Supporting Information

Hydrodeoxygenation of ethyl stearate over Re-promoted Ru/TiO_2 catalyst: Rate enhancement and selectivity control by the addition of Re

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Table S1 Results of hydrodeoxygenation of ethyl stearate on various Re-modified Ru(1)/TiO_2 catalysts at low conversion levels

Entry	Catalyst	Time (min)	Conversion (%)	Selectivity (%) [a]			Carbon balance [b] (%)	Reaction rate [c] (mol min^{-1} g_{cat}^{-1})
				$C_{18}H_{37}OH$	*n*-$C_{17}H_{36}$	*n*-$C_{18}H_{38}$		
1	Ru(1)	60	19.3	26.4	28.7	16.9	72.0	53.6
2	Ru(1)Re(0.5)	45	20.3	35.0	22.6	23.6	81.2	75.2
3	Ru(1)Re(1)	30	25.5	30.6	22.0	30.7	83.3	142
4	Ru(1)Re(2)	20	22.6	41.4	17.9	31.6	90.9	188
5	Ru(1)Re(5)	20	24.0	55.7	12.8	30.2	98.7	200
6	Ru(1)Re(10)	10	24.8	38.2	15.7	32.3	86.2	413
7	Ru(1)Re(15)	5	16.6	38.5	21.3	36.3	96.1	553
8	Re(10)	120	18.6	34.0	0.6	3.4	38.0	25.8

Reaction conditions: 1 mmol ethyl stearate, 60 mg catalyst (reduced at 300 °C), 10 mL hexane, 3 MPa H_2, 220 °C.

a. Small amounts of other alkane products of *n*-$C_{15}H_{32}$ and *n*-$C_{16}H_{34}$ were detected to form.

b. The amount of $C_{18}H_{37}OH$, *n*-$C_{17}H_{36}$, *n*-$C_{18}H_{38}$ against the amount of ethyl stearate consumed. A deviation from 100% carbon balance may be due to the undesired consumption of the substrate of ethyl stearate via transesterification with a product of 1-octadecanol producing a larger molecule that cannot be detected by the present GC analysis.

c. Amount of ethyl stearate consumed per 1 min per 1 g catalyst.

Table S2 Hydrodeoxygenation of ethyl stearate on Ru(1)Re(10)/TiO_2 catalyst reduced at different temperatures

Temperature (ºC)	Conversion (%)	Selectivity (%) [a]			C_{18}/C_{17} [b]
		$C_{18}H_{37}OH$	*n*-$C_{17}H_{36}$	*n*-$C_{18}H_{38}$	
200	98.5	n.d.	23.0	62.0	2.7
300	99.9	n.d.	22.2	69.7	3.2
400	96.4	5.6	27.4	64.2	2.3

Reaction conditions:1 mmol ethyl stearate, 60 mg catalyst, 10 mL hexane, 3 MPa H_2, 220 °C, 2 h.

a. Small amounts of other alkane products of *n*-$C_{15}H_{32}$ and *n*-$C_{16}H_{34}$ were detected to form. “n.d.” indicates “not detected”.

b. *n*-$C_{18}H_{38}$/ *n*-$C_{17}H_{36}$

Table S3 Results of hydrodeoxygenation of ethyl stearate on different catalysts

Entry	Catalyst	Conversion (%)	Selectivity (%) [a]		
			$C_{18}H_{37}OH$	*n*-$C_{17}H_{36}$	*n*-$C_{18}H_{38}$
1	5%Ru/C[b]	14.0	n.d.	99.0	n.d.
2	5%Ru/Al_2O_3[b]	95.0	n.d.	93.5	1.6
3	Ru(1)Re(10)/TiO_2	99.9	n.d.	22.2	69.7

Reaction conditions: 1 mmol ethyl stearate, 60 mg catalyst, 10 mL *n*-hexane, 3 MPa H_2, 220 °C.

a. Small amounts of other alkane products of *n*-$C_{15}H_{32}$ and *n*-$C_{16}H_{34}$ were detected to form. "n.d." indicates "not detected".

b. The commercial Ru/C and Ru/Al_2O_3 were obtained from Wako Co. Ltd. The Ru content was 5 wt%.

Table S4 Hydrodeoxygenation of a possible intermediate of 1-octadecanol ($C_{18}H_{37}OH$) on various catalysts at low conversion levels

Catalyst	Conversion (%)	Selectivity (%)[a]		C_{18}/C_{17} [b]
		n-$C_{17}H_{36}$	*n*-$C_{18}H_{38}$	
Ru(1)Re(1)	35.7	34.1	57.9	1.70
Ru(1)Re(2)	72.6	26.5	65.2	2.46
Ru(1)Re (10)	83.2	18.7	74.4	3.99

Reaction conditions: 2 mmol 1-octadecanol, 30 mg catalyst (reduced at 300 °C), 10 mL hexane, 3 MPa H_2, 0.5 h, 220 °C.

a. Some minor amount of other productions ($C_{15}H_{32}$ and $C_{16}H_{34}$) were detected.

b. *n*-$C_{18}H_{38}$/ *n*-$C_{17}H_{36}$

Table S5 Hydrodeoxygenation of a possible intermediate of stearic acid ($C_{18}H_{35}COOH$) on the selected catalysts

Entry	Catalyst	time (h)	Conversion (%)	Selectivity (%)[a]			C_{18}/C_{17} [b]
				$C_{18}H_{37}OH$	*n*-$C_{17}H_{36}$	*n*-$C_{18}H_{38}$	
1	Ru(1)	2	59.6	33.7	17.9	5.4	0.30
2	Ru(1)Re(10)	0.5	93.6	63.4	9.5	13.9	1.46
3	Ru(1)Re(10)	2	99.9	n.d.	27.3	52.7	1.93

Reaction conditions: 1 mmol Stearic acid, 60 mg catalyst (reduced at 300 °C),10 mL hexane, 3 MPa H_2, 220 °C.

a. Some minor amount of other productions ($C_{15}H_{32}$ and $C_{16}H_{34}$) were detected.

b. *n*-$C_{18}H_{38}$/ *n*-$C_{17}H_{36}$

Table S6 Results of hydrodeoxygenation of ethyl stearate over Ru(1)Re(10)/TiO_2 catalyst

Entry	Catalyst (mg)	Conversion (%)	Selectivity (%)[b]			n-$C_{18}H_{38}$/ n-$C_{17}H_{36}$
			$C_{18}H_{37}OH$	n-$C_{17}H_{36}$	n-$C_{18}H_{38}$	
1	30	45.4	22.3	22.9	54.5	2.38
2	45	65.7	18.0	24.4	55.3	2.13
3	60	99.9	n.d	22.2	69.7	3.15

Reaction conditions: 1 mmol ethyl stearate, Ru(1)Re(10)/TiO_2 (reduced at 300 °C), 10 mL hexane, 3 MPa H_2, 220 °C, 2 h.

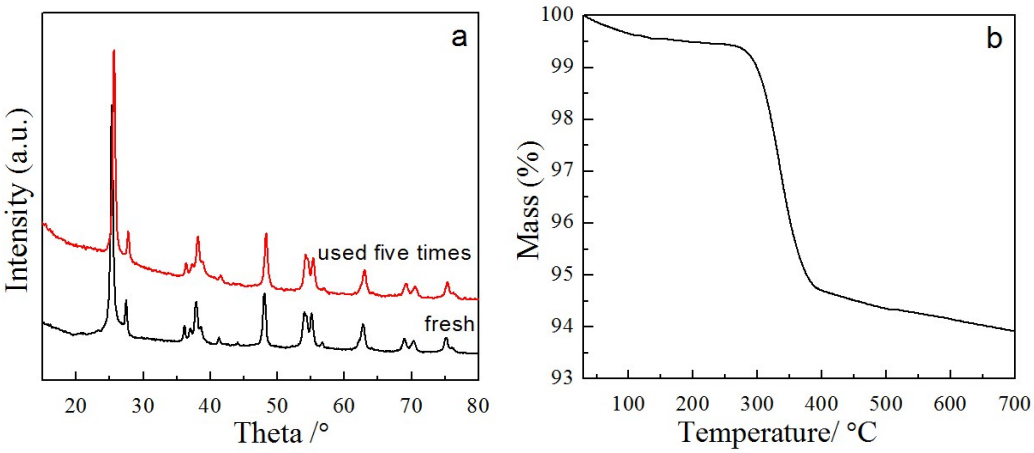

Fig. S1 (a) XRD patterns of fresh and used catalysts and (b) TGA of Ru(1)Re(10)/TiO_2 used five times.

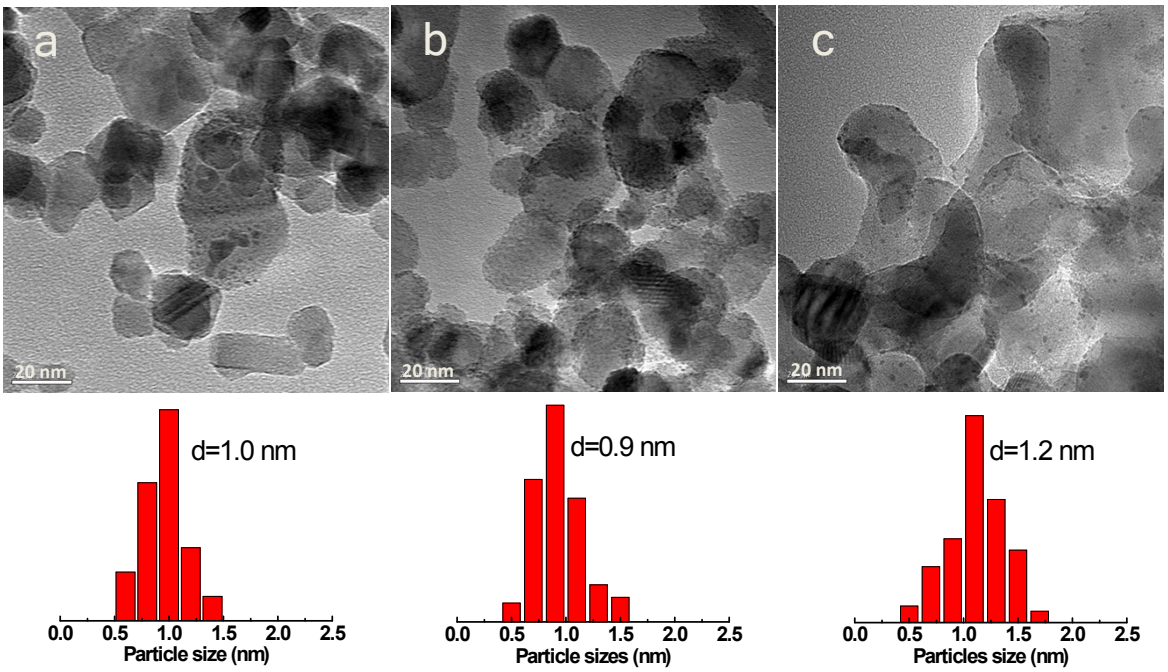

Fig. S2 TEM images and histograms of metal particle size distribution of (a) Ru(1)/TiO_2, (b) Re(10)/TiO_2 and (c) Ru(1)Re(10)/TiO_2 catalysts reduced at 300 °C.

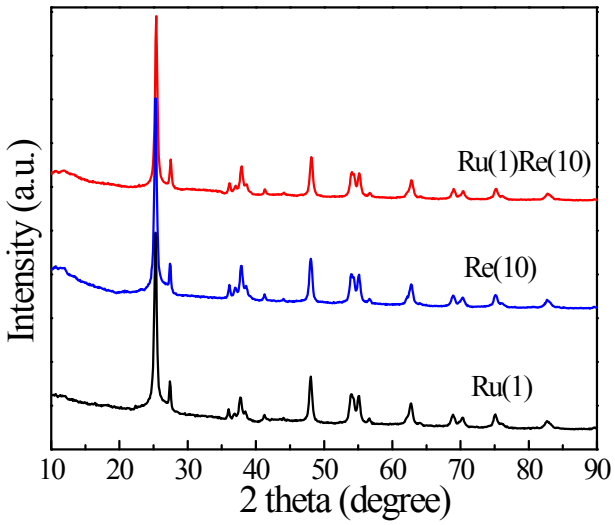

Fig. S3 XRD patterns of Ru(1)/TiO_2, Re(10)/TiO_2 and Ru(1)Re(10)/TiO_2 catalysts reduced at 300 °C.

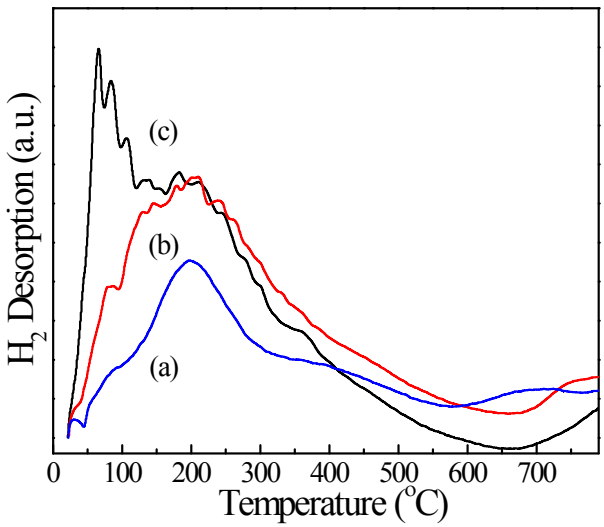

Fig. S4 H_2-TPD results of (a) Ru(1)/TiO_2, (b) Re(10)/TiO_2 and (c) Ru(1)Re(10)/TiO_2 catalysts.

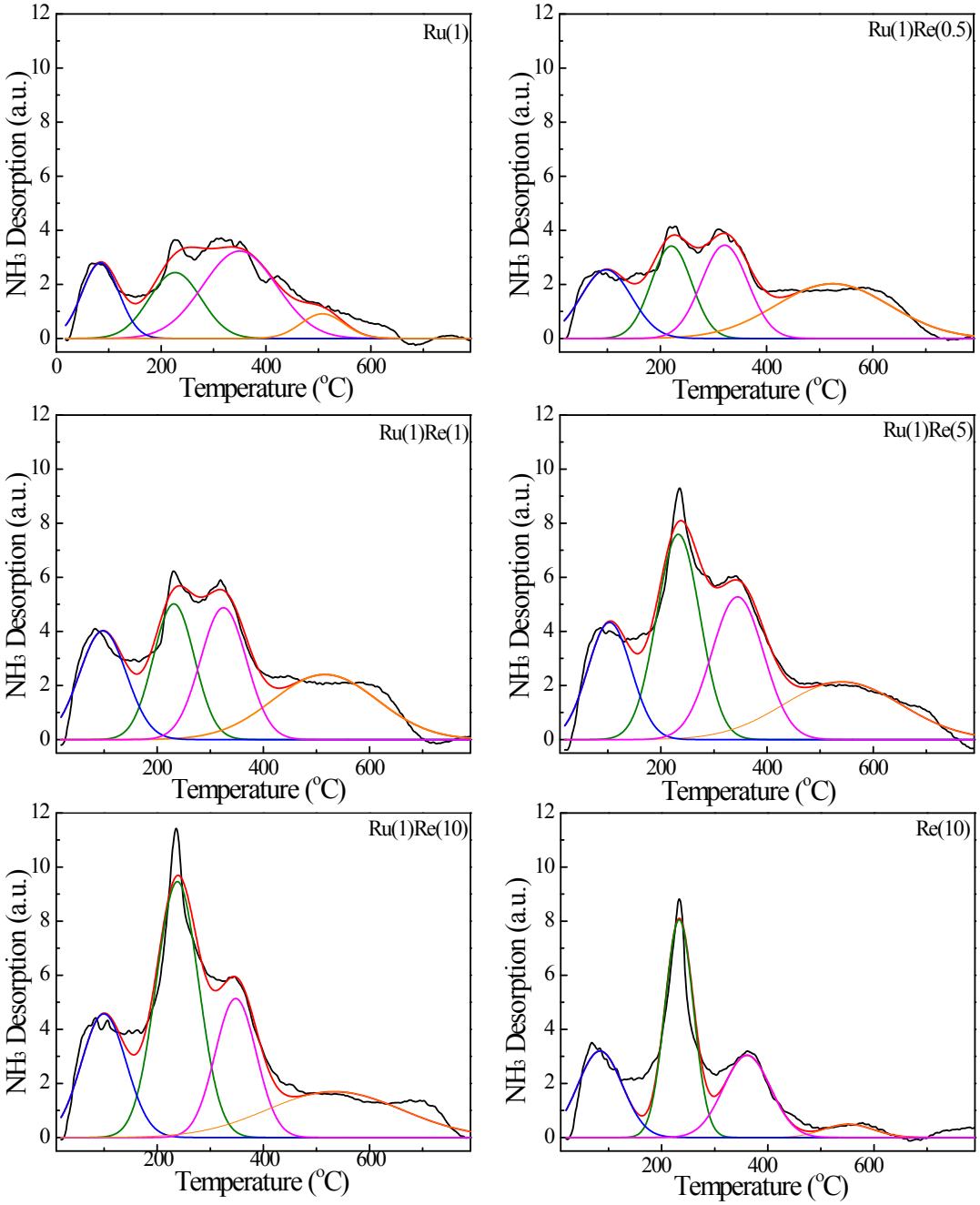

Fig. S5 NH_3-TPD profiles of TiO_2-supported catalysts. Each TPD desorption profile is divided into four regions depending on desorption temperatures.