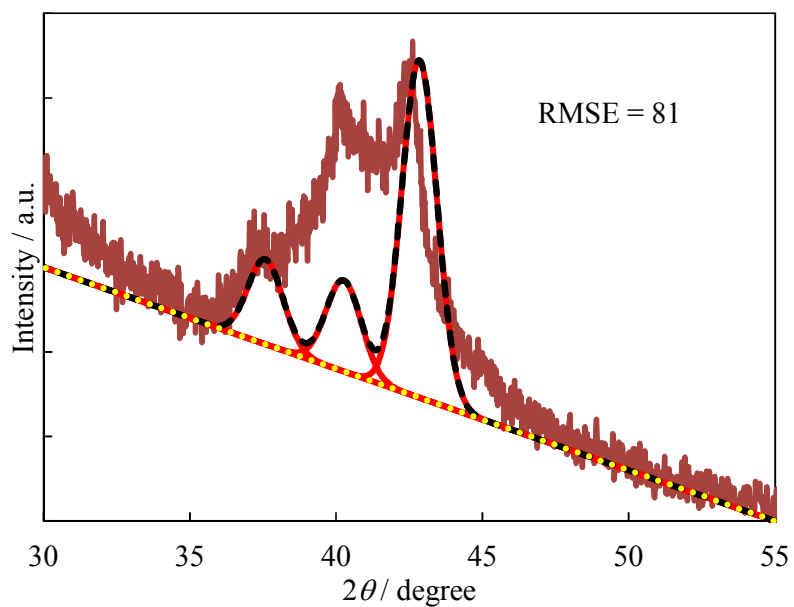


Figure S5. A fitting result of XRD peaks of Re (L, 413, Reaction) (Re=14 wt%) using Re(HCP) metal species.

Brown line: raw data (Figure 1 (g)), yellow dotted line: background, red line: Re(HCP), black dotted line: the result of curve fitting. Fitting range: $2\theta = 35 - 55^\circ$.

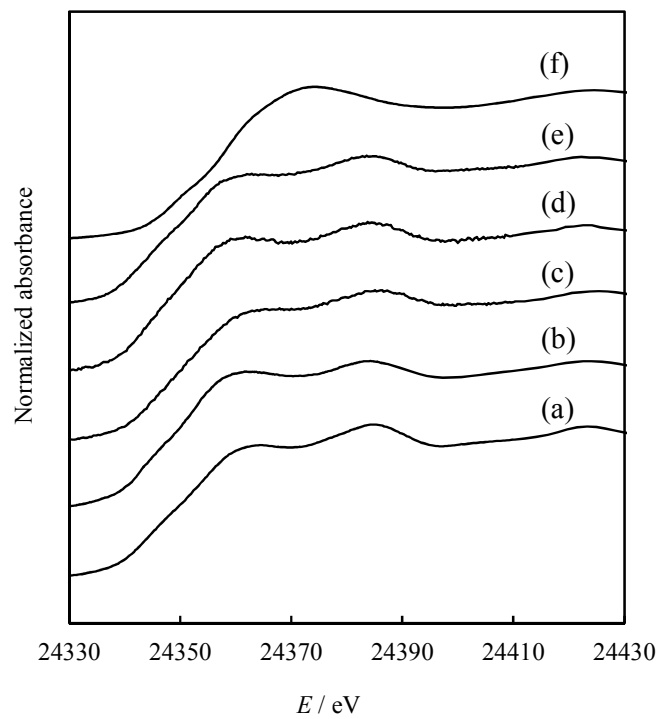


Figure S6. Pd *K*-edge XANES spectra of Pd and Re-Pd catalysts after the reaction or reduction.

(a) Pd foil, (b) Pd(L, 413, Reaction), (c) Re-Pd(L, 413, Reaction) (Re/Pd = 8), (d) Re-Pd(G, 473) (Re/Pd = 8), (e) Re-Pd(G, 473, Reaction) (Re/Pd = 8), (f) PdO.

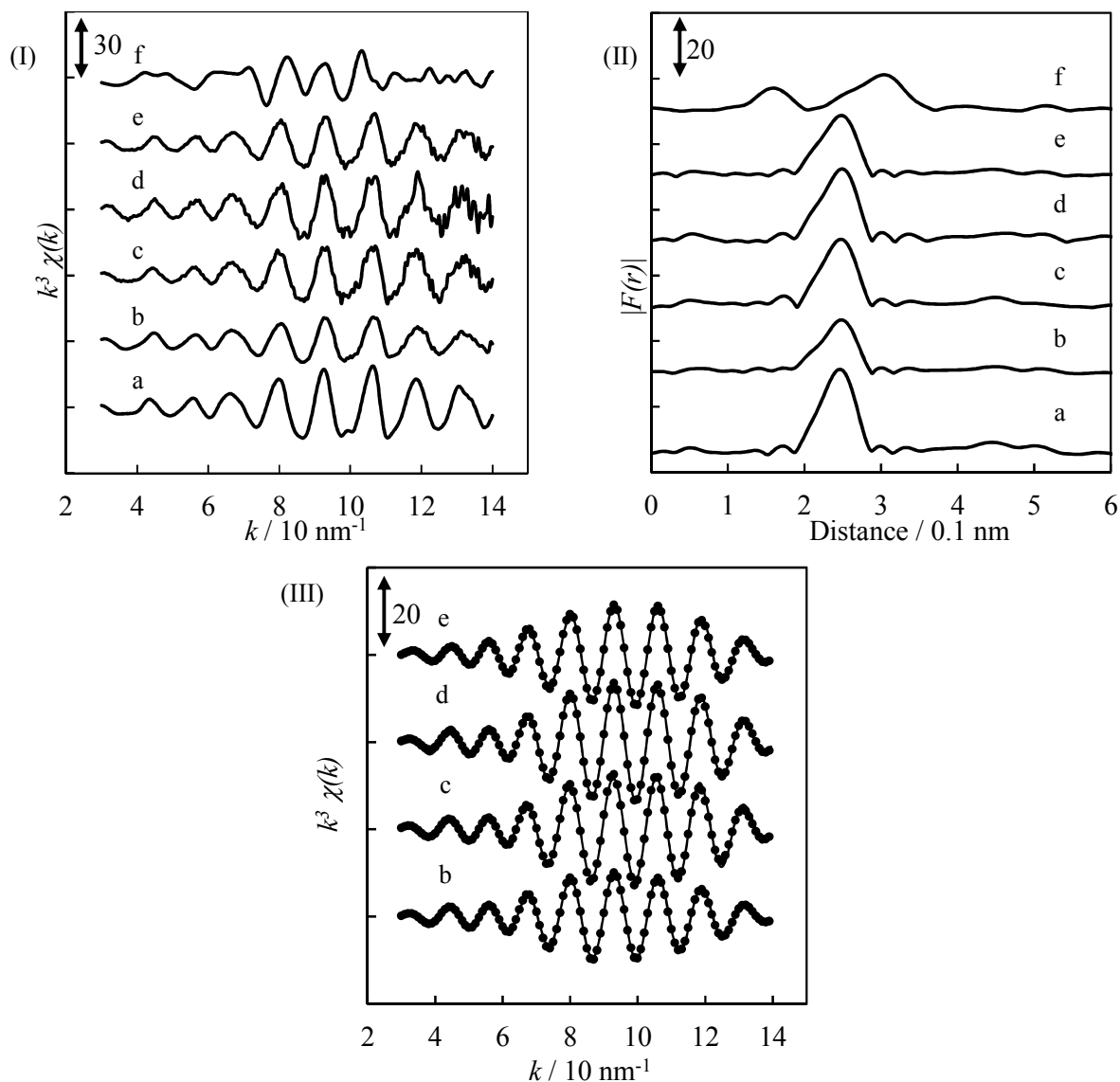


Figure S7. Results of Pd *K*-edge EXAFS analysis of Pd and Re-Pd (Re/Pd = 8) catalysts after reaction and flow reduction.

(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) Pd(L, 413, Reaction), (c) Re-Pd(L, 413, Reaction) (Re/Pd = 8), (d) Re-Pd(G, 473) (Re/Pd = 8), (e) Re-Pd(G, 473, Reaction) (Re/Pd = 8), (f) PdO.

Table S5 Curve fitting results for the Pd *K*-edge EXAFS analysis of Pd and Re-Pd (Re/Pd = 8) catalysts after the reaction and H₂ reduction treatment^a.

Entry	Catalyst	Re/Pd	Shells	CN ^b	$R / 10^{-1} \text{ nm}^c$	$\sigma / 10^{-1} \text{ nm}^d$	$\Delta E_0 / \text{eV}^e$	$R_f / \%^f$
	PdO		Pd-O	4	2.02	0.060	0.0	
1 ^g	Pd(L, 413, Reaction) ^h		Pd-Pd	11.3	2.74	0.076	2.5	0.4
2 ^g	Re-Pd(L, 413, Reaction) ⁱ	8	Pd-Pd	11.7	2.76	0.067	2.8	1.0
3 ^j	Re-Pd(G, 473) ⁱ	8	Pd-Pd	11.7	2.75	0.065	3.3	0.4
4 ^{g, j}	Re-Pd(G, 473, Reaction) ⁱ	8	Pd-Pd	11.6	2.75	0.071	3.3	0.4
	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 Pd = 1 wt%.ⁱ Re: 14 wt%, Pd = 1 wt%.^j Reduction conditions: 100% H₂ 30 mL/min, time 1 h.

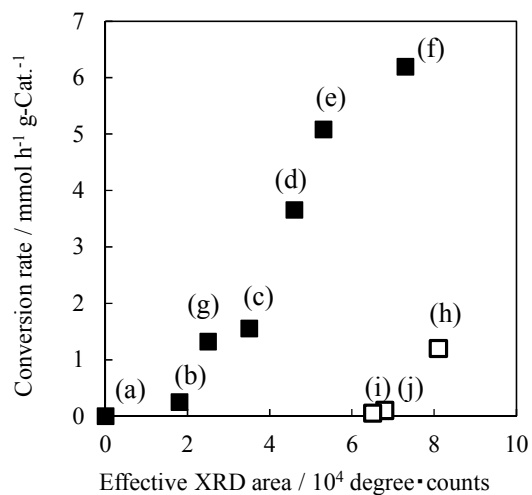


Figure S8. Conversion rate of STA hydrogenation as a function of effective XRD area of Pd, Re-Pd and Re catalysts.

(a) Pd(L, 413, Reaction), (b) Re-Pd(L, 413, Reaction) (Re/Pd = 2). (c) Re-Pd(L, 413, Reaction) (Re/Pd = 4), (d) Re-Pd(L, 413, Reaction) (Re/Pd = 6), (e) Re-Pd(L, 413, Reaction) (Re/Pd = 8), (f) Re-Pd(L, 413, Reaction) (Re/Pd = 12), (g) Re(L, 413, Reaction), (h) Re-Pd(G, 473) (Re/Pd = 8), (i) Re(G, 473), (j) Re(G, 473).

Effective XRD area = XRD area \times Re dispersion (Figure 1, Table 4).

Conversion rate is based on Table 1 and 2.

Table S6 Effect of STA concentration in the hydrogenation of STA over Re-Pd(L, 413) (Re/Pd = 8) and Re(L, 413) catalysts.

Entry	Catalyst	Cat. amount / g	STA / g	1,4-dioxane / g	Initial STA conc. / wt%	Time / h	Conv. / %	Selectivity / %				Conversion rate / mmol • g-Cat ⁻¹ • h ⁻¹
								C ₁₈ H ₃₇ OH	C ₁₈ H ₃₈	C ₁₇ H ₃₆	Others	
1	Re-Pd(L, 413)	0.060	0.60	19	3	2	25	96	3.1	0.7	0.5	4.3
2	$\left(\begin{array}{l} \text{Re/Pd} = 8 \\ \text{Re} = 14 \text{ wt\%} \\ \text{Pd} = 1 \text{ wt\%} \end{array} \right)$	0.10	1.0	19	5	2	29	97	2.4	0.6	0.2	5.2
3		0.10	1.0	13	7	2	28	97	2.3	0.5	0.4	5.0
4		0.10	1.0	9.0	10	2	31	96	2.9	0.6	0.3	5.5
5		0.10	1.0	5.7	15	2	29	97	2.0	0.5	0.2	5.1
6	Re(L, 413)	0.061	0.61	20	3	4	8.6	91	4.7	1.4	3.1	0.8
7	(Re = 14 wt%)	0.10	1.0	19	5	4	15	92	3.9	0.9	2.8	1.3
8		0.10	1.0	13	7	4	19	94	3.5	0.7	1.5	1.6
9		0.10	1.0	9.0	10	4	23	95	3.6	0.8	0.8	2.1
10		0.10	1.0	5.7	15	4	30	96	2.8	0.5	0.4	2.8

Reaction conditions: 3~15 wt% STA solution, 1,4-dioxane solvent 5.7-20 g, STA 0.60-1.0 g, catalyst 0.060-0.10 g, reaction temperature 413 K, H₂ pressure 8.0 MPa, Others: CO₂, CH₄ and C₂H₆.

Table S7 The calculation result for reaction order with respect to initial STA concentration over Re-Pd(L, 413) catalysts.

Entry	Run time	Calculated initial conversion rate / mmol • g-Cat ⁻¹ • h ⁻¹					Calculated reaction order	Figure S9
		(3 wt%) ^a	(5 wt%) ^a	(7 wt%) ^a	(10 wt%) ^a	(15 wt%) ^a		
1	1st (zero order assumption)	4.4	5.3	5.0	5.5	5.1	0.087	(a)
2	2nd (+0.087 order assumption)	4.4	5.2	5.1	5.6	5.1	0.097	(b)
3	3rd (+0.097 order assumption)	4.4	5.2	5.1	5.6	5.1	0.097	(c)

Reaction conditions: 3~15 wt% STA solution, 1,4-dioxane solvent 5.7-20 g, STA 0.60-1.0 g, catalyst 0.060-0.10 g, reaction temperature 413 K, H₂ pressure 8.0 MPa.

^a STA concentration

Calculation method for reaction order:

- (1) The reaction order was decided from the slope of double logarithmic plot for conversion rate vs initial STA concentration by using least-square approach, where the conversion rate was calculated assuming the zero reaction order (the slope obtained from the data at the specific reaction time and the origin) (entry 1).
- (2) The reaction rate constant in this reaction order was evaluated from each data point at the specific reaction time and concentration, and the initial conversion rate was estimated again from the rate constant (entry 2).
- (3) The calculations of (1) and (2) were repeated until the reaction order converged (entries 2-4).

Table S8 The calculation result for reaction order with respect to initial STA concentration over Re(L, 413) catalysts.

Entry	Run time	Calculated initial conversion rate / mmol • g-Cat ⁻¹ • h ⁻¹					Calculated reaction order	Figure S10
		(3 wt%) ^a	(5 wt%) ^a	(7 wt%) ^a	(10 wt%) ^a	(15 wt%) ^a		
1	1st (zero order assumption)	0.75	1.3	1.6	2.1	2.8	0.74	(a)
2	2nd (+0.79 order assumption)	0.79	1.4	1.8	2.3	3.0	0.82	(b)
3	3rd (+0.82 order assumption)	0.79	1.4	1.8	2.3	3.1	0.83	(c)
4	4th (+0.83 order assumption)	0.79	1.4	1.8	2.3	3.1	0.83	(d)

Reaction conditions: 3~15 wt% STA solution, 1,4-dioxane solvent 5.7-20 g, STA 0.60-1.0 g, catalyst 0.060-0.10 g, reaction temperature 413 K, H₂ pressure 8.0 MPa.

^a STA concentration

Calculation method for reaction order:

- (1) The reaction order was decided from the slope of double logarithmic plot for conversion rate vs initial STA concentration by using least-square approach, where the conversion rate was calculated assuming the zero reaction order (the slope obtained from the data at the specific reaction time and the origin) (entry 1).
- (2) The reaction rate constant in this reaction order was evaluated from each data point at the specific reaction time and concentration, and the initial conversion rate was estimated again from the rate constant (entry 2).
- (3) The calculations of (1) and (2) were repeated until the reaction order converged (entries 2-4).

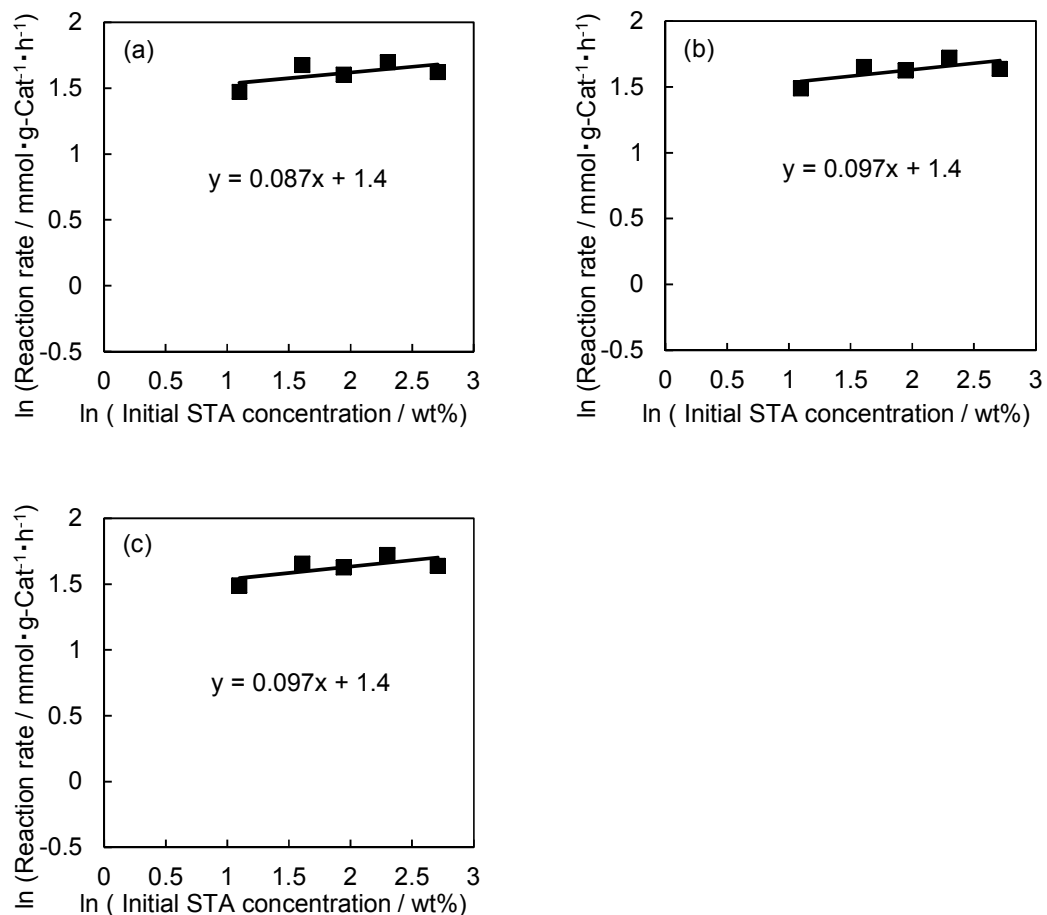


Figure S9. The comparison of reaction orders with respect to the initial STA concentration over Re-Pd(L, 413) catalysts.

Reaction conditions: 3~15 wt% STA solution, 1,4-dioxane solvent 5.7-20 g, STA 0.60-1.0 g, catalyst 0.060-0.10 g, reaction temperature 413 K, H₂ pressure 8.0 MPa.

(a) zero order assumption (Table S7, entry 1), (b) +0.093 order assumption (Table S7, entry 2), (c) +0.094 order assumption (Table S7, entry 3).

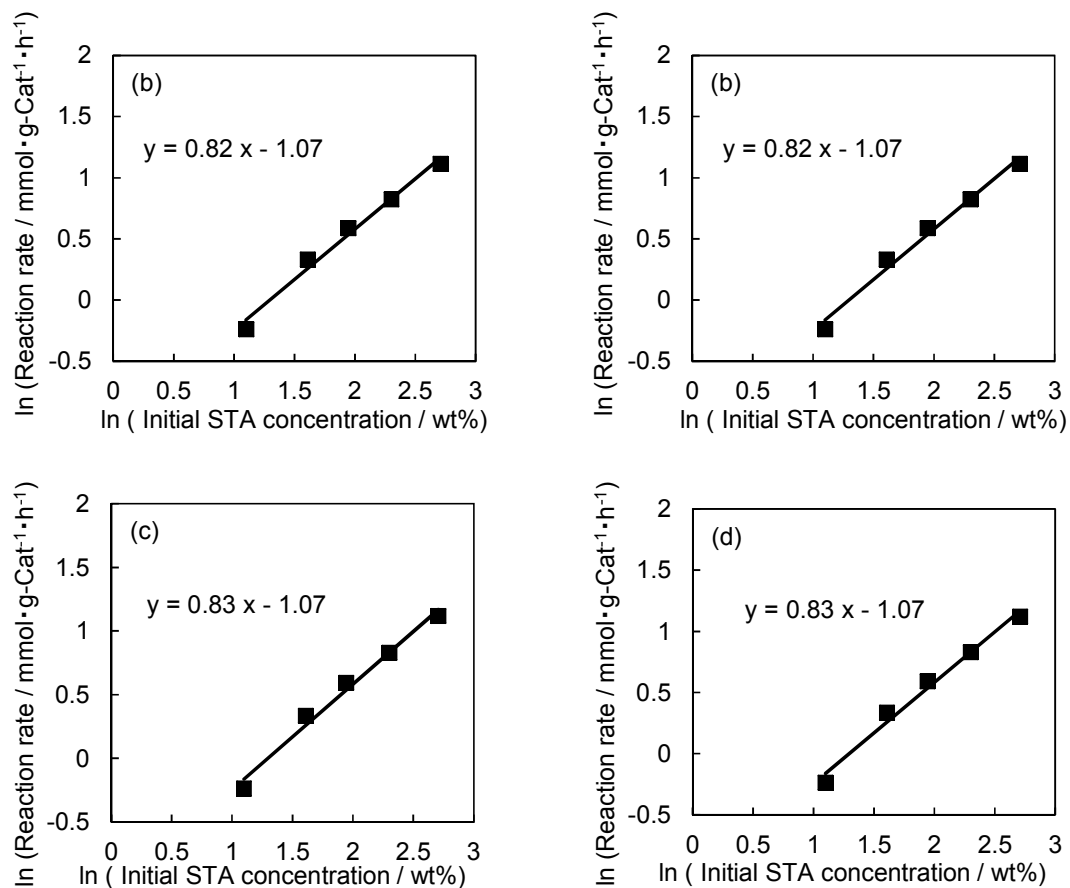


Figure S10. The comparison of reaction orders with respect to the initial STA concentration over Re(L, 413) catalysts.

Reaction conditions: 3~15 wt% STA solution, 1,4-dioxane solvent 5.7-20 g, STA 0.60-1.0 g, catalyst 0.060-0.10 g, reaction temperature 413 K, H_2 pressure 8.0 MPa.

(a) zero order assumption (Table S8, entry 1), (b) +0.74 order assumption (Table S8, entry 2), (c) +0.82 order assumption (Table S8, entry 3), (d) +0.83 order assumption (Table S8, entry 4).

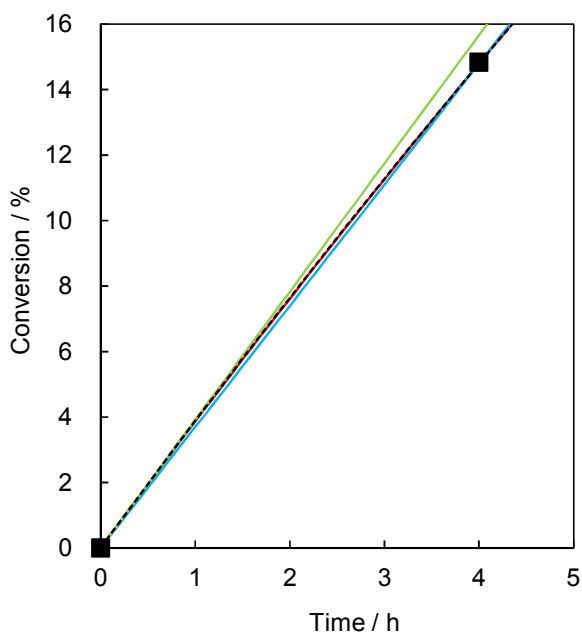


Figure S10. Time dependence for hydrogenation of STA over Re(L, 413) and the determination of the initial reaction rate.

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

■: conversion; blue line: zero order line for STA concentration; red line: 0.74 order line for STA concentration; green line: tangent line for red line at origin; black broken line: the converged order line (0.83) for STA concentration.

Table S9 Effect of H₂ pressure in the hydrogenation of STA over Re-Pd(L, 413) (Re/Pd = 8) and Re(L, 413) catalysts.

Entry	Catalyst	H ₂ pressure	Time	Conversion	Selectivity / %				Conversion rate
		/ MPa	/ h	/ %	C ₁₈ H ₃₇ OH	C ₁₈ H ₃₈	C ₁₇ H ₃₆	Others	/ mmol•g-Cat ⁻¹ •h ⁻¹
1	Re-Pd(L, 413)	1	8	16	97	2.0	0.6	0.5	0.7
2	$\left(\begin{array}{l} \text{Re/Pd} = 8 \\ \text{Re} = 14 \text{ wt\%} \\ \text{Pd} = 1 \text{ wt\%} \end{array} \right)$	2	4	7.5	95	2.2	1.4	1.0	0.7
3		4	4	18	96	2.4	0.7	0.6	1.6
4		6	4	31	96	2.6	0.6	0.5	2.7
5		8	2	29	97	2.4	0.6	0.2	5.2
6	Re(L, 413)	1	16	11	93	2.8	0.8	3.1	0.2
7	(Re = 14 wt%)	2	8	8.6	90	3.0	1.1	5.9	0.2
8		4	8	11	93	3.9	1.2	2.2	0.5
9		6	8	14	93	4.0	1.0	1.6	0.6
10		8	8	24	92	5.0	0.9	2.2	1.0

Reaction conditions: 5 wt% STA solution 20 g (STA 1 g, 1,4-dioxane 19 g), catalyst amount 0.1 g, reaction temperature 413 K, Others: CO₂, CH₄ and C₂H₆.