Electronic Supplementary Information

Alcohol amination over titania-supported ruthenium nanoparticles

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Table S1: Parameters in controllable preparation of Ru particle with different size.

Catalyst	$RuCl_3$ concentration (mmol/L)	PVA/Ru mass ratio	Reduce temperature (^oC)
5Ru/TiO_2-1.4	10	1.2	0
5Ru/TiO_2-3.5	10	1.2	25
5Ru/TiO_2-5.8	10	1.2	50
5Ru/TiO_2-9.9	20	1.2	50

Table S2: Catalytic performance for octanol amination over the catalysts (100 mg catalyst, 1.0 mL 1-octanol, NH_3/octanol = 7, $P(H_2)$ = 2.0 bar, T = 180 °C)

Catalyst	Reaction time (h)	Conversion (%)	Selectivity (%)	
			Octylamine	Di-octylamine
5Ru/TiO_2-1.4	1	25.3	99.5	0.5
	3	79.6	98.5	1.5
	5	96.5	96.1	3.9
5Ru/TiO_2-3.5	1.5	36.8	99.4	0.6
	2.5	64.3	98.6	1.4
	6	92.5	83.2	6.8
5Ru/TiO_2-5.8	1	21.2	99.6	0.4
	3	70.8	99.1	0.8
	8	91.5	73.2	26.8
5Ru/TiO_2-9.9	1	15.2	99.1	0.9
	3	61.7	95.8	4.2
	10	93.1	55.3	44.7

Table S3: Catalytic performance for octanol amination and coupling of octylamine over the catalysts with different Ru particle size (30 mg catalyst, 1.0 mL 1-octanol or 1-octylamine, NH_3/reactant = 7, $P(H_2)$ = 2.0 bar, T = 180°C)

Catalyst	Reaction time (h)	Octanol conversion[a] (%)	Octylamine conversion[b] (%)	Selectivity in coupling of octylamine (%)		
				Di-octylamine	Imine	Octylnitrile
5Ru/TiO_2-1.4	1.5	4.1	0.6	32.7	57.3	10
	2	5.7	0.8	67.3	32.7	0
	2.5	6.9	0.9	69.6	30.4	0
5Ru/TiO_2-3.5	1.5	2.9	0.7	21.2	64.3	14.5
	2	3.9	0.9	45.7	49.3	5.0
	2.5	4.7	1.1	51.3	48.7	0
5Ru/TiO_2-5.8	1.5	1.8	0.9	6.4	82	11.6
	2	2.5	1.2	10.6	75.6	13.8
	2.5	3.0	1.3	26.4	63.1	10.5
5Ru/TiO_2-9.9	2.5	0.7	0.8	21.6	61.9	16.5
	3	0.8	1.0	31.6	56.9	11.4
	4	1.0	1.3	74	26	0

[a] Conversion for octanol amination (selectivity to octylamine is 100 percent under the conditions);
[b] Conversion for coupling of octylamine.

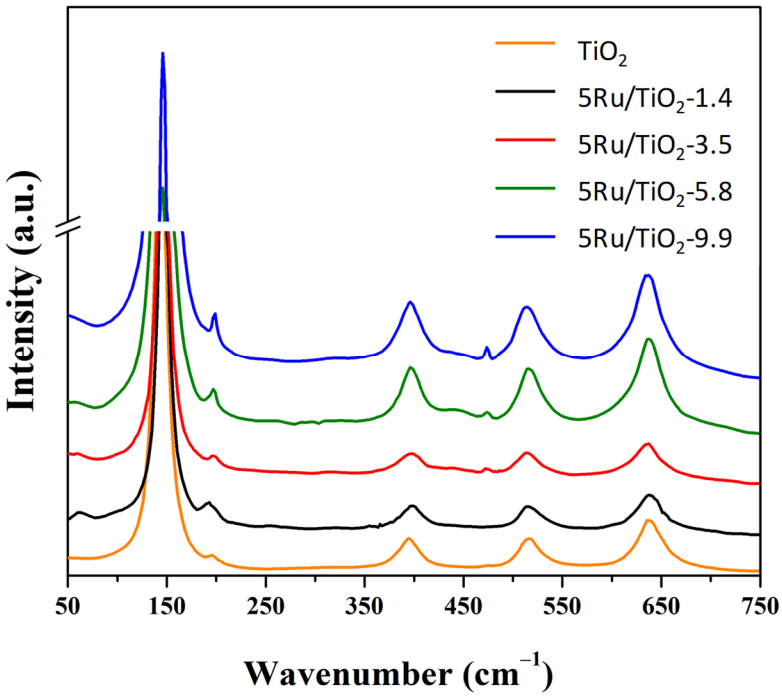

Figure S1: Raman spectra of the catalysts with different Ru particle size

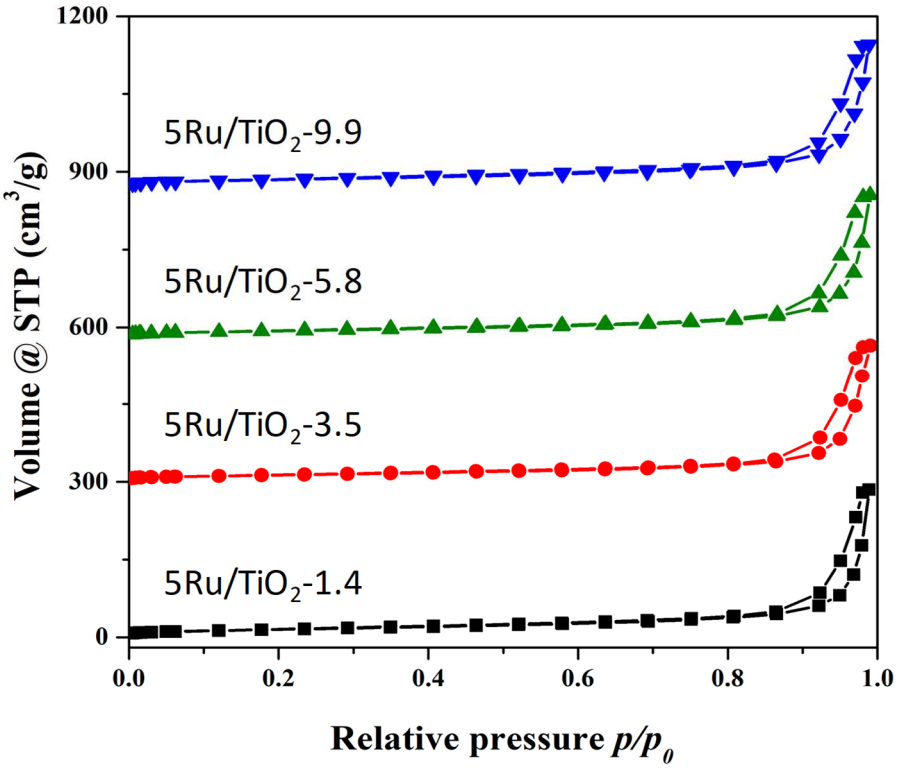

Figure S2: Nitrogen adsorption-desorption isotherms of the as-prepared catalysts

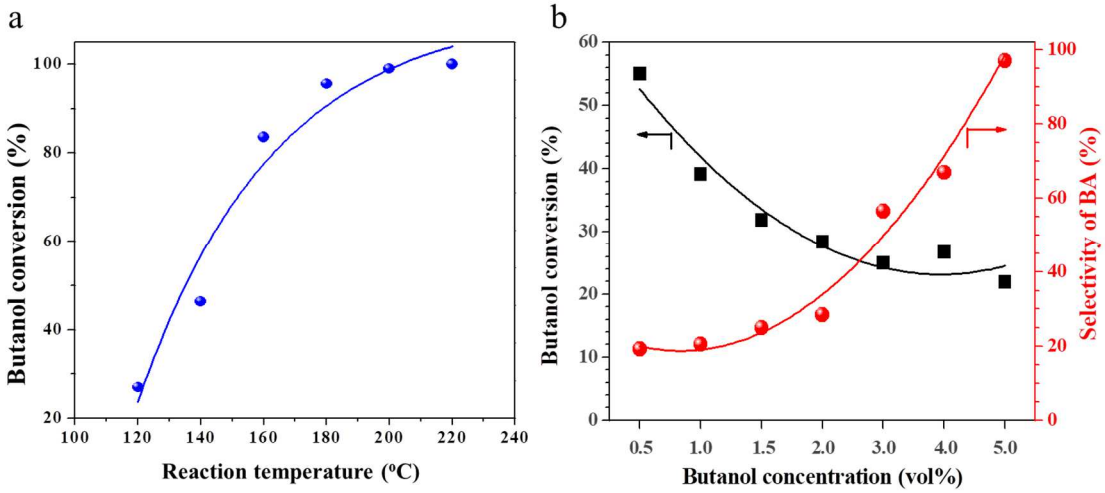

Figure S3: Effect of (a) reaction temperature and (b) 1-butanol concentration and butylamine selectivity on gas-phase amination of 1-butanol over 5Ru/TiO_2-5.8. (Conditions: catalyst 10-100 mg, GHSV = 20 L/g·h, 40 v/v % of H_2, 2 v/v % of 1-butanol, NH_3/butanol molar ratio = 7, reaction temperature 120-220 ºC, b was obtained at 180 ºC)

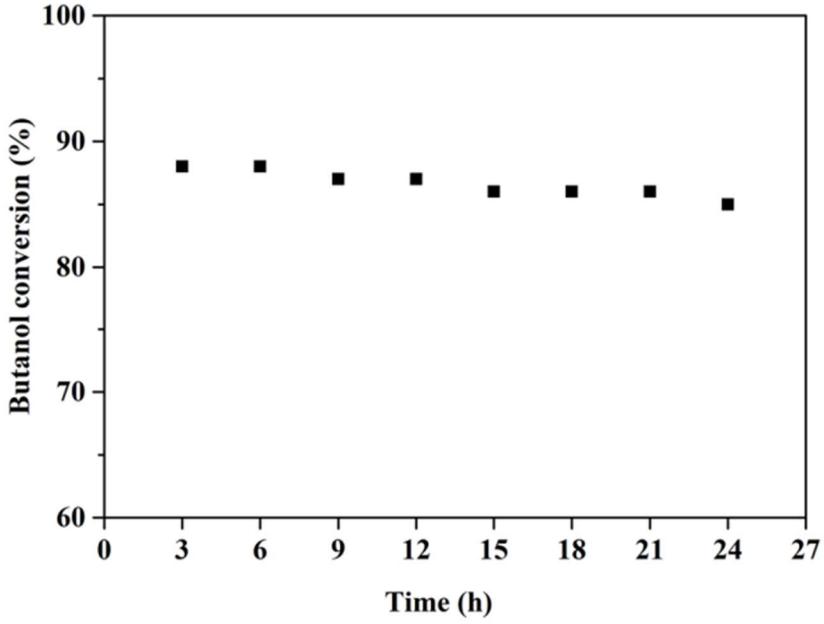

Figure S4: Conversion versus time over 5Ru/TiO_2-1.4 in gas phase butanol amination (180°C, NH_3/butanol molar ratio = 7, GHSV = 4 L(STP)/g•h)

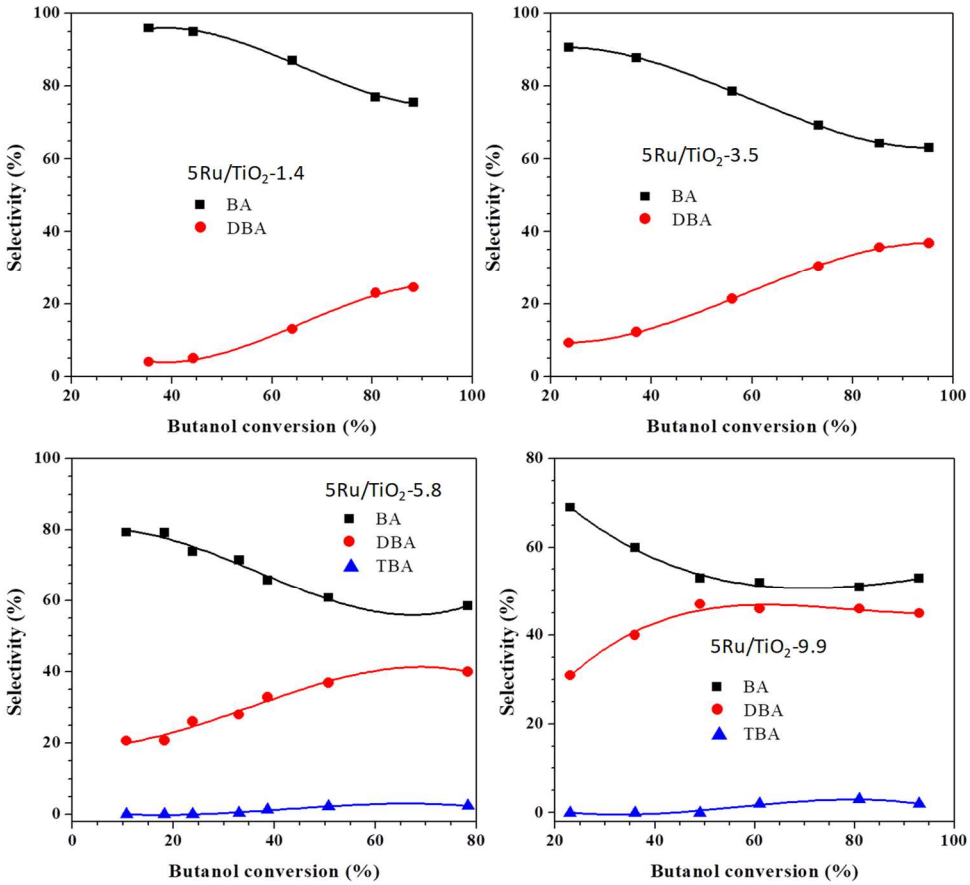

Figure S5: Selectivity-conversion curves for gas-phase amination of 1-butanol over the as-prepared catalysts. (Conditions: catalyst 10-100 mg, GHSV = 0-50 L/g·h, 40 v/v % of H_2, 2 v/v % of 1-butanol, NH_3/butanol molar ratio = 7, reaction temperature 180 ^oC)

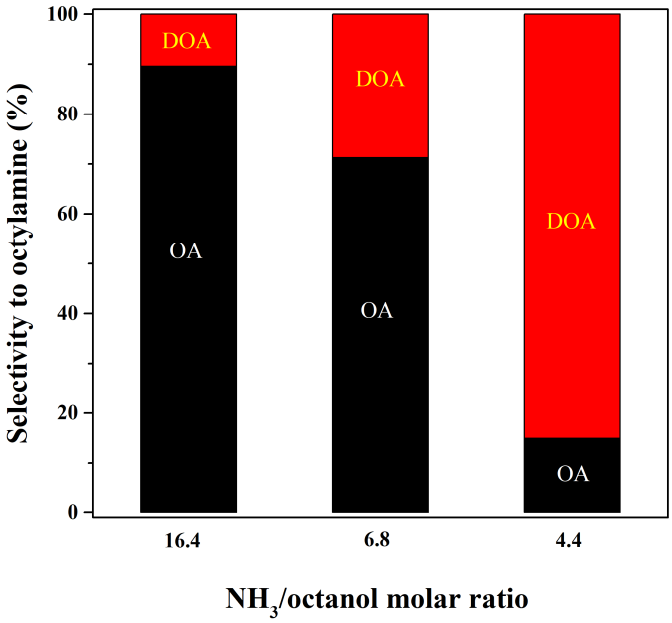

Figure S6: Effect of the NH_3/octanol ratio on the selectivity to octylamine at 90-95% conversion over the 5Ru/TiO_2-5.8 catalyst. (Conditions: 100 mg of catalyst, 1.0 mL of 1-octanol, $P(H_2)$ = 2.0 bar, T = 180 °C)

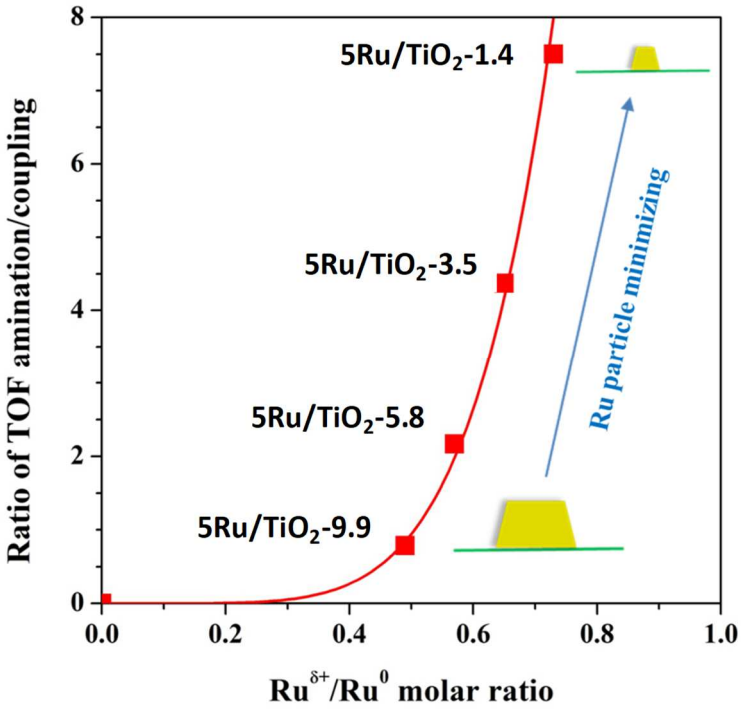

Figure S7: Ratio of TOF amination to TOF coupling as a function of $Ru^{\delta+}/Ru^{0}$ molar ratio over the Ru catalysts with different Ru particle sizes

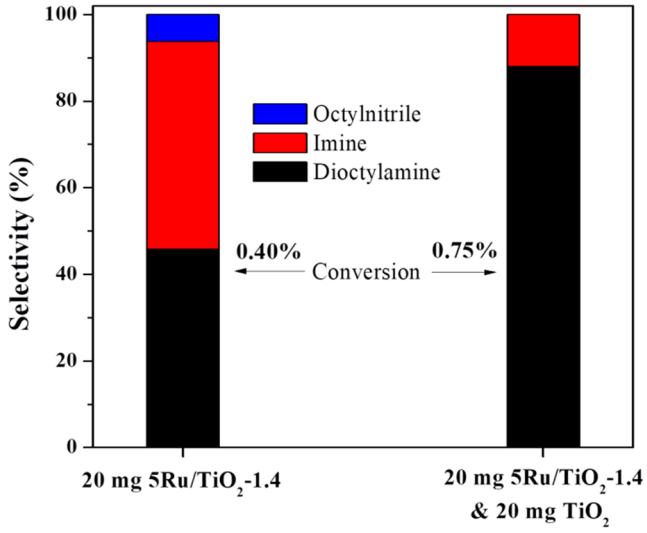

Figure S8: Effect of adding TiO_2 support on conversion and selectivity of products in octylamine coupling. (1.5 or 1.0 mg Ru catalyst, 1.0 mL of octylamine, NH_3/octylamine ratio of 6.8, $P(H_2)$ = 2.0 bar, T = 180 ºC, time of 1.0-2.5 h)