Electronic Supplementary Information for

Thermocatalytic synthesis of 2-butanol from biomass-derived levulinic acid using carbon-doped titania supported ruthenium

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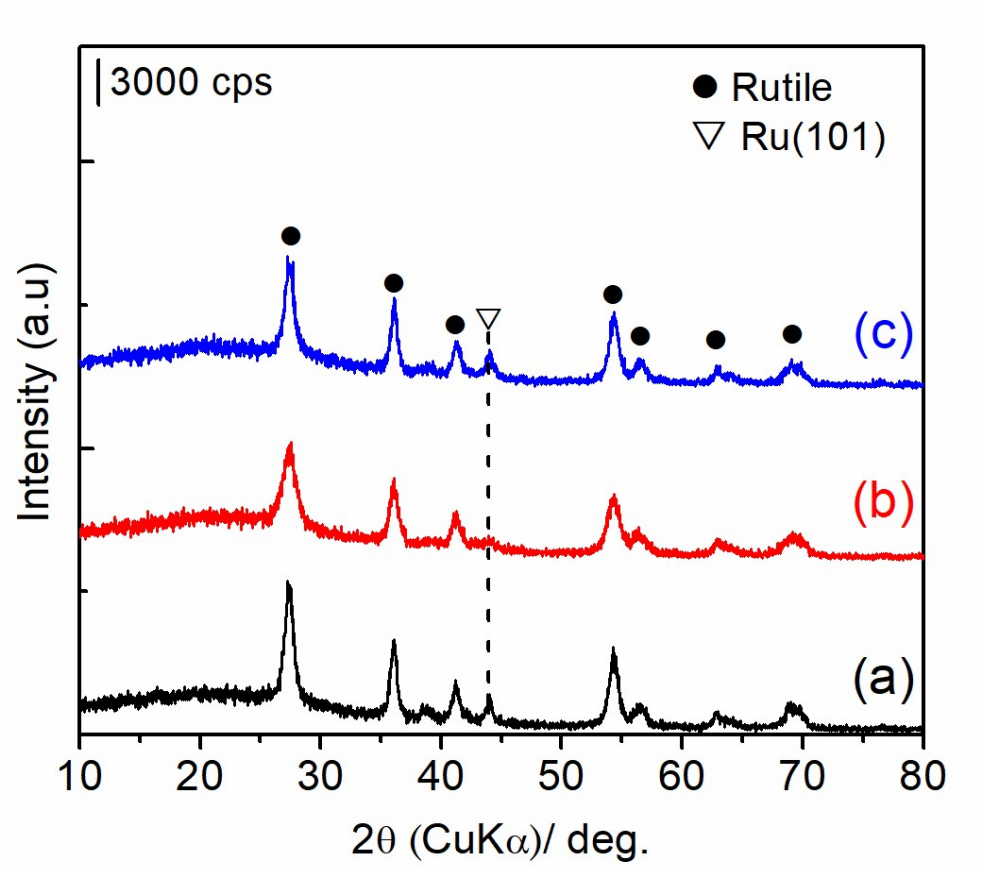

Fig. S1 XRD pattern of (*op*)Ru@C-TiO_2 catalysts with different amount of carbon doping ((a) 1.0 wt%, (b) 2.0 wt%, (c) 3.0 wt%) after reduction with H_2 at 400 ^oC for 2 h.

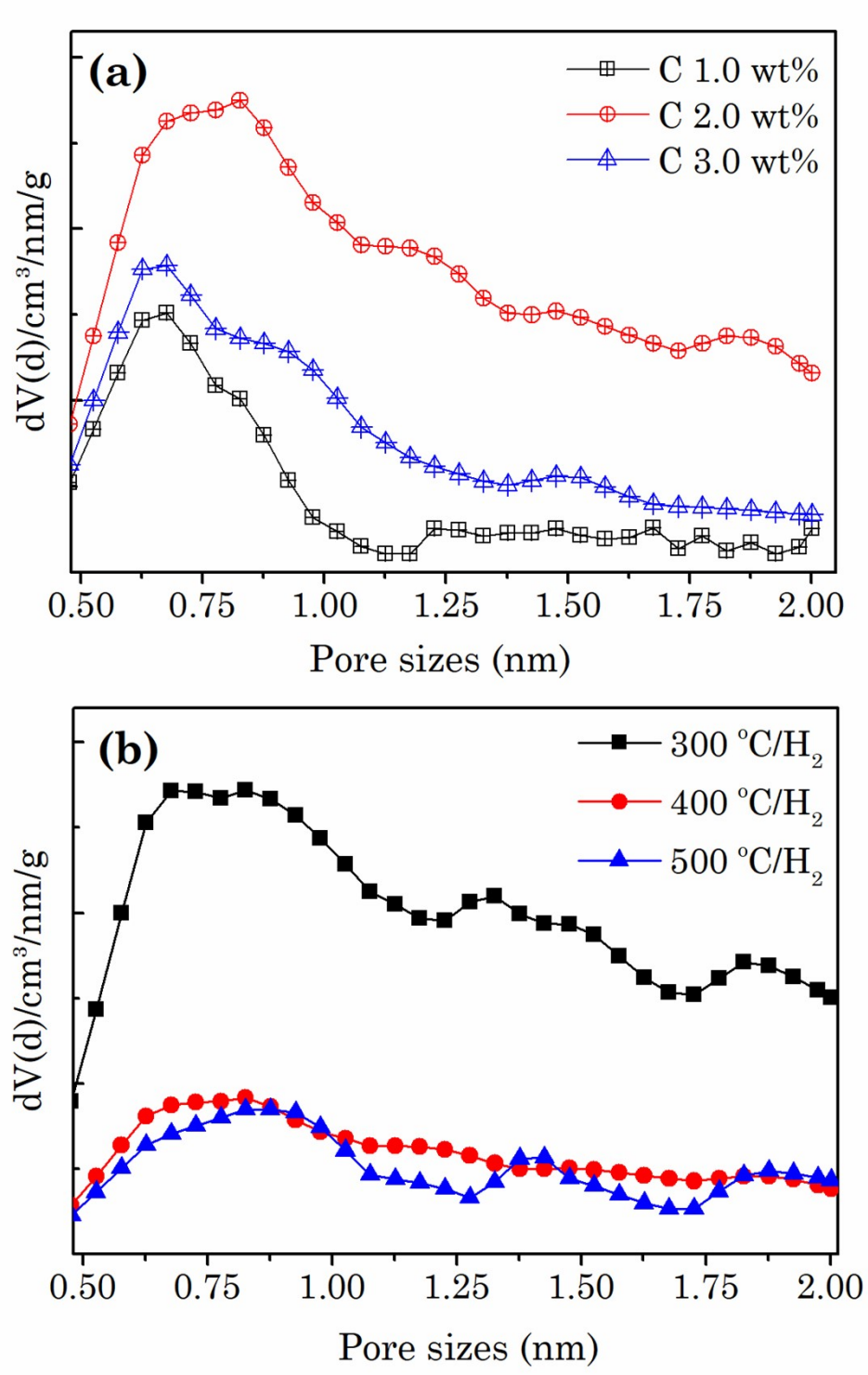

Fig. S2 Pore sizes distribution calculated by using Hovartz-Kawazoe (HK) method for (*op*)Ru@C-TiO_2 sample with (a) different amount of C-doping and (b) different reduction temperature with H_2 for 2 h.

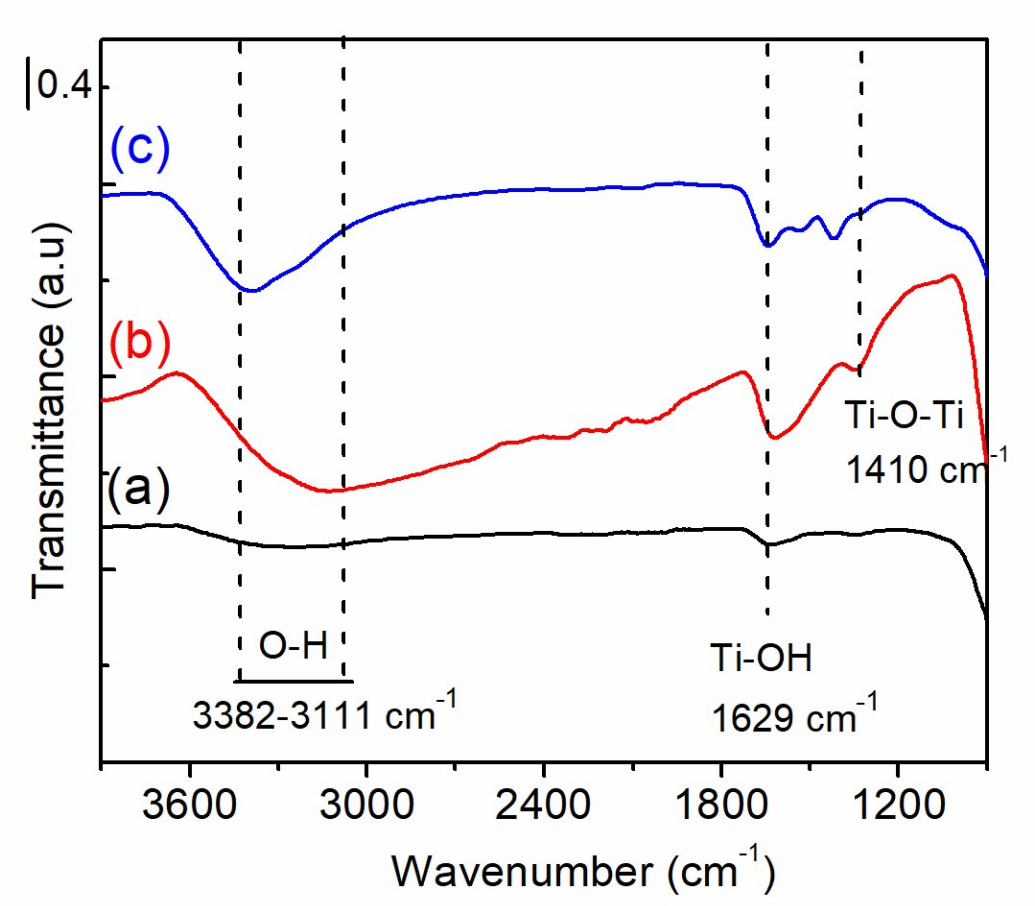

Fig. S3 ATR-IR spectra of (a) @TiO_2, (b) @C-TiO_2 (2.0 wt%), and (c) (*op*)Ru@C-TiO_2 (2.0 wt%) catalysts after drying at room temperature.

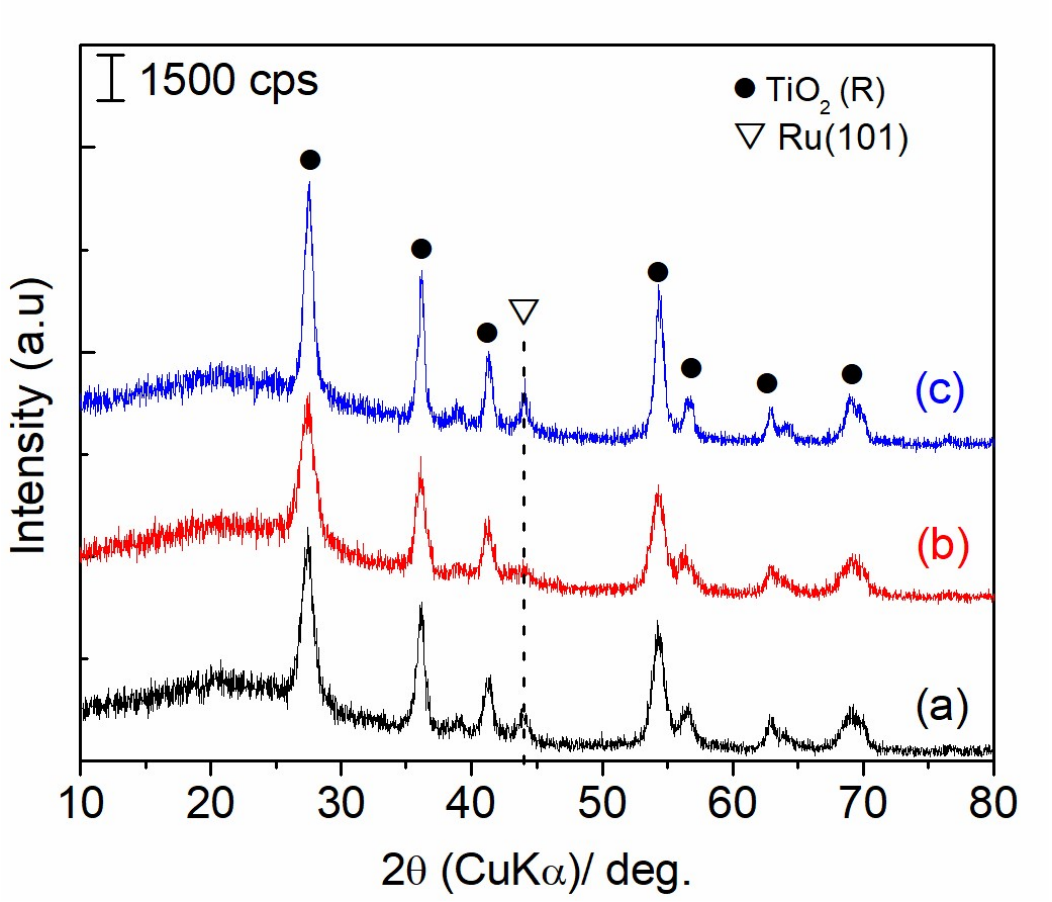

Fig. S4 XRD patterns of (op)Ru@C-TiO2 (C = 2.0 wt%) after reduction with H_2 at different temperatures of (a) 300 °C, (b) 400 °C, and (c) 500 °C for 2 h.

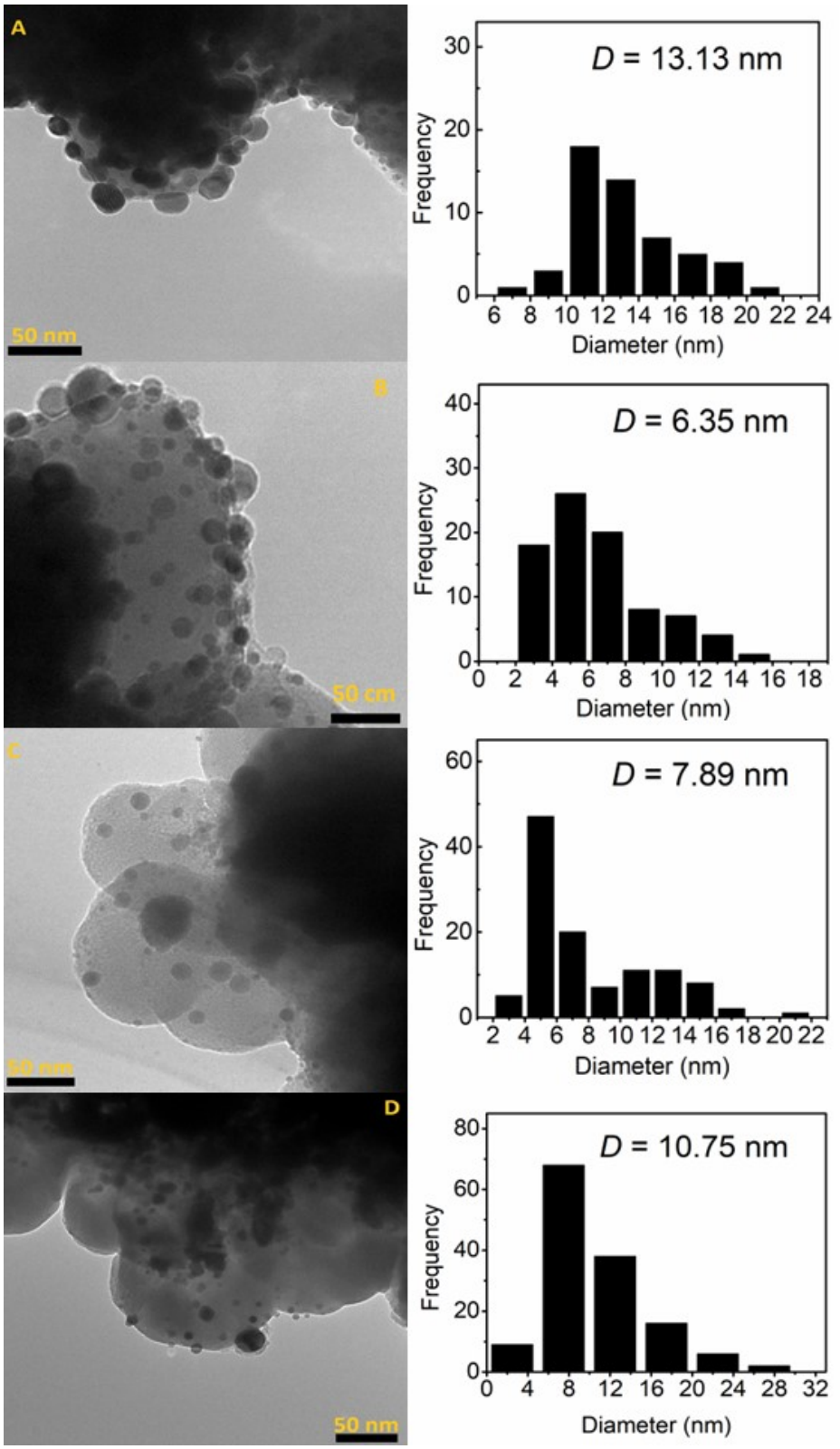

Fig. S5 TEM analysis of (*op*)Ru@C-TiO_2 (2.0 wt%) catalysts after reduction with H_2 at (a) 300 °C, (b) 400 °C and (c) 500 °C for 2 h, and (d) recovered (*op*)Ru@C-TiO_2 400 °C/H_2 catalyst.

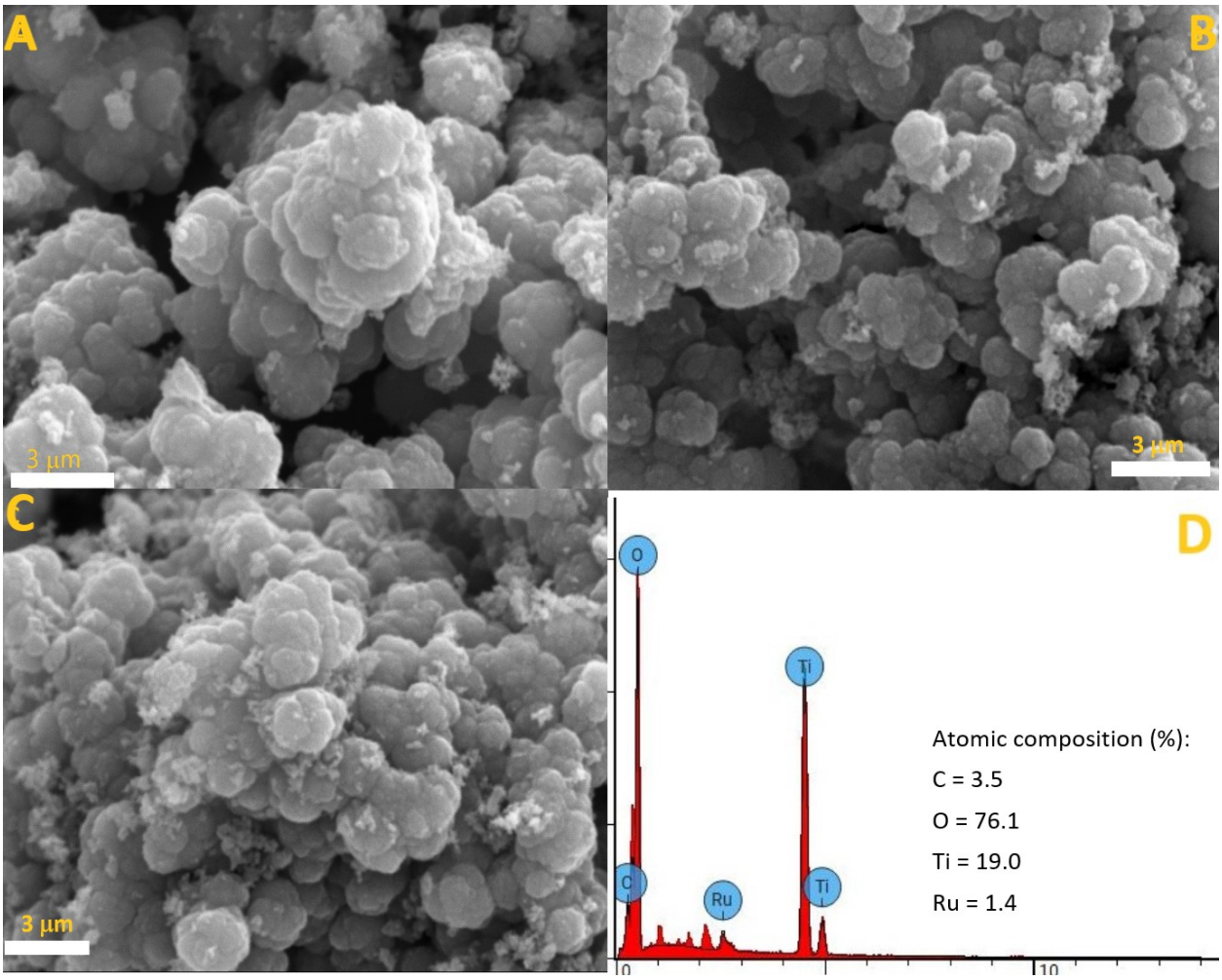

Fig. S6 SEM analysis of (*op*)Ru@C-TiO_2 with different amount of C-doping (a) 1.0 wt%; (b) 2.0 wt%) and (c) 3.0 wt%, and (d) typical EDS spectra of (*op*)Ru@C-TiO_2 (1.0 wt%) catalysts after reduction with H_2 at 400 ^oC for 2 h.

Table S1 Overall carbon content and bulk composition (%) of synthesised Ru@C-TiO_2 catalyst

Entry	Sample	Ru[a] (wt%)	Ti[a] (wt%)	C[b] (wt%)
1	(*op*)Ru@C-TiO_2 (1.0 wt%)	4.91	53.12	0.29
2	(*op*)Ru@C-TiO_2 (2.0 wt%)	4.92	50.23	1.05
3	(*op*)Ru@C-TiO_2 (3.0 wt%)	4.89	51.72	1.72
4	(*cop*)Ru@C-TiO_2	4.54	57.21	1.17

[a]The bulk composition (%) was determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). [b]Overall carbon contents were obtained by performing an elemental analysis.

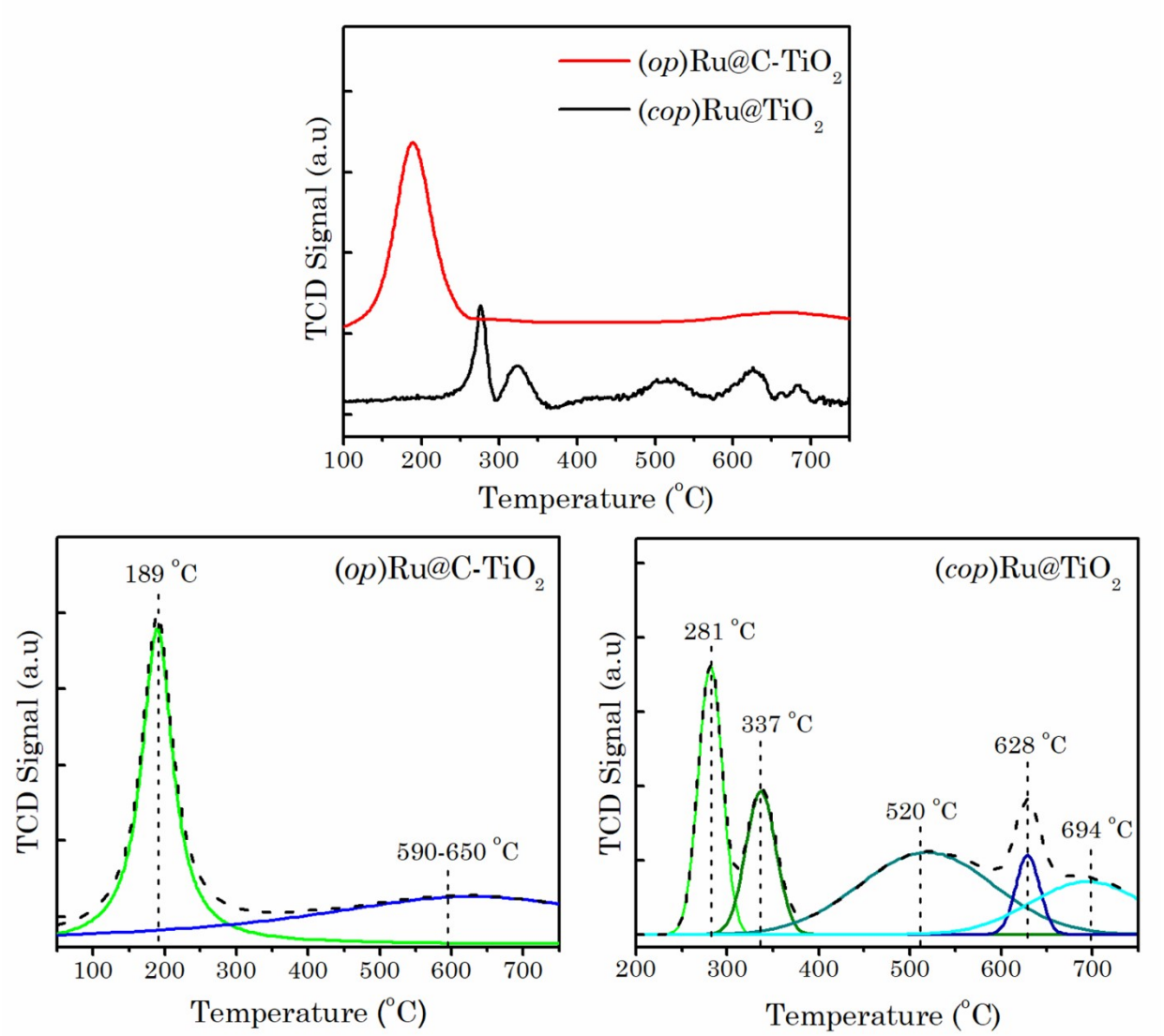

Fig. S7 The H_2-TPR profiles of Ru@TiO_2 and (*op*)Ru@C-TiO_2 (2.0 wt%) catalysts and their deconvoluted spectra.

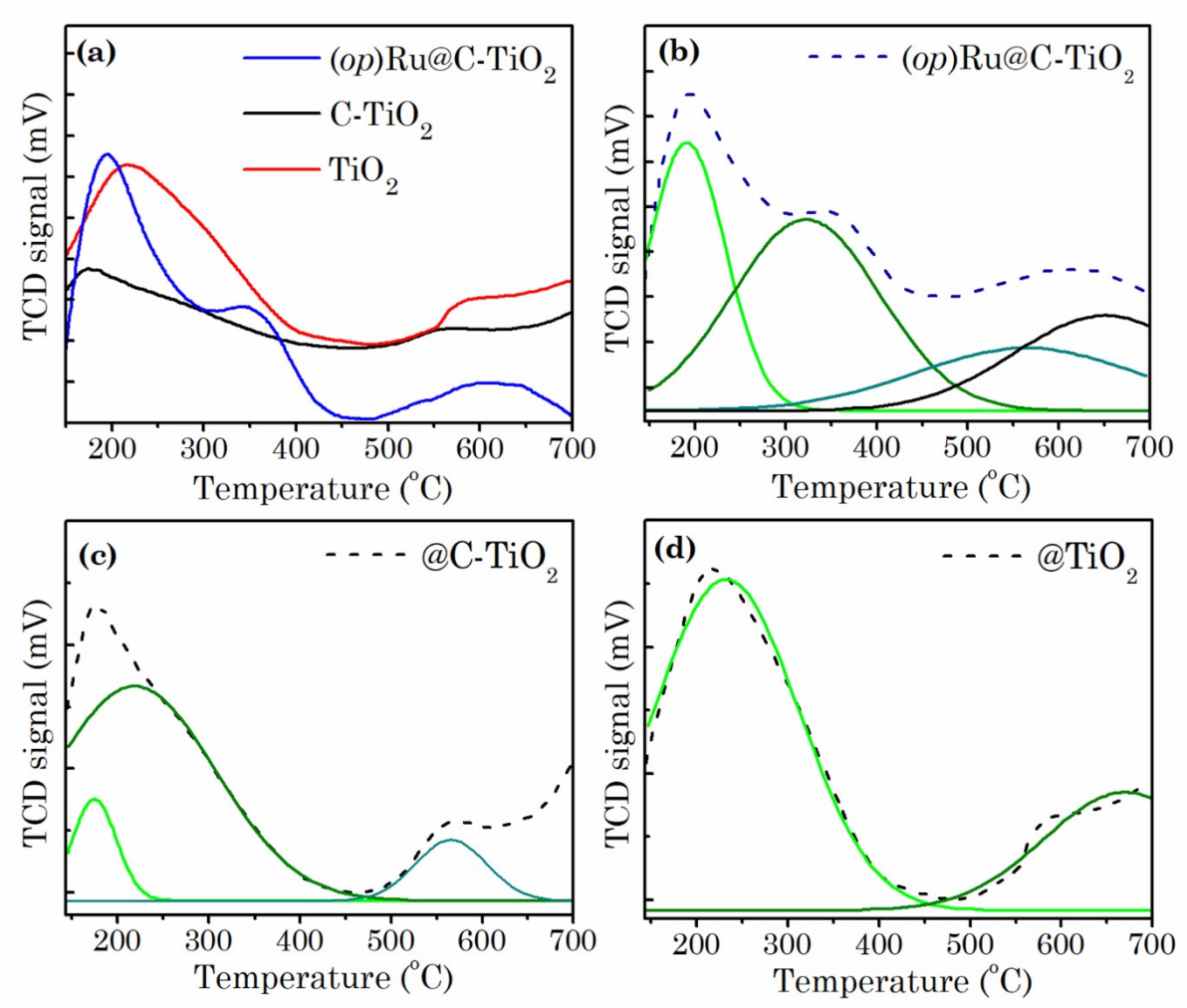

Fig. S8 NH_3-TPD spectra of @TiO_2, @C-TiO_2 supports and (*op*)Ru@C-TiO_2 (2.0 wt%) catalysts and their deconvoluted spectra.

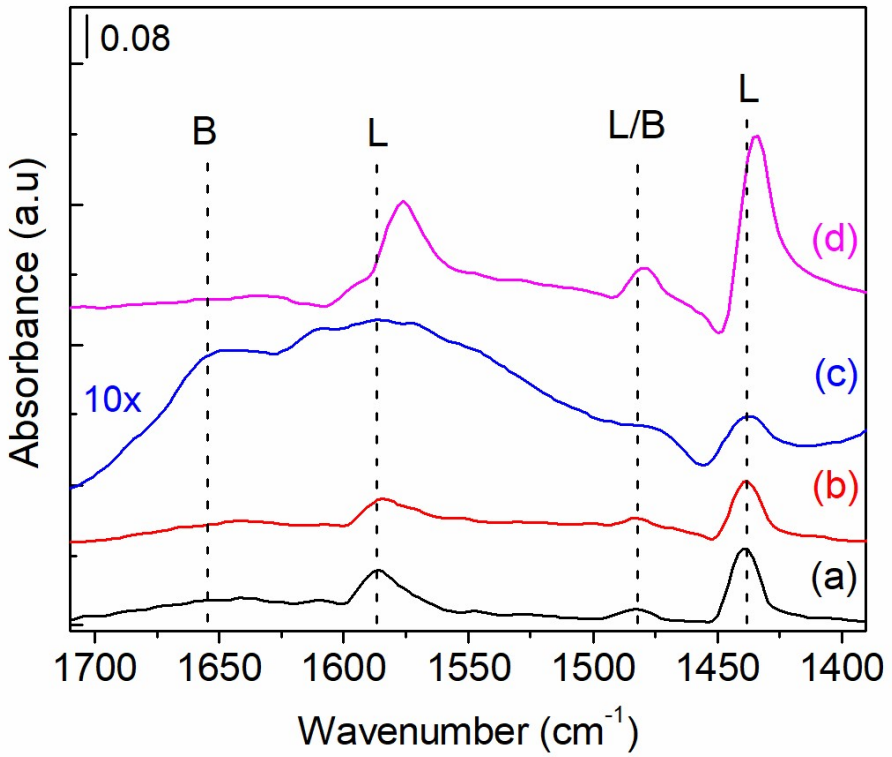

Fig. S9 ATR-IR spectra of adsorbed pyridine on the surface of (a) (*cop*)Ru@TiO_2 (*op*)Ru@C-TiO_2 (1.0 wt%), (c) (*op*)Ru@C-TiO_2 (2.0 wt%), and (d) (*op*)Ru@C-TiO_2 (3.0 wt%) catalysts.

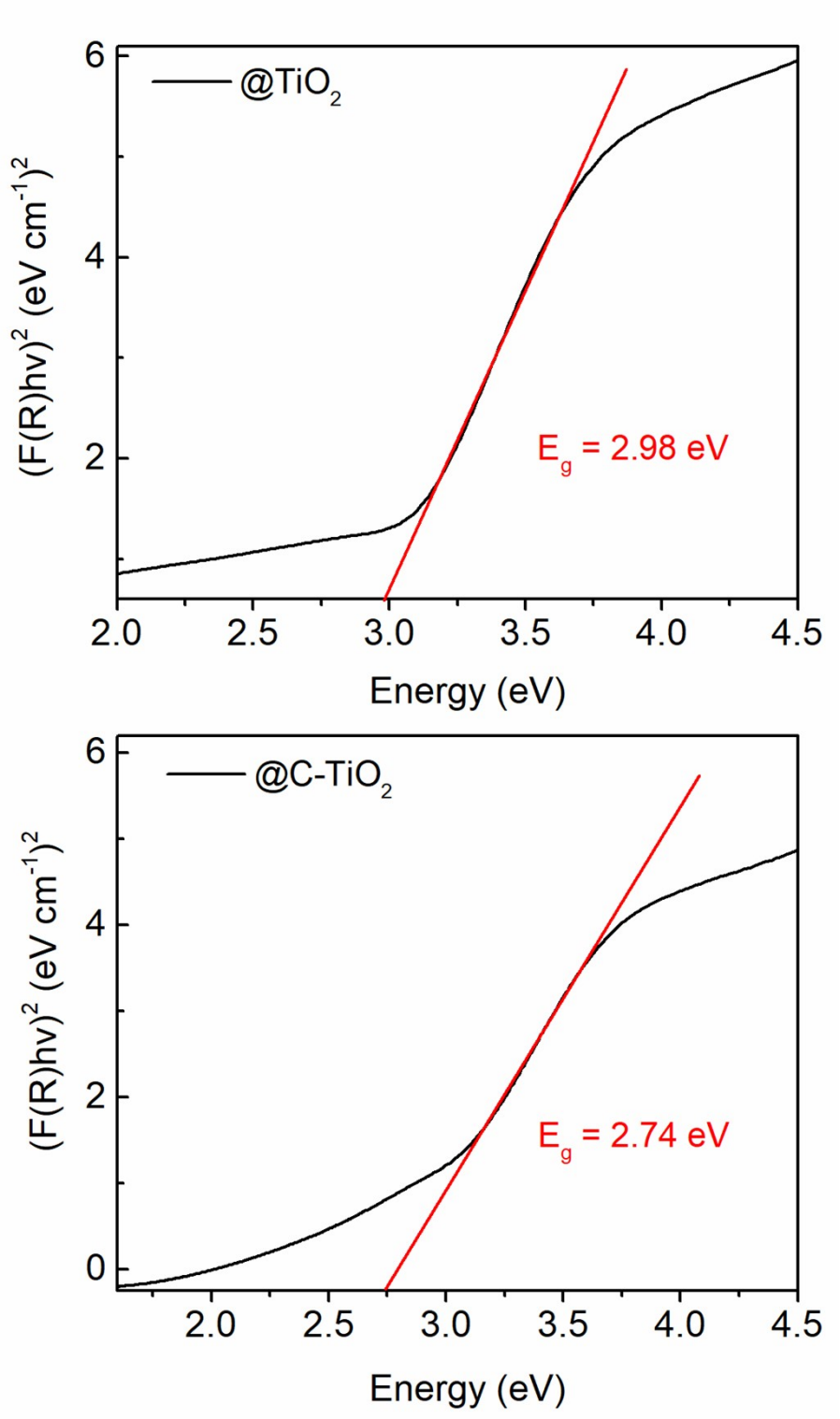

Fig S10. The Kubelka-Munk profiles of (a) @TiO_2 and (b) @C-TiO_2 powders derived from UV-Vis DRS spectra.

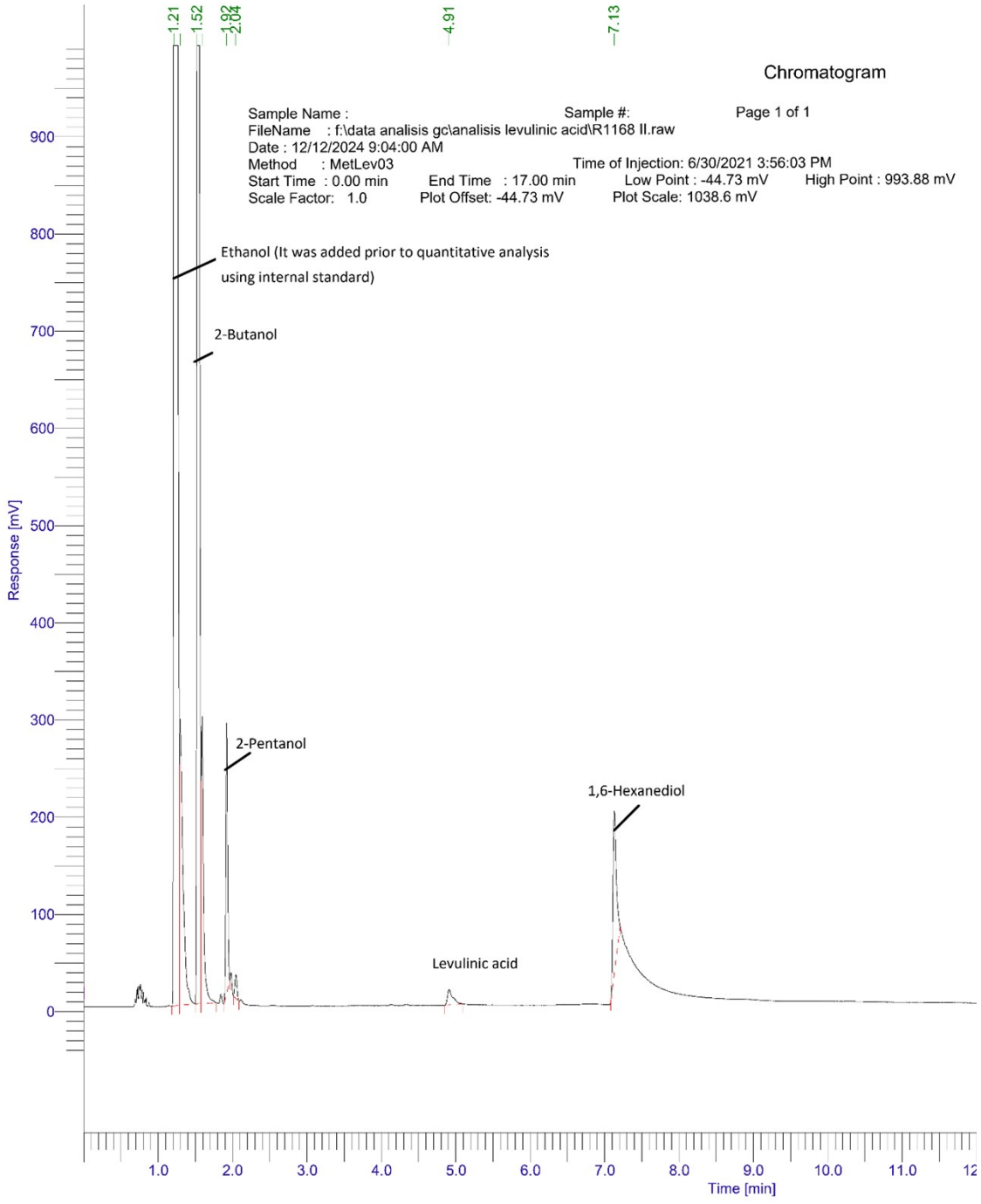

Fig. S11 GC chart of reaction mixture obtained from LA reaction using (*op*)Ru@C-TiO_2 (2.0 wt%) catalyst at 200 ^{o}C, H_2 30 bar after 180 min.

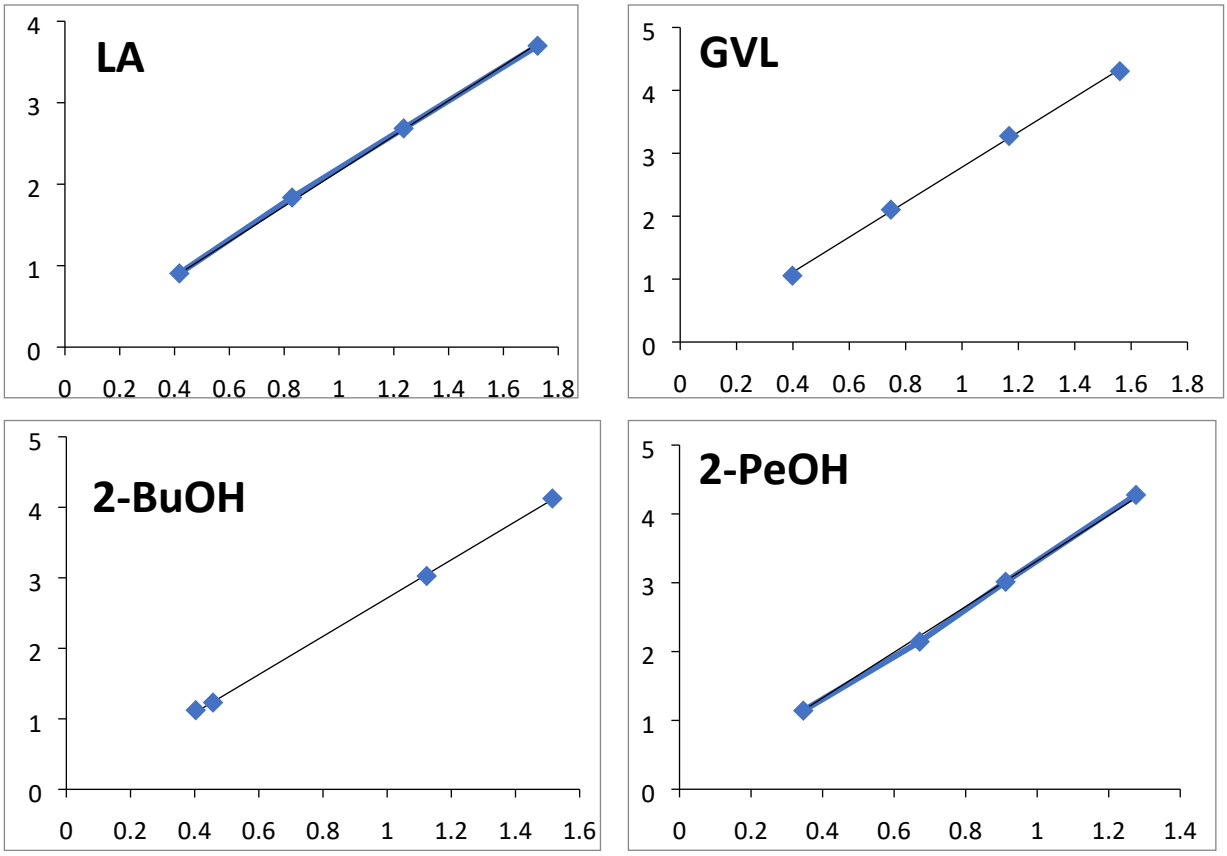

Fig. S12 Calibration curves of reactant (LA) and products (GVL, 2-BuOH, and 2-PeOH) to obtain their response factors.

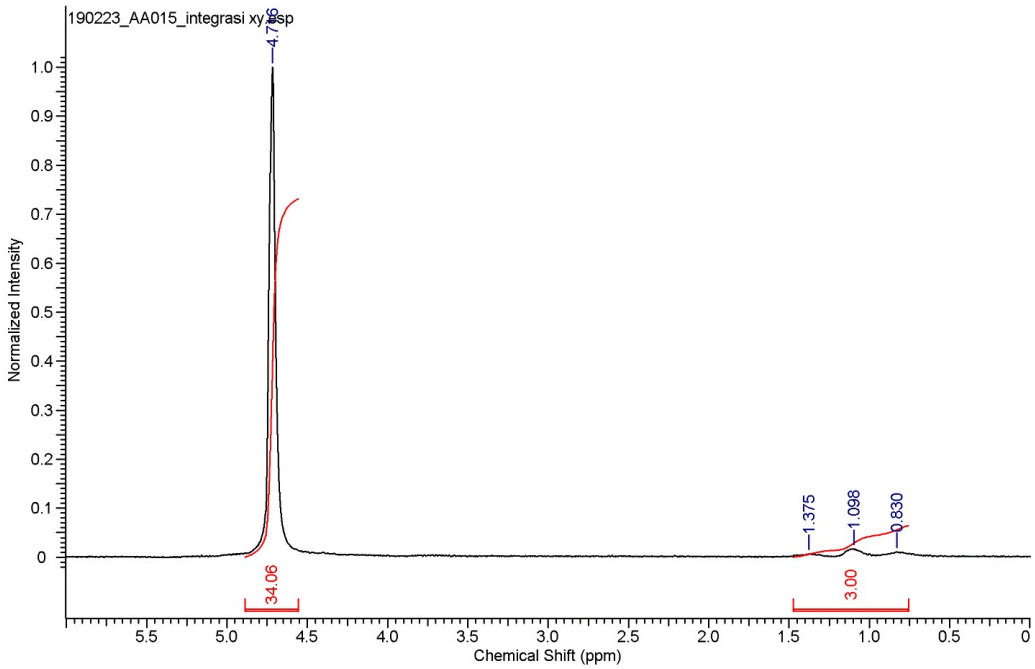

Fig. S13 ^{1}H-NMR spectra of reaction mixture obtained from LA reaction to 2-BuOH in D_2O solvent using (*op*)Ru@C-TiO_2 (2.0 wt%) catalyst at 200 ^{o}C, H_2 30 bar after 3 h.

Table S2 Results of LA catalytic conversion over various supported Ru-based catalysts

Entry	Catalyst	Conv.[a] (%)	Yield[a](%)				
			2-BuOH	2-PeOH	1,4-PeD	GVL	Others[b]
1	(*op*)Ni@C-TiO_2	100	2	0	6	85	8
2	(*op*)Cu@C-TiO_2	41	0	0	4	31	6
3	(*op*)Co@C-TiO_2	34	4	0	26	4	0
4	Ru/ZrO_2	97	11	0	10	74	2
5	Ru/γ–Al_2O_3	100	25	0	5	36	27
6	Ru/Al_2O_3-500	100	32	0	1	58	15
7	Ru-Sn/γ–Al_2O_3	100	0	0	0	98	2
8	Ru-Sn/C	100	1	0	31	63	5
9	Ru-Ni/C	100	1	0	0	88	11
10	Ru-MoOx/C	100	2	0	0	83	15
11	Ru-MoOx/TiO_2	86	2	0	0	78	6
12	Ru-MoOx/SiO_2	100	1	0	0	95	4
13	@C-TiO_2	30	0	0	0	0	30
14	@TiO_2	23	0	0	0	0	23

Reaction conditions: catalyst (50 mg), LA (2 mmol), H_2O (3 mL), 200 °C, 30 bar H_2, 3 h. [a]Conversion of LA and Yield of products were determined by GC using an internal standard technique. [b]Others (include 2-methyltetrahydrofuran (2-MeTHF) and 1-Pentanol (1-PeOH)) were determined by GC using total area to the LA conversion. 2-BuOH = 2-Butanol. 2-PeOH = 2-Pentanol. 1,4-PeD = 1,4-Pentanediol. GVL = γ–Valerolactone.

Table S3. Effect of catalyst dosage on the conversion of LA to 2-BuOH.

Entry	Catalyst dosage (g)	LA/Ru (molar ratio)[a]	Conv.[b] (%)	Yield[b](%)				
				2-BuOH	2-PeOH	1,4-PeD	GVL	Others[c]
1	0.0522	75	100	87	11	0	2	0
2	0.0251	159	100	37	11	0	40	12
3	0.0126	324	100	2	0	0	93	5

Reaction conditions: catalyst = (*op*)Ru@C-TiO_2 (2.0 wt%) 400 °C/H_2, LA (2 mmol), solvent (3 mL), 200 °C, 30 bar H_2, 3 h. [a]The molar ratio of reactant to catalyst was estimated based on the rough amount of Ru precursor in the (*op*)Ru@C-TiO_2. [b]Conversion of LA and yield of products were determined by GC using an internal standard technique. [c]Others (include 2-methyltetrahydrofuran (2-MeTHF) and 1-Pentanol (1-PeOH)) were determined by GC using total area to the LA conversion. 2-BuOH = 2-Butanol. 2-PeOH = 2-Pentanol. 1,4-PeD = 1,4-Pentanediol. GVL = γ–Valerolactone.