Electronic Supplementary Information

Efficient Ru-Fe catalyzed selective hydrogenolysis of carboxylic acids to alcoholic chemicals

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Table 1S Catalytic performance and metal dispersion of as-reduced 5% Ru_x-Fe_y/SBA-15 catalysts[a]

Catalyst	Conversion / %	Selectivity / %				D_{Ru} (%)		TOF[d] / h^{-1}
		EtOH	AH	Gas	Others	TEM[b]	H/Ru[c]	
Ru/SBA-15	15.5	22.6	1.4	74.5	1.5	7.3	1.22	637.1
Ru_{15}-Fe_1/SBA-15	16.4	68.0	1.3	30.3	0.4	7.4	2.10	827.4
Ru_{10}-Fe_1/SBA-15	21.1	68.3	18.7	7.6	5.4	7.7	2.38	939.3
Ru_3-Fe_1/SBA-15	23.2	65.1	22.1	7.2	5.6	7.8	1.76	1396.6
Ru_2-Fe_1/SBA-15	25.5	62.0	26.8	6.8	4.4	8.0	1.38	1957.8
$Ru_{1.5}$-Fe_1/SBA-15	26.5	63.5	18.9	6.5	11.1	7.1	0.78	1799.8
Ru_1-Fe_1/SBA-15	21.7	64.9	16.2	6.4	12.5	6.9	0.65	1768.6
Fe/SBA-15	1.3	37.5	12.2	7.6	42.7	–	0.14	491.9

[a] Reaction conditions: catalyst weight = 0.20 g, T = 493 K, $P(H_2)$ = 3.0 MPa, H_2/Acid = 80, AcOH conversion was controlled below 30%. [b] The Ru nanoparticles were regarded as the spheres. Therefore, the Ru dispersion, D_{Ru} was calculated as D = 1.32/d, according to literature[1]. [c] The D_{Ru} was calculated by H_2 adsorption as described in literature. [d] The TOF was calculated by metal dispersion from H_2 adsorption.

Table 2S Catalytic performance of supported 5% Ru_x-Fe_y catalysts for AcOH hydrogenolysis[a]

Catalyst (Ru loading = 5 wt%)	Particle size / nm	Conversion / %	Selectivity / %				
			EtOH	EtOAc	AH	Acetone	Gases[b]
Ru/SBA-15	18.1	71.0	0.6	0.3	0.9	0	98.2
Ru_{15}-Fe_1/SBA-15	17.8	92.8	49.4	0.6	0.5	0	49.5
Ru_{10}-Fe_1/SBA-15	17.1	91.5	83.6	3.1	1.6	0	11.7
Ru_3-Fe_1/SBA-15	16.9	91.0	82.8	5.2	2.3	0	9.7
Ru_2-Fe_1/SBA-15	16.5	91.6	86.2	6.1	2.5	0	5.2
$Ru_{1.5}$-Fe_1/SBA-15	18.7	75.1	67.7	22.4	4.3	0	5.6
Ru_1-Fe_1/SBA-15	19.2	66.5	58.7	30.0	5.1	0	6.2
Fe/SBA-15	–	1.8	6.2	6.3	15.8	61.3	10.4
Ru_2-Fe_1/SiO_2	29.6	46.2	14.0	56.2	0.8	0	29.0
Ru_2-Fe_1/SBA-15-CoIm-773 K	29.3	69.5	67.8	17.3	2.5	0	12.4
Ru_2-Fe_1/SBA-15-CoIm-573 K	3.2	99.9	0.3	0	0	0	99.7

[a] Reaction conditions: catalyst weight = 0.20 g, $P(H_2)$ = 3.0 MPa, T = 533 K, $LHSV_{(AcOH)}$ = 1.5 h^{-1}, H_2/Acid = 80.

[b] Gases include methane, ethane, and CO_x.

Table 3S Catalytic performance of supported 5% Ru_x-Fe_y catalysts with different supports for AcOH hydrogenolysis[a]

Catalyst (Ru loading = 5 wt%)	Conversion / %	Selectivity / %				
		EtOH	EtOAc	AH	Acetone	Gases[b]
Ru_2-Fe_1/SBA-15	91.6	86.2	6.1	2.5	0	5.2
Ru_2-Fe_1/ZSM-5 (Si/Al=50)	88.7	55.1	2.3	3.8	0	38.8
Ru_2-Fe_1/ZSM-5 (Si/Al=25)	84.7	52.5	8.1	12.3	0.0	27.1
Ru_2-Fe_1/HY (Si/Al=30)	62.7	30.3	48.3	4.2	0.1	17.1
Ru_2-Fe_1/SiO_2	46.2	14.0	56.2	0.8	0	29.0
Ru_2-Fe_1/Al_2O_3	87.3	60.0	1.8	2.0	0.1	36.1

[a] Reaction conditions: catalyst weight = 0.20 g, $P(H_2)$ = 3.0 MPa, T = 533 K, $LHSV_{(AcOH)}$ = 1.5 h^{-1}, H_2/Acid = 80.

[b] Gases include methane, ethane, and CO_x.

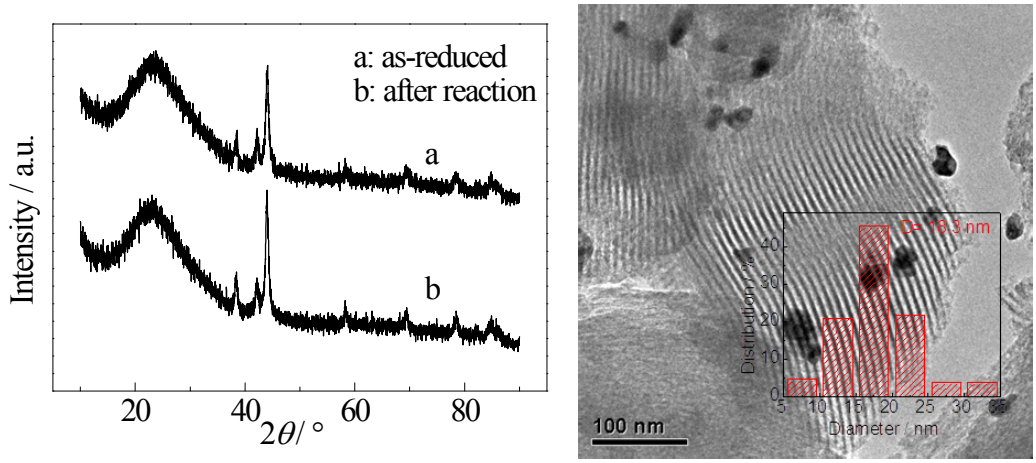

Fig. 1S The XRD patterns of 5% Ru_2-Fe_1/SBA-15 catalyst before and after the catalytic run for 300 h and the TEM image after the long-term run.

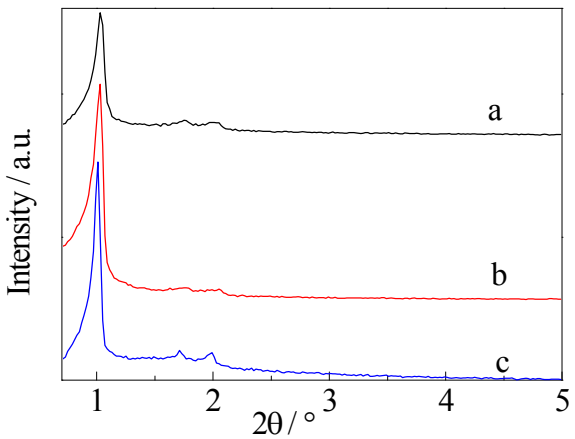

Fig. 2S The low-angle XRD pattern: (a) 5% Ru_2-Fe_1/SBA-15, (b) 5% Ru_2-Fe_1/SBA-15 after the catalytic run on stream for 300 h, and (c) SBA-15.

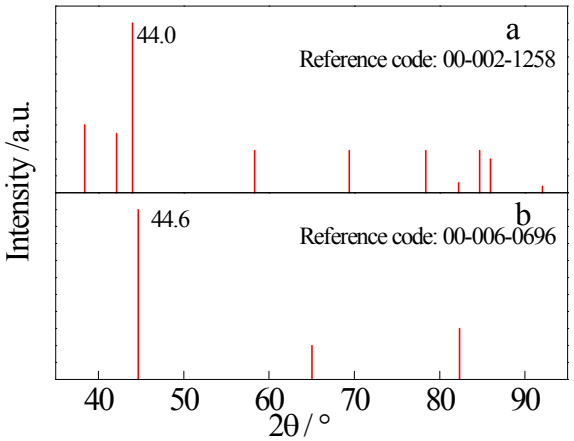

Fig. 3S The standard XRD data files of Ru and Fe: (a) Ru, (b) Fe.

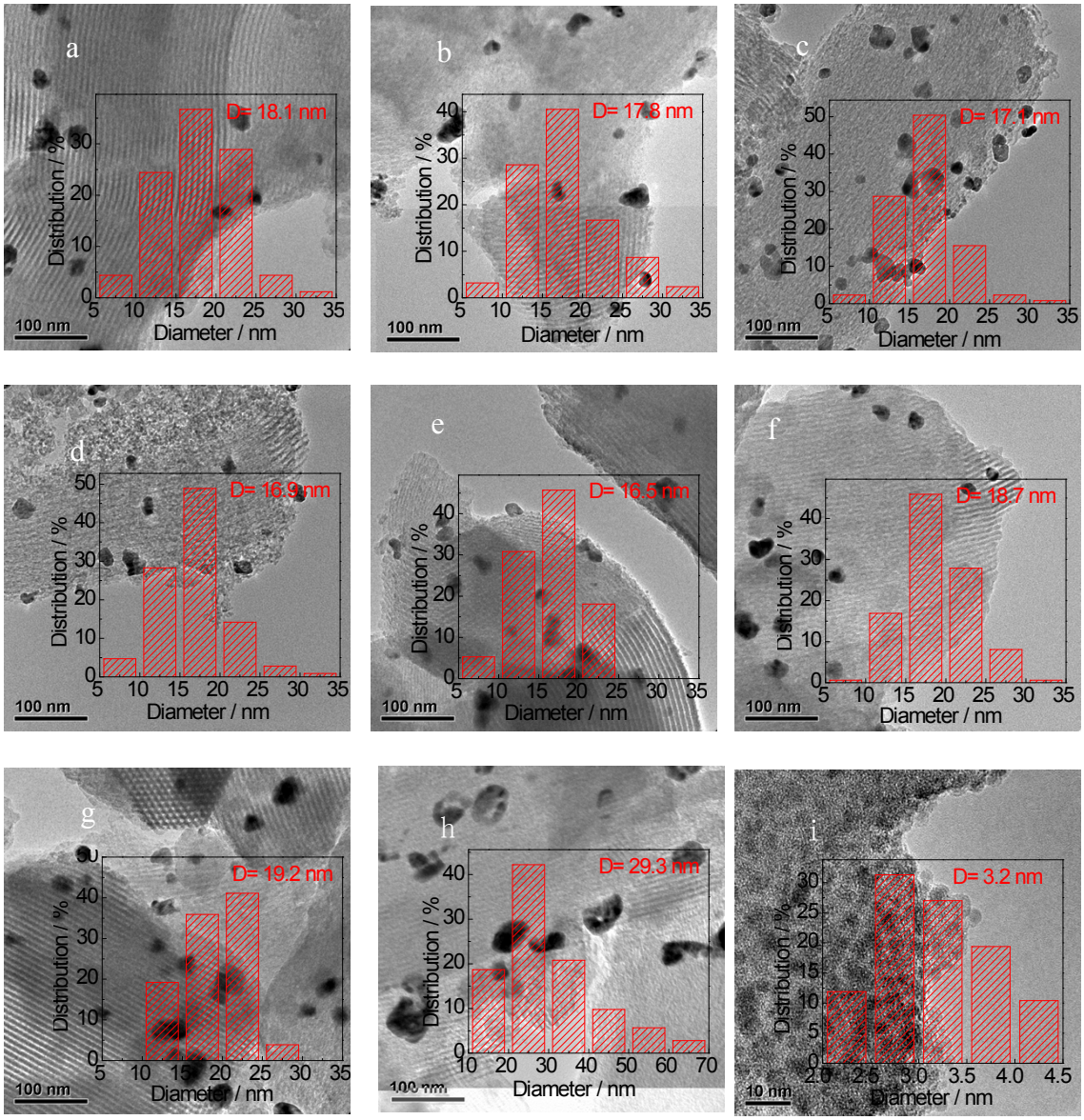

Fig. 4S TEM images and particle size distribution of 5% Ru_x-Fe_y/SBA-15 catalysts with different Ru/Fe atomic ratios: (a) Ru/SBA-15, (b) Ru_{15}-Fe_1/SBA-15, (c) Ru_{10}-Fe_1/SBA-15, (d) Ru_3-Fe_1/SBA-15, (e) Ru_2-Fe_1/SBA-15, (f) $Ru_{1.5}$-Fe_1/SBA-15, and (g) Ru_1-Fe_1/SBA-15, (h) Ru_2-Fe_1/SBA-15-773 K, (i) Ru_2-Fe_1/SBA-15-573 K.

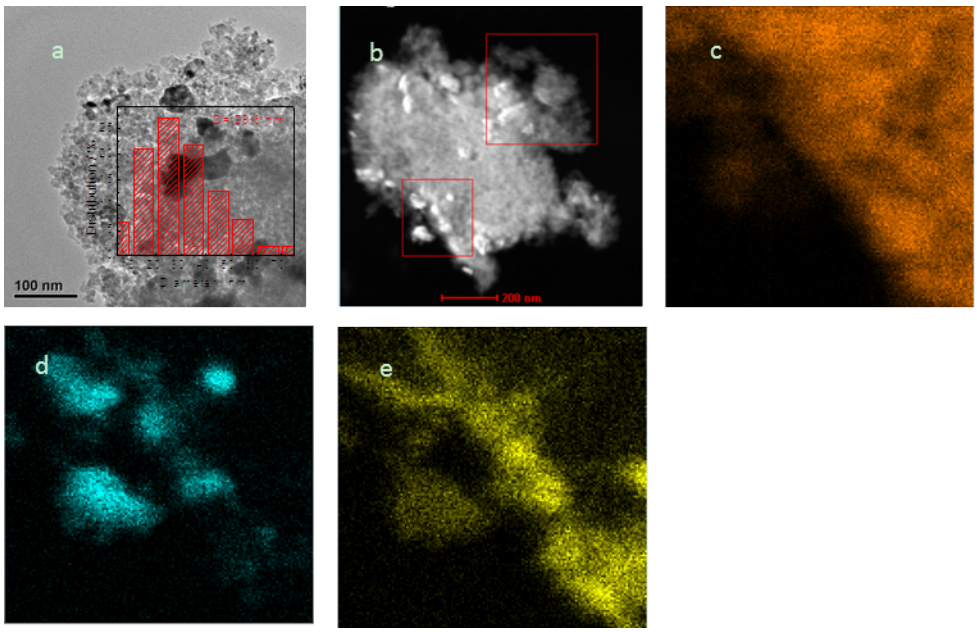

Fig. 5S TEM image, STEM-EDX elemental mappings of 5% Ru_2-Fe_1/SiO_2 catalyst: (a) TEM image, (b) dark-field image, (c) STEM-EDX elemental mappings for Si, (d) STEM-EDX elemental mappings for Ru, and (e) STEM-EDX elemental mappings for Fe.

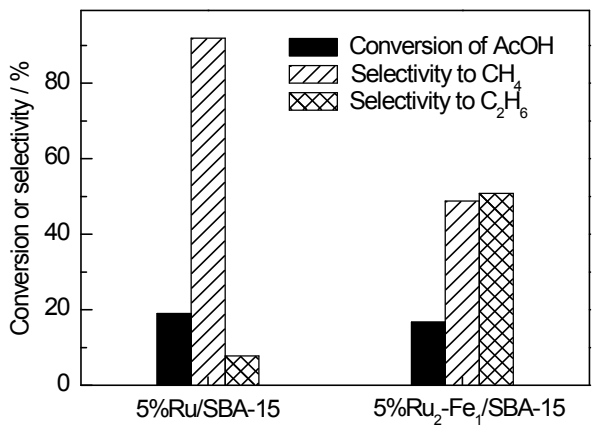

Fig. 6S Hydrogenolysis of EtOH over 5% Ru/SBA-15 and 5% Ru_2-Fe_1/SBA-15 catalysts at 463 K.

Reference

1 B. D. Li, J. Wang, Y. Z. Yuan, H. Ariga, S. Takakusagi and K. Asakura, *ACS Catal.*, 2011, **1**, 1521–1528.