Supporting Information

Activity enhancement of Ru/TiO_2 catalyst for catalytic hydrogenation of amides to amines through controlling strong metal-support interaction

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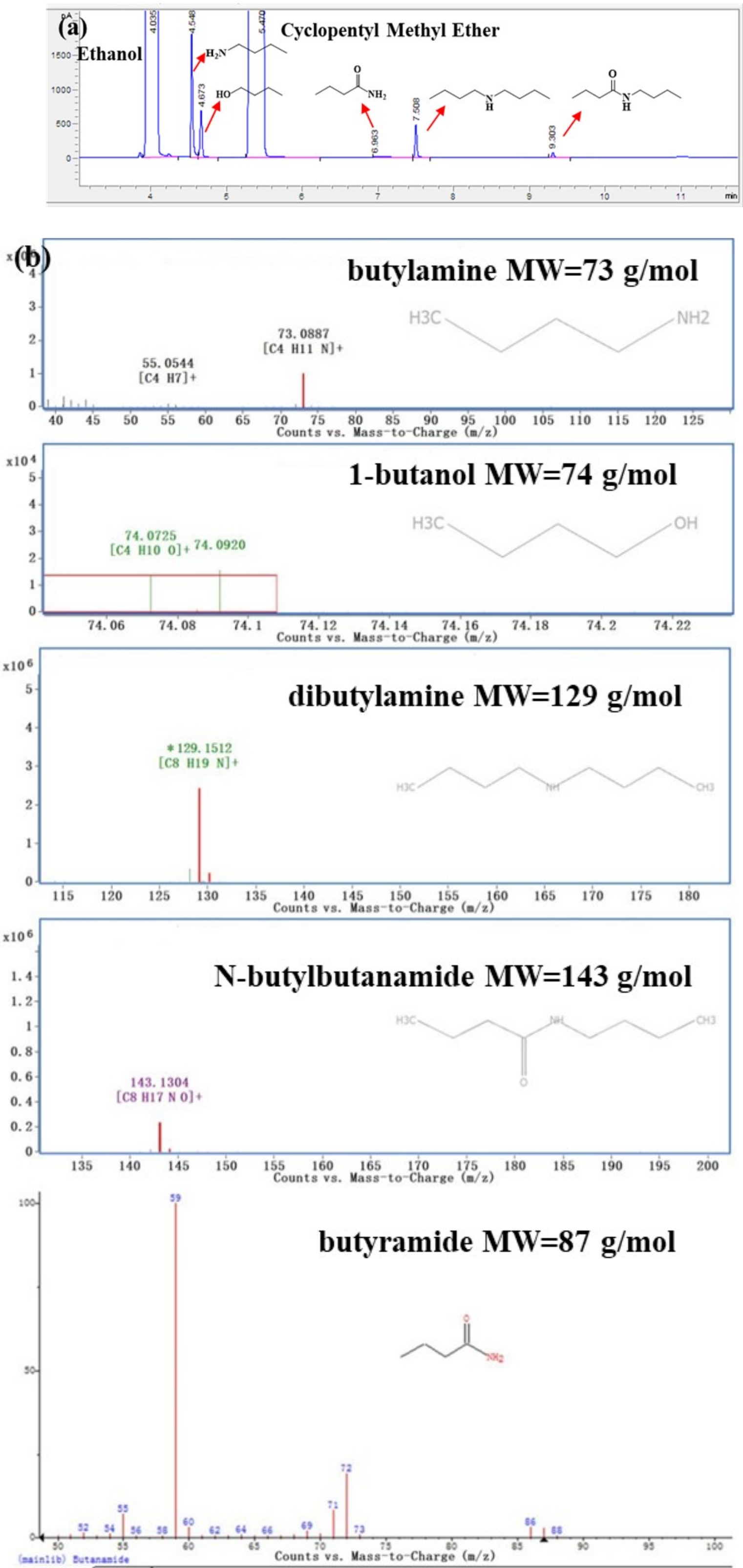

Fig. S1 (a) The GC trace of the liquid mixture after the reaction and (b) the MS spectra of the liquid mixture after the reaction.

The retention times were used to determine the GC peak positions of reactant and products, and the MS spectra were used to confirm the information of the reactant and products accurately.

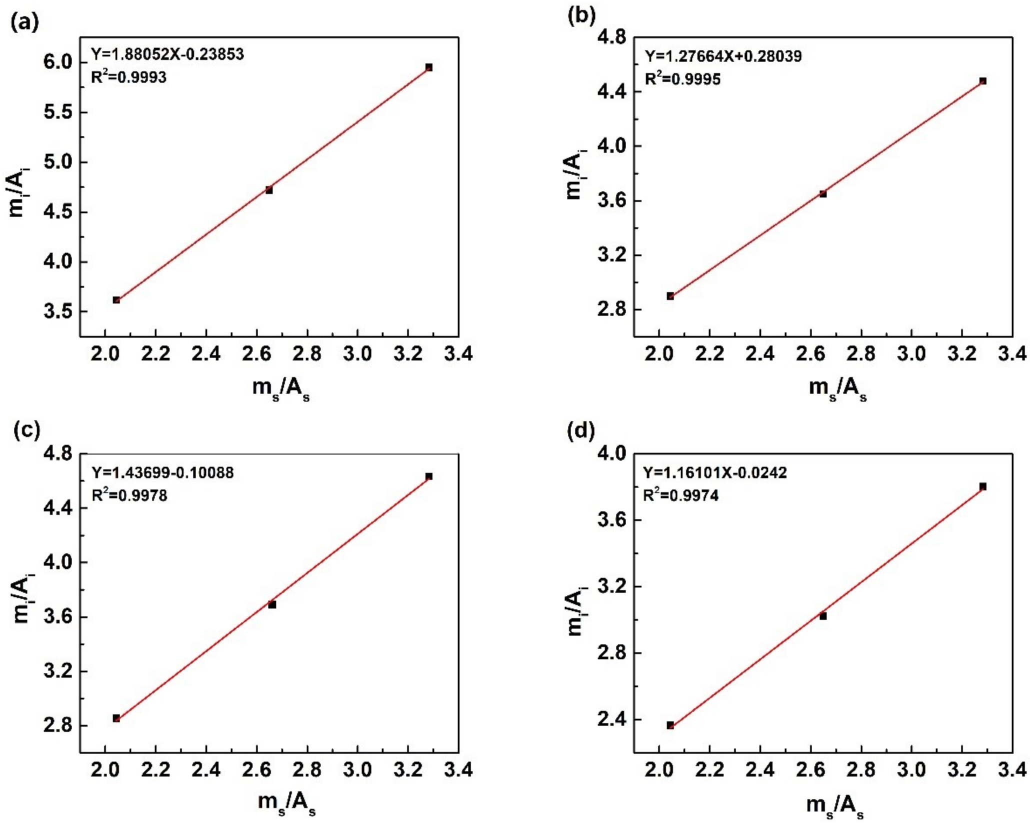

Fig. S2 Internal standard curve and relative correction factor of standards. (a) butyramide; (b) butylamine; (c) 1-butanol; (d) dibutylamine

Table S1 The chemical properties of Ru/Rutile catalysts reduced at different temperatures.

Catalysts	d_{Ru} [a]	H_2 consumption	Ru reduction degree [b]
	nm	mmol/g	
Ru/TiR-200C-500	2.60	0.425	0.456
Ru/TiR-300C-500	2.55	0.571	0.532
Ru/TiR-400C-500	3.24	0.591	0.573
Ru/TiR-500C-500	4.48	0.670	0.601
Ru/TiR-600C-	5.59	0.609	0.578

500

[a] Ru particle size is calculated by the TEM images according to $d = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

[b] Ru reduction degree is calculated based on the ratios of amount of H_2 consumption to the theoretical H_2 consumption value.

Table S2 XPS analysis results of Ru/Rutile catalysts with different calcination and reduction temperatures.

Catalysts	$Ru^{X+}3d_{5/2}$ eV	$Ru^{0}3d_{5/2}$ eV	$Ru^{0}3p_{3/2}$ eV	$Ti^{4+}2p_{3/2}$ eV	$Ru^0/(Ru^0+Ru^{X+})$ [a]	I_{Ru3d}/I_{Ti2p} [b]
Ru/TiR-200C-500	281.3	280.3	461.9	458.5	0.507	0.246
Ru/TiR-300C-500	281.2	280.2	461.8	458.5	0.534	0.259
Ru/TiR-400C-500	280.6	279.7	461.6	458.5	0.568	0.199
Ru/TiR-500C-500	280.4	279.6	461.5	458.5	0.575	0.139
Ru/TiR-600C-500	280.2	279.3	461.4	458.5	0.554	0.128
Ru/TiR-200C-200	281.3	280.3	461.9	458.5	0.540	0.247
Ru/TiR-200C-300	281.3	280.3	461.9	458.6	0.560	0.218
Ru/TiR-200C-400	281.3	280.3	461.9	458.6	0.540	0.205
Ru/TiR-200C-600	281.1	280.1	461.7	458.5	0.497	0.223

[a] $Ru^0/(Ru^0+Ru^{X+})$ is calculated based on the XPS peak fitting area ratio of Ru3d.

[b] I_{Ru3d}/I_{Ti2p} is calculated based on the XPS peak area ratio of Ru3d and Ti2p.

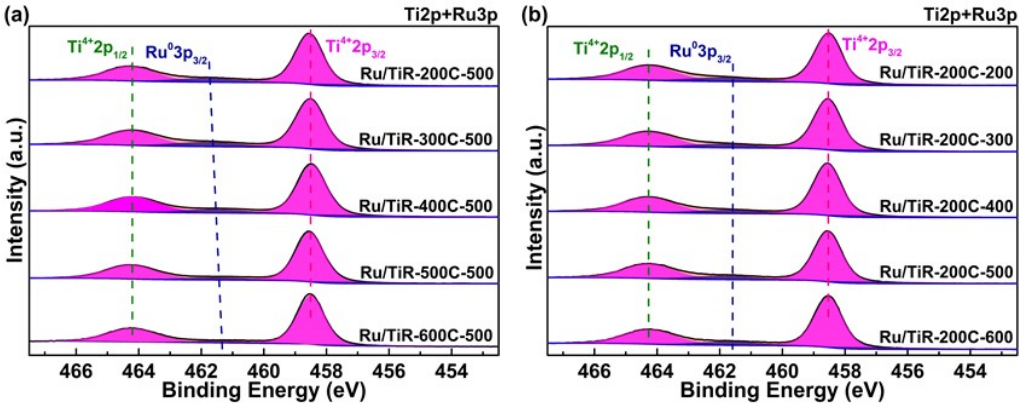

Fig. S3 Ti 2p XPS results of (a) Ru/TiR-XC-500 and (b) Ru/TiR-200C-Y catalysts.

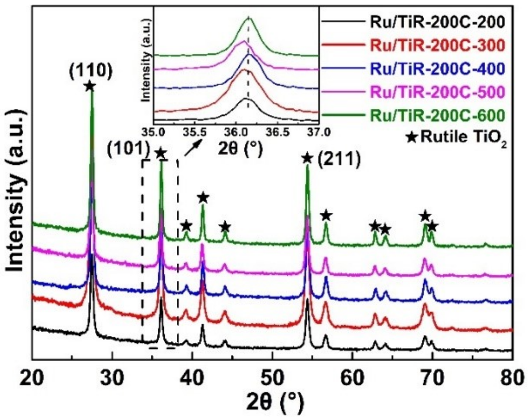

Fig. S4 XRD patterns of Ru/Rutile catalysts with different reduction temperature.

Table S3. Hydrogenation of butyramide over Ru/TiR-200C-Y catalysts at various butyramide concentrations and H_2 pressures [a].

Catalysts	Butyramide amount (mmol)	H_2 pressure (MPa)	Reaction time (h)	Catalyst mass (mg)	Con. (%)	Rate $mol^{-1}\cdot g^{-1}\cdot s^{-1}$
Ru/TiR-200C-200	1	5	0.5	100	14	7.7×10^{-4}
	3	5	1	100	16	1.35×10^{-3}
	5	5	1	100	13	1.85×10^{-3}
	3	3	1	100	5	4.5×10^{-4}
	3	7	1	100	21	1.74×10^{-3}
Ru/TiR-200C-300	1	5	0.5	50	17	2.01×10^{-3}
	3	5	1	100	27	2.29×10^{-3}
	5	5	1	100	18	2.52×10^{-3}
	3	3	1	100	13	1.06×10^{-3}
	3	7	1	100	30	2.49×10^{-3}
Ru/TiR-200C-400	1	5	0.5	50	24	2.70×10^{-3}
	3	5	1	100	28	2.35×10^{-3}
	5	5	1	100	15	2.11×10^{-3}
	3	3	1	100	22	1.82×10^{-3}
	3	7	1	100	34	2.81×10^{-3}
Ru/TiR-200C-500	1	5	0.5	50	16	1.74×10^{-3}
	3	5	1	100	25	2.07×10^{-3}
	5	5	1	100	15	2.15×10^{-3}
	3	3	1	100	18	1.52×10^{-3}
	3	7	1	100	32	2.65×10^{-3}

	1	5	0.5	50	18	2.00×10^{-3}
Ru/TiR-	3	5	1	100	20	1.66×10^{-3}
200C-	5	5	1	100	11	1.59×10^{-3}
600	3	3	1	100	16	1.36×10^{-3}
	3	7	1	100	25	2.07×10^{-3}

[a] Reaction conditions: 50 ~ 100 mg catalyst, 1 ~ 3 mmol butyramides, 25 mL CPME, 150 °C, 3 ~ 7 MPa H_2 and 0.5 ~ 1 h.

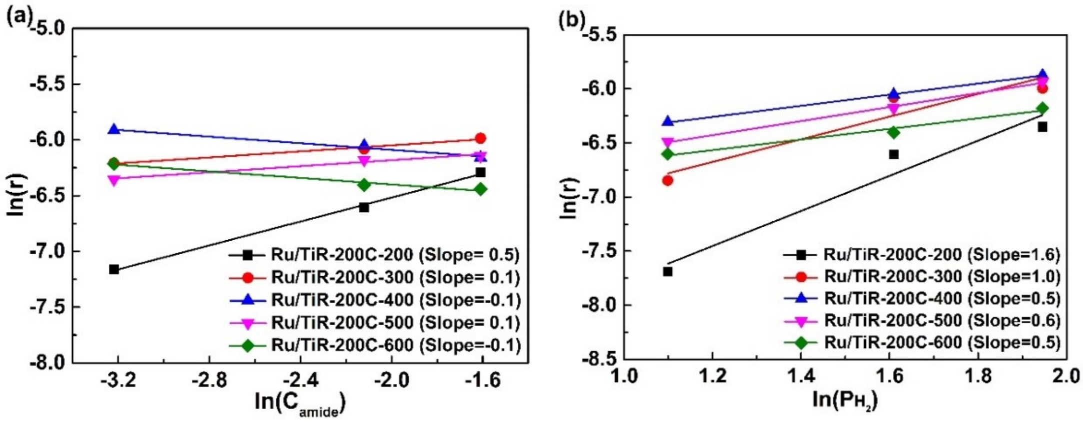

Fig. S5 The reaction orders of (a) butyramide and (b) H_2 for butyramide hydrogenation reaction over Ru/Rutile catalysts with different reduction temperatures.

Reaction conditions: 300 mg catalyst, 1 ~ 5 mmol butyramides, 25 mL CPME, 150 °C, 3 ~ 7 MPa H_2, and 0.5 ~ 1 h.

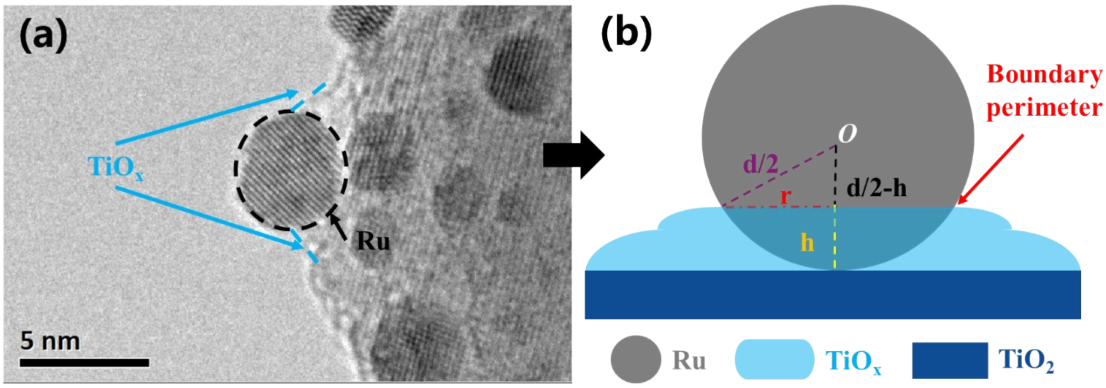

Fig. S6 (a) The observed structures and (b) the proposed structural model of the Ru/Rutile catalyst at different reduction temperature.

$$\theta = \frac{S_{cap}}{S_{sphere}} = \frac{2\pi\cdot\frac{d}{2}\cdot h}{\pi d^2} \qquad (1)$$

$$(\frac{d}{2})^2 = (\frac{d}{2} - h)^2 + r^2 \qquad (2)$$

$$P = 2\pi r = 2\pi d\sqrt{\theta - \theta^2} \qquad (3)$$

The θ is the coverage of TiO_x species on Ru particle; S_{cap} is the Ru particle surface area covered by TiO_x overlayer to Ru particle; S_{sphere} is the total Ru particle surface area; d is the diameter of Ru particle; h is the height of the cap; r is the radius of boundary perimeter. As the reduction temperature increases, the coverage of TiO_x species to Ru particle increases and the length of Ru-TiO_x boundary grow correspondingly.

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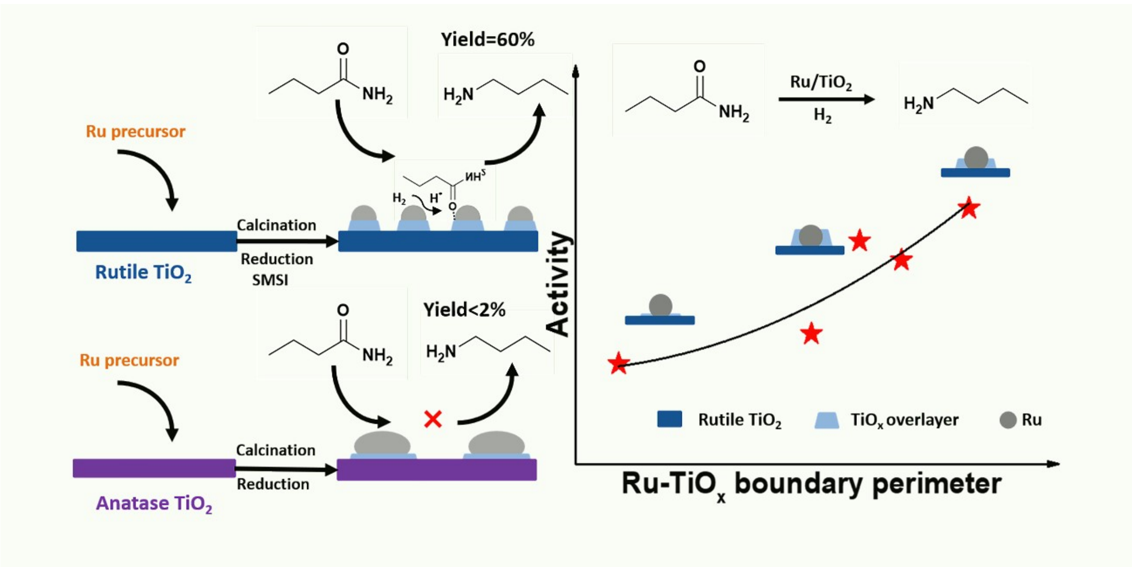

Rutile TiO_2 is in favor of highly dispersed Ru particles and Ru-TiO_x boundary is responsible for the catalytic amide hydrogenation.