Selective hydrogenolysis of bio-renewable tetrahydrofurfurylamine to piperidine on ReO_x-modified Rh catalysts

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ReO_x/SiO_2 (2 wt% Rh, 1.4 wt% Re).

Fig. S5 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for (a) Ir-ReO_x/SiO_2 (2 wt% Ir, 2.2 wt% Re), (b) Pd-ReO_x/SiO_2 (2 wt% Pd, 2.2 wt% Re) and (c) Pt-ReO_x/SiO_2 (2 wt% Pt, 2.2 wt% Re).

Fig. S6 FT-IR spectrum of pyridine adsorbed at 250 ^{o}C on Rh-ReO_x/SiO_2 (2 wt% Rh, 2.2 wt% Re).

Fig. S7 Conversion and selectivity in THFAM conversion to piperidine on Rh-ReO_x/SiO_2 (2 wt% Rh, 1.4 wt% Re) for four reaction cycles. Reaction conditions: 1 mmol THFAM, 1 mmol HCl, 0.1 g catalyst, 10 mL H_2O, 2.0 MPa H_2, 200 ^{o}C, 3 h.

Fig. S8 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for the spent Rh-ReO_x/SiO_2 (2 wt% Rh, 1.4 wt% Re) catalyst.

Table S1 Turnover rate and selectivity in 5-amino-1-pentanol (APO) amination on various supported catalysts.

General procedure for synthesis of N,N,N-trimethyl-1-(tetrahydrofuran-2-yl)methanaminium chloride. N,N,N-Trimethyl-1-(tetrahydrofuran-2-yl)methanaminium chloride (TMTHFAM) was synthesized by treatment of THFAM with iodomethane in ethanol. Iodomethane (4.00×10^{-2} mol) was added to an ethanol solution (20 mL) of THFAM (1.00×10^{-2} mol) and sodium bicarbonate (3.00×10^{-2} mol) with vigorous stirring at 25 ^{o}C. After reaction at 25 ^{o}C for 12 h, the resulting precipitate N,N,N-trimethyl-1-(tetrahydrofuran-2-yl)methanaminium iodide was collected by filtration, washing with diethyl ether and drying at 60 ^{o}C and ambient atmosphere. Afterward, N,N,N-trimethyl-1-(tetrahydrofuran-2-yl)methanaminium iodide was exchanged with 5.0 g Amberlite IRA402-Cl three times in water at 25 ^{o}C for 12 h. The reaction mixture was filtrated and the filtrate of TMTHFAM was evaporated to dryness at 65 ^{o}C under vacuum. The resulting powder TMTHFAM was dried in a vacuum at 60 ^{o}C.

^{1}H and ^{13}C NMR data for N,N,N-trimethyl-1-(tetrahydrofuran-2-yl)methanaminium chloride: ^{1}H NMR (600 MHz, Deuterium Oxide) δ 4.48 (dt, J = 11.5, 5.7 Hz, 1H), 3.93 – 3.80 (m, 2H), 3.50 – 3.42 (m, 2H), 3.18 (s, 9H), 2.23 – 2.13 (m, 1H), 1.99 – 1.83 (m, 2H), 1.60 (dq, J = 12.7, 8.0 Hz, 1H); ^{13}C NMR (151 MHz, Deuterium Oxide) δ 72.93, 69.38, 69.36, 69.34, 68.83, 54.11, 54.09, 54.06, 29.97, 24.49.

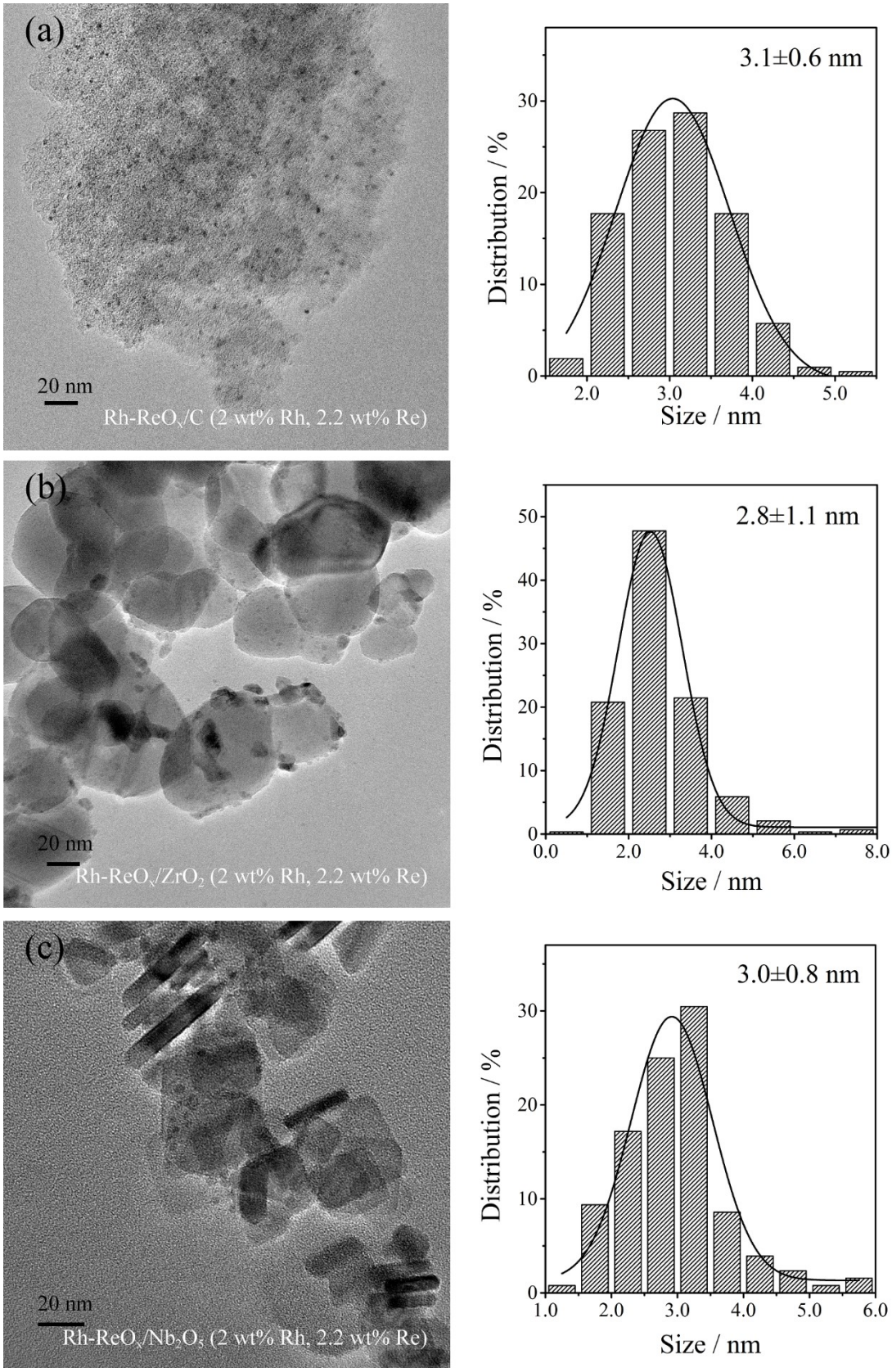


Fig. S1 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for (a) Rh-ReO_x/C (2 wt% Rh, 2.2 wt% Re), (b) Rh-ReO_x/ZrO_2 (2 wt% Rh, 2.2 wt% Re) and (c) Rh-ReO_x/Nb_2O_5 (2 wt% Rh, 2.2 wt% Re).

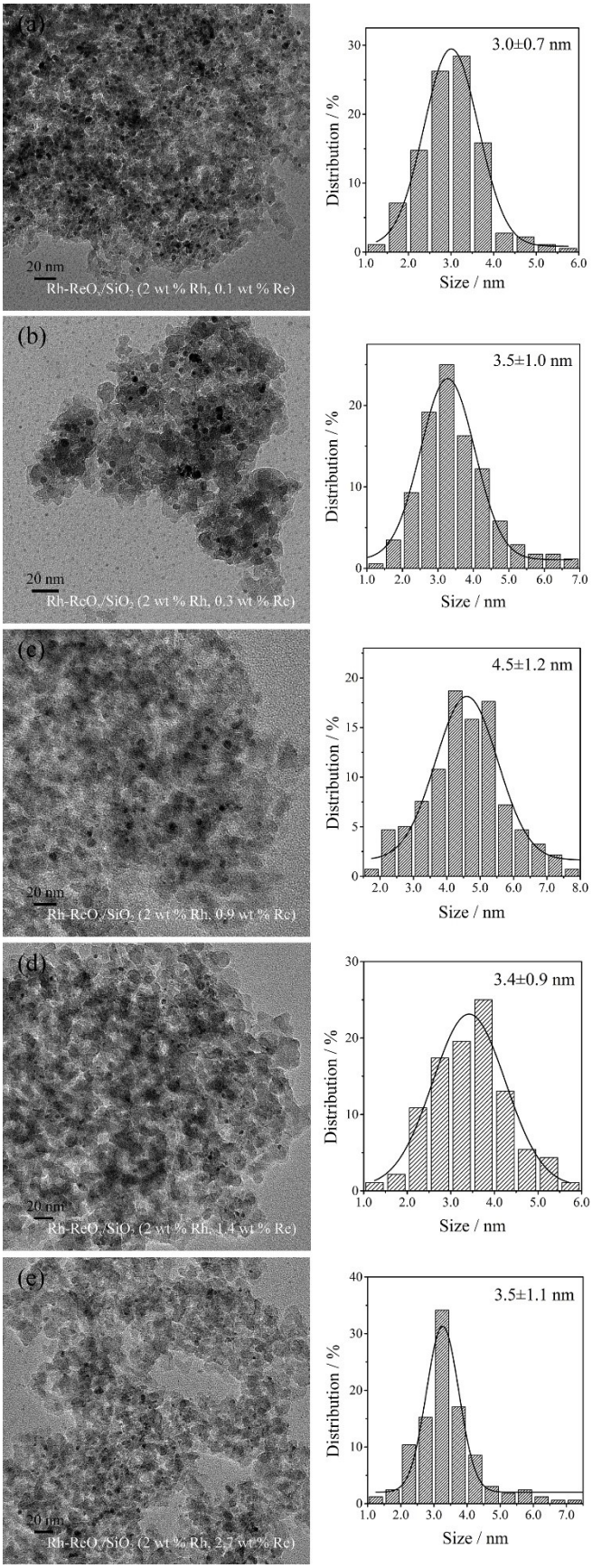
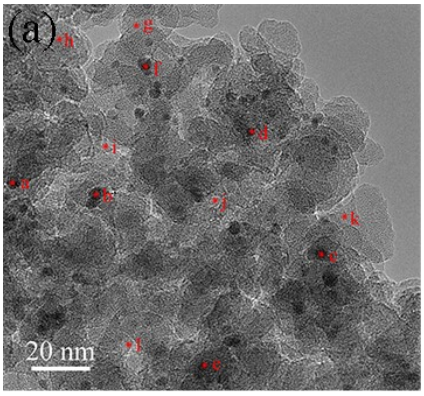
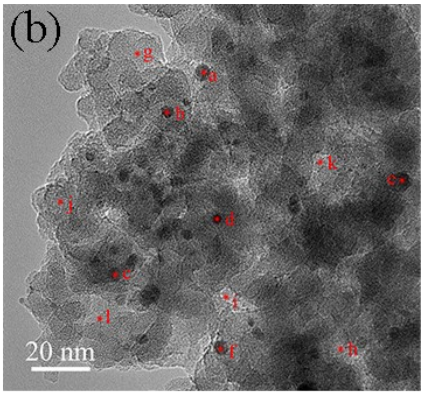


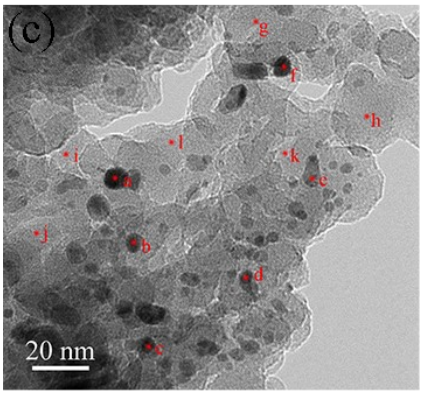
Fig. S2 Transmission electron microscopy (TEM) micrographs (scale bar = 20 nm) and histograms of metal particle size distribution for Rh-ReO_x/SiO_2 (2 wt% Rh, (a) 0.1 wt% Re, (b) 0.3 wt% Re, (c) 0.9 wt% Re, (d) 1.4 wt% Re and (e) 2.7 wt% Re).



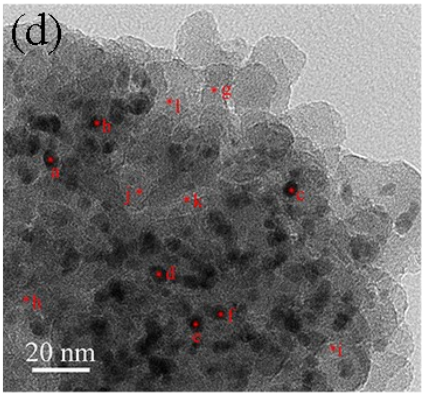
Point	a	b	c	d	e	f	g-l
Rh / atom %	1.63	3.05	1.35	1.40	1.75	1.58	0
Re / atom %	0.14	0.05	0.08	0.02	0.04	0.06	0



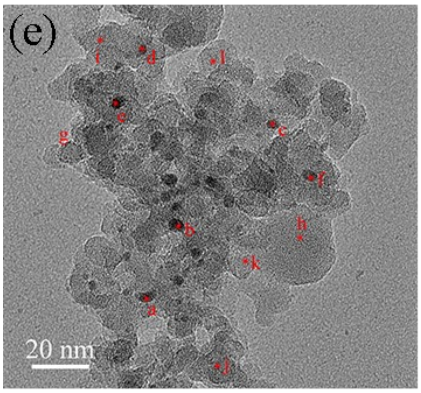
Point	a	b	c	d	e	f	g-l
Rh / atom %	2.63	1.54	1.74	1.70	1.11	0.72	0
Re / atom %	0.24	0.10	0.12	0.17	0.09	0.07	0



Point	a	b	c	d	e	f	g-l
Rh / atom %	1.07	1.11	1.18	1.20	1.05	1.20	0
Re / atom %	0.13	0.15	0.15	0.17	0.15	0.18	0



Point	a	b	c	d	e	f	g-l
Rh / atom %	0.50	0.46	0.46	0.55	0.57	0.38	0
Re / atom %	0.09	0.08	0.08	0.10	0.10	0.07	0



Point	a	b	c	d	e	f	g-l
Rh / atom %	0.19	0.18	0.21	0.25	0.20	0.17	0
Re / atom %	0.08	0.10	0.11	0.09	0.10	0.06	0

Fig. S3 High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs (scale bar = 20 nm) and electron dispersive X-ray (EDX) microanalyses of Rh-ReO_x/SiO_2 (2 wt% Rh, (a) 0.1 wt% Re, (b) 0.3 wt% Re, (c) 0.9 wt% Re, (d) 1.4 wt% Re and (e) 2.7 wt% Re).

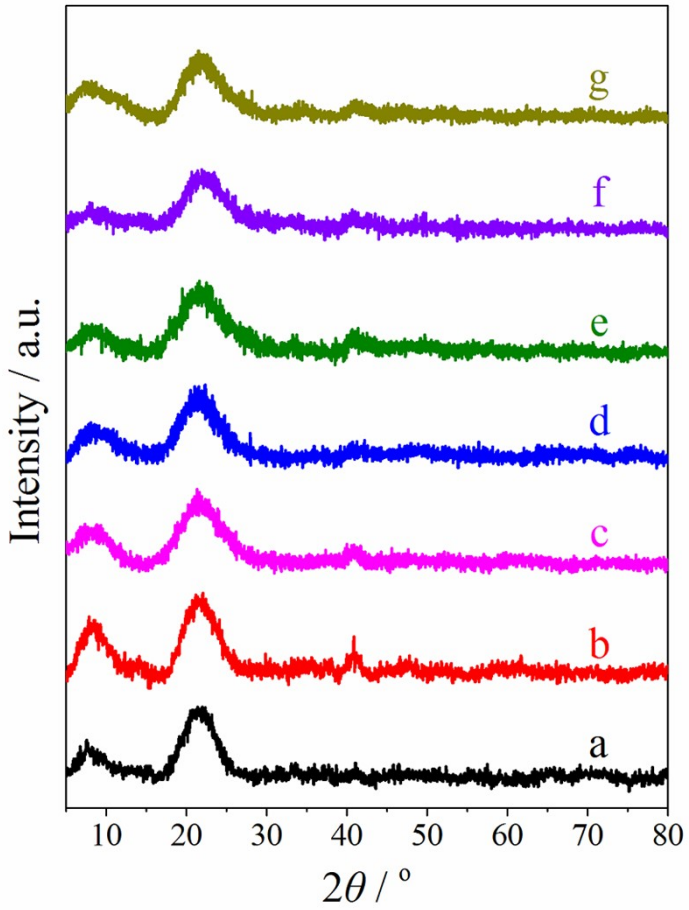
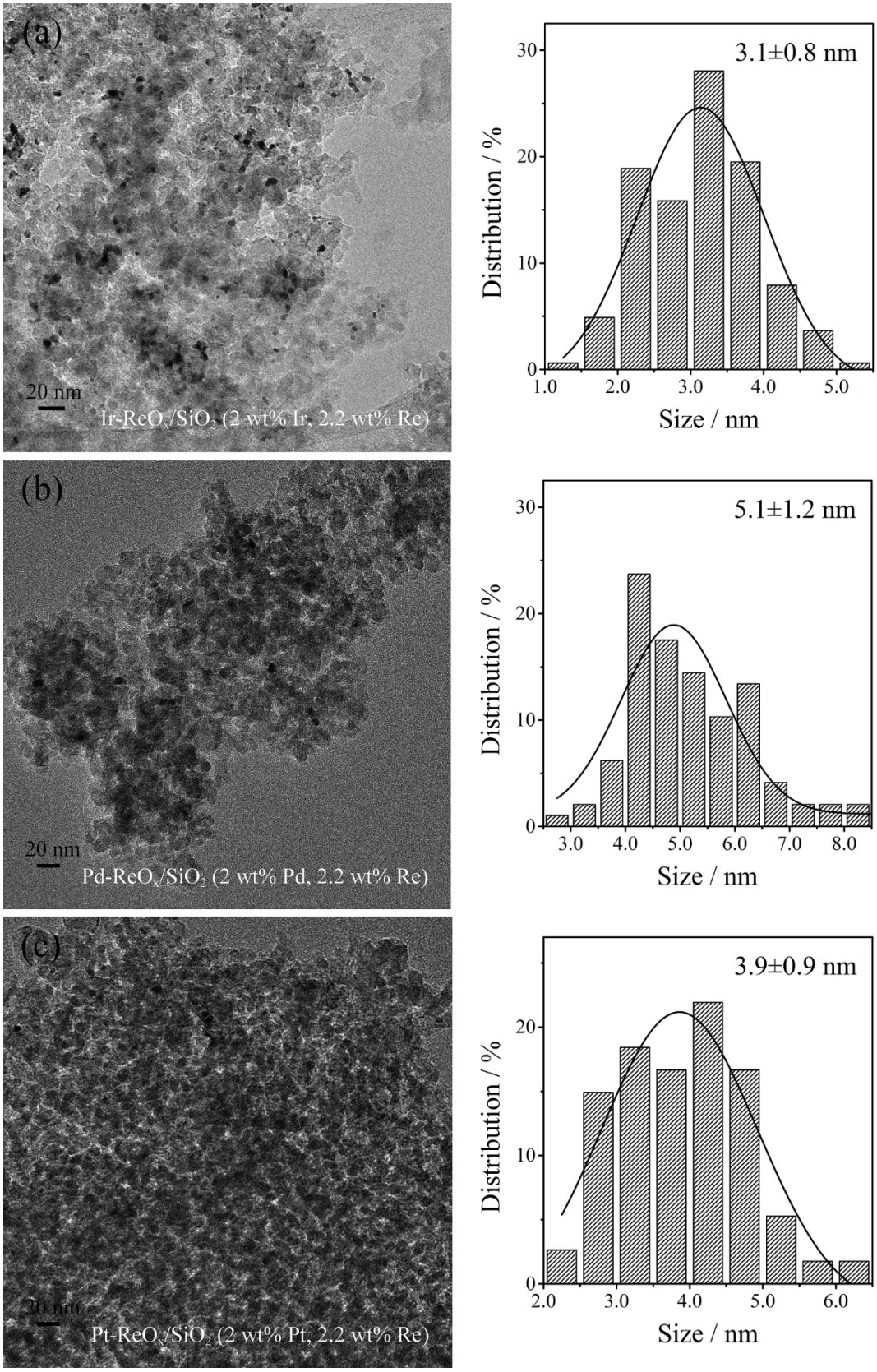


Fig. S4 XRD patterns of Rh-ReO_x/SiO_2 (2 wt% Rh, (a) 0.1 wt% Re, (b) 0.3 wt% Re, (c) 0.9 wt% Re, (d) 1.4 wt% Re, (e) 2.2 wt% Re, (f) 2.7 wt% Re) and (g) the spent Rh-ReO_x/SiO_2 (2 wt% Rh, 1.4 wt% Re).



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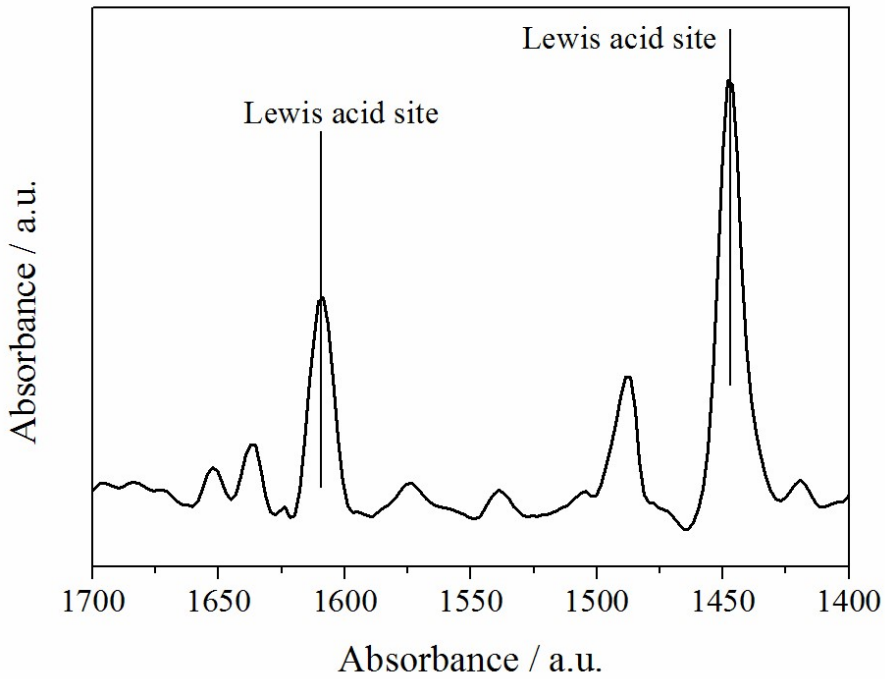
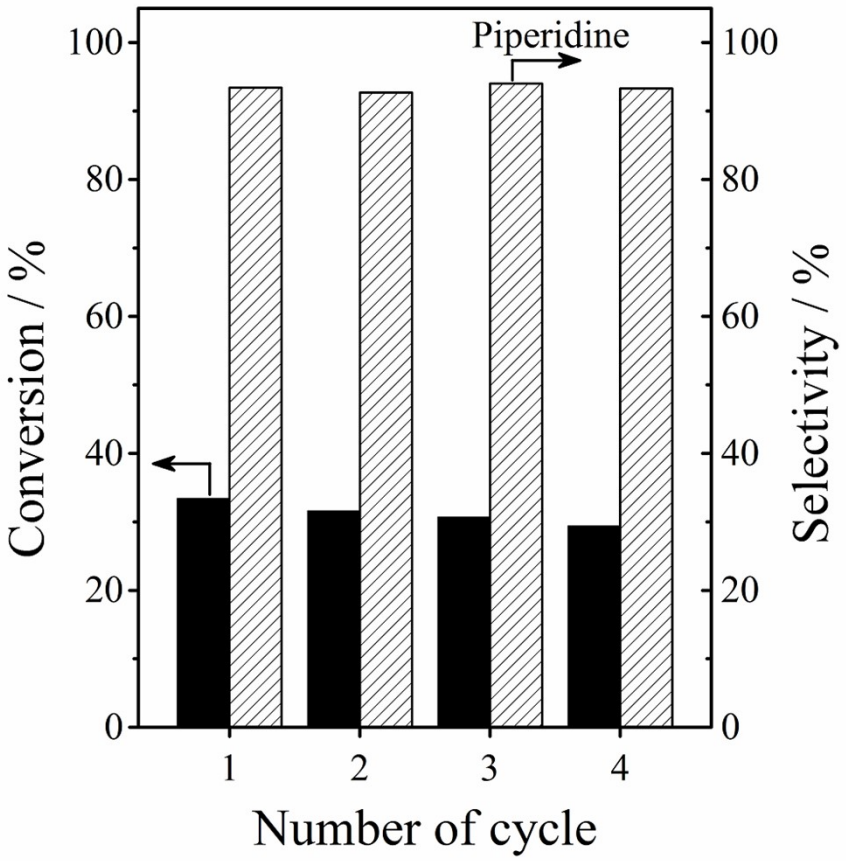


Fig. S6 FT-IR spectrum of pyridine adsorbed at 250 °C on Rh-ReO_x/SiO_2 (2 wt% Rh, 2.2 wt% Re).



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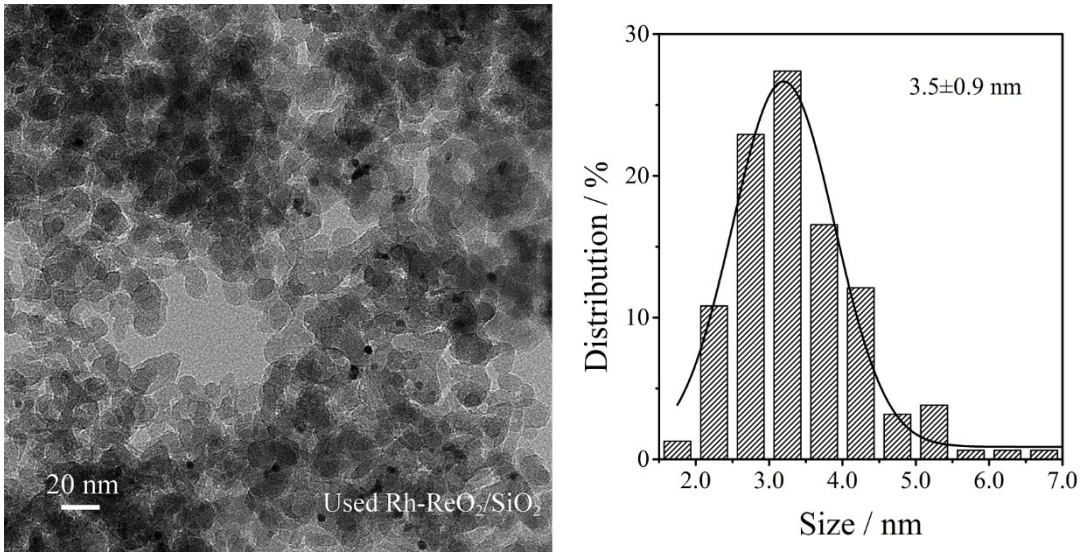

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Table S1 Turnover rate and selectivity in 5-amino-1-pentanol (APO) amination on various supported catalysts [a]

Entry	Catalyst	Turnover rate ($mol_{piperidine}$ $mol_{surface\text{-}Rh}^{-1}$ h^{-1})	Molar selectivity (%)	
			Piperidine	Pentylamine
1	ReO_x/SiO_2 (5 wt% Re)	0 [b]	-	-
2	Rh/SiO_2 (2 wt% Rh)	79.6	94.1	1.5
3	$Rh\text{-}ReO_x/SiO_2$ (2 wt% Rh, 2.2 wt% Re)	152.5	97.4	0.7
4	$Ir\text{-}ReO_x/SiO_2$ (2 wt% Ir, 2.2 wt% Re)	92.5	75.6	20.5

[a]Reaction conditions: 1 mmol APO, 1 mmol HCl, 0.05 g catalysts, 10 mL H_2O, 2 MPa H_2, 200 ^oC. 20-30% APO conversions obtained by varying reaction time. [b]No products were detected at 200 ^oC for 10 h.