

## Electronic Supplementary Information (ESI)

### Catalytic transfer hydrogenation of levulinate esters to $\gamma$ -valerolactone over supported ruthenium hydroxide catalysts

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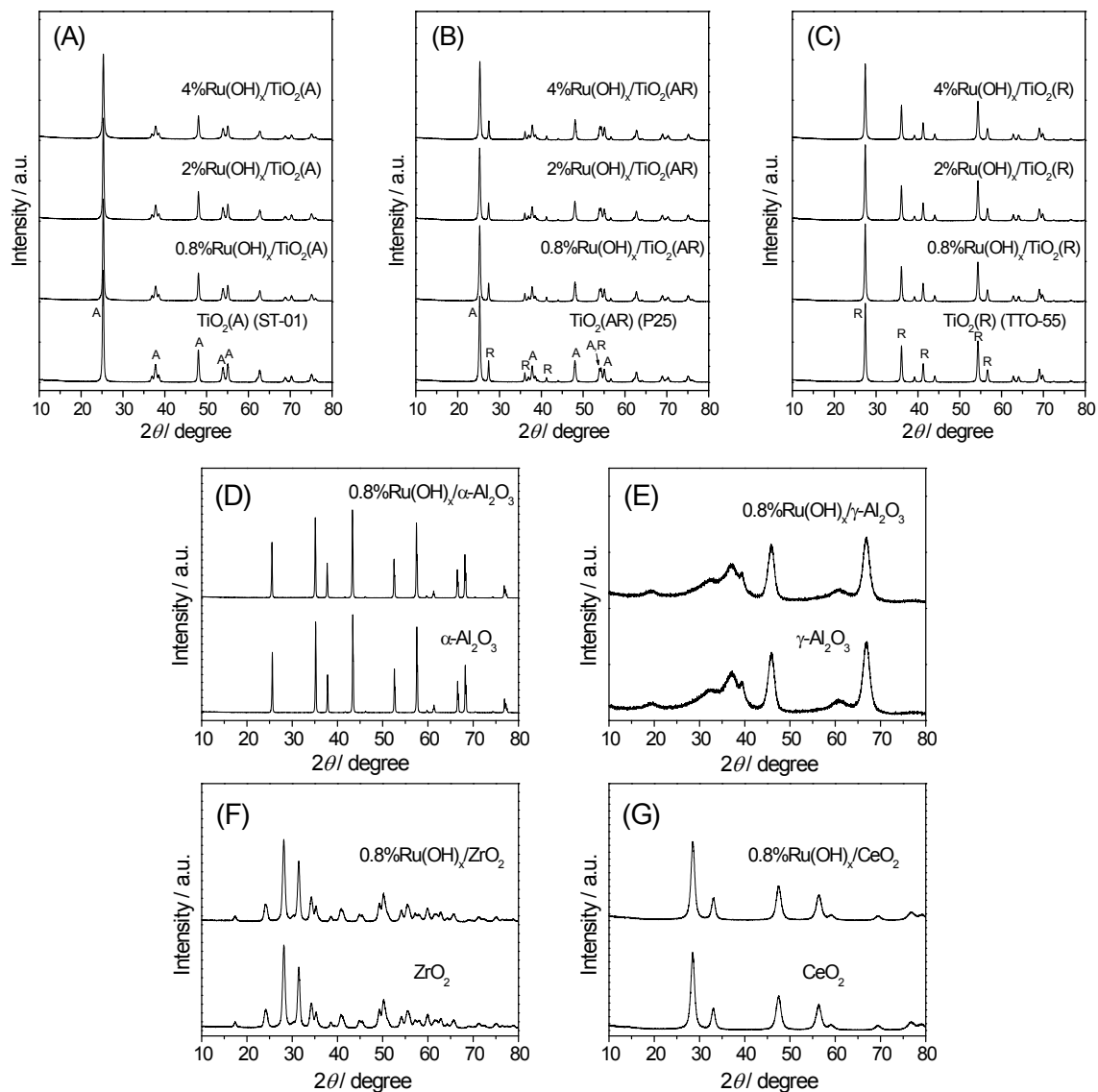
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## Characterization

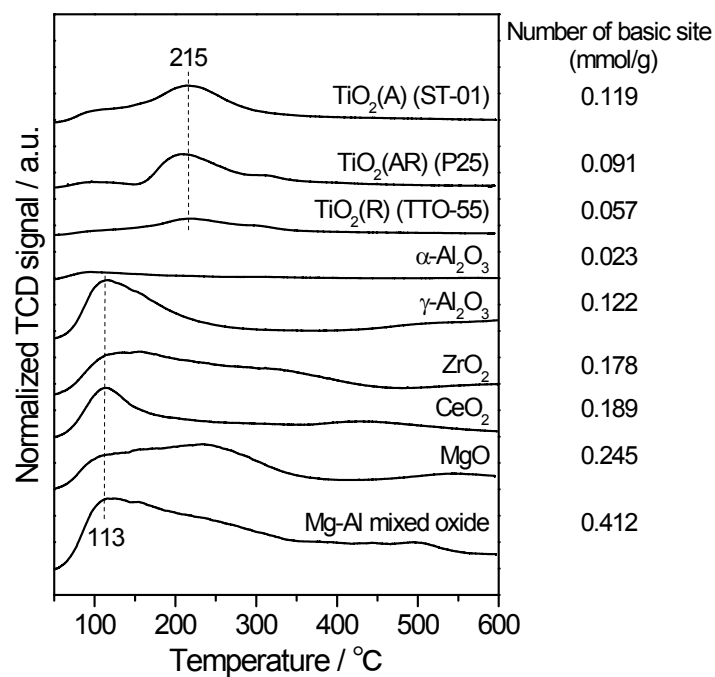
**CO<sub>2</sub>-TPD:** The basicity of the support oxides was studied by temperature programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) by using a BELCAT-B system (BEL Japan, Inc.). Approximately 100 mg of each sample was mounted in a quartz tube and was preheated under a He flow (50 mL/min) at 600 °C for 1 h, allowed to cool to 50 °C, and subsequently exposed to flowing CO<sub>2</sub> (50 mL/min) for 1 h. After being purged at 50 °C for 0.5 h with He to eliminate weakly-adsorbed CO<sub>2</sub>, CO<sub>2</sub>-TPD was carried out between 50 and 600 °C under a He flow (30 mL/min) with a ramping rate of 10 °C/min, and the desorbed CO<sub>2</sub> was quantified by an on-line thermal conductivity detector.

**In-situ FTIR:** FTIR spectroscopy was performed by using a Cary 670-IR (Agilent technology, Inc.) instrument with a D-TGS detector in the spectral range 4000–1000 cm<sup>-1</sup>. For in situ FTIR spectroscopy of 2-propanol adsorption/desorption, 10 mg of sample was pressed into a self-supported wafer (diameter: 10 mm) prior to analysis. The wafer was loaded into a high-vacuum transmission FTIR cell and was heated to 90 °C in a flow of He (100 mL/min) for 1 h, and the baseline spectrum was collected. After exposing to a flow of 25 mbar 2-propanol in He (100 mL/min) for 1 h, FTIR difference spectra of 2-propanol adsorbed on the sample were obtained under flushing in He flow (100 mL/min) by subtracting the baseline spectrum from the 2-propanol-adsorbed spectrum.

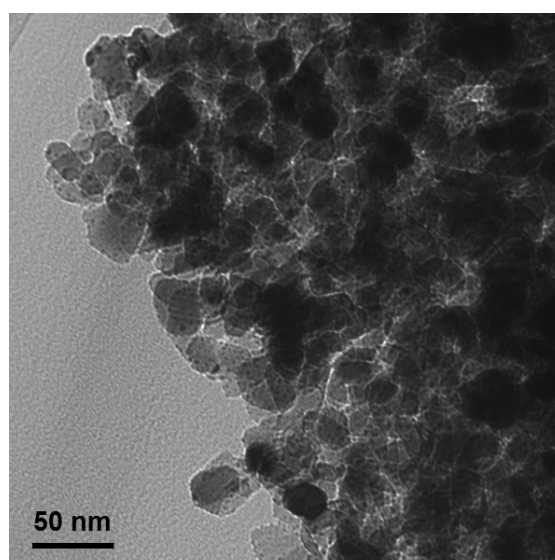
**TEM observation:** TEM images were obtained with a Hitachi HF-2000 TEM operated at 200 kV. The sample was suspended in EtOH using ultrasound, and then a droplet of the suspension was dried on a carbon grid.



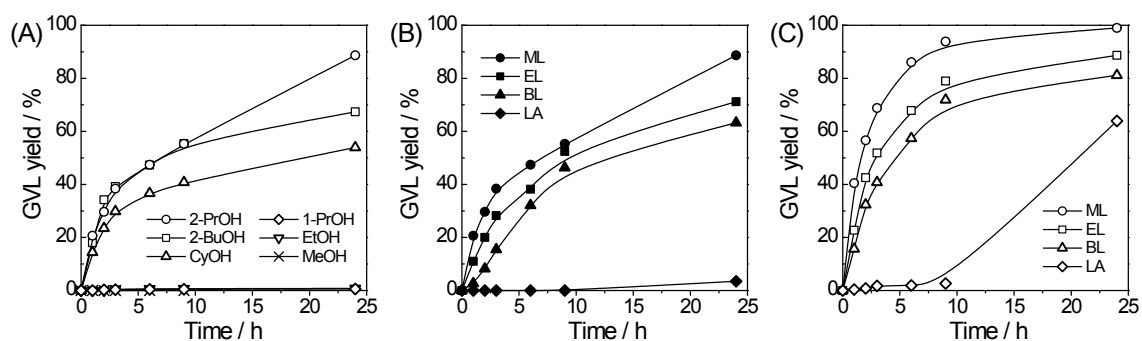
**Fig. S1** X-ray diffraction patterns of (A) Ru(OH)<sub>x</sub>/TiO<sub>2</sub>(A), (B) Ru(OH)<sub>x</sub>/TiO<sub>2</sub>(AR), (C) Ru(OH)<sub>x</sub>/TiO<sub>2</sub>(R) with varied Ru content (0.8–4 wt.%), (D) 0.8%Ru(OH)<sub>x</sub>/α-Al<sub>2</sub>O<sub>3</sub>, (E) 0.8%Ru(OH)<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, (F) 0.8%Ru(OH)<sub>x</sub>/ZrO<sub>2</sub>, (G) 0.8%Ru(OH)<sub>x</sub>/CeO<sub>2</sub>. Several diffraction planes associated with anatase and rutile TiO<sub>2</sub> crystals are indicated as “A” and “R”, respectively.



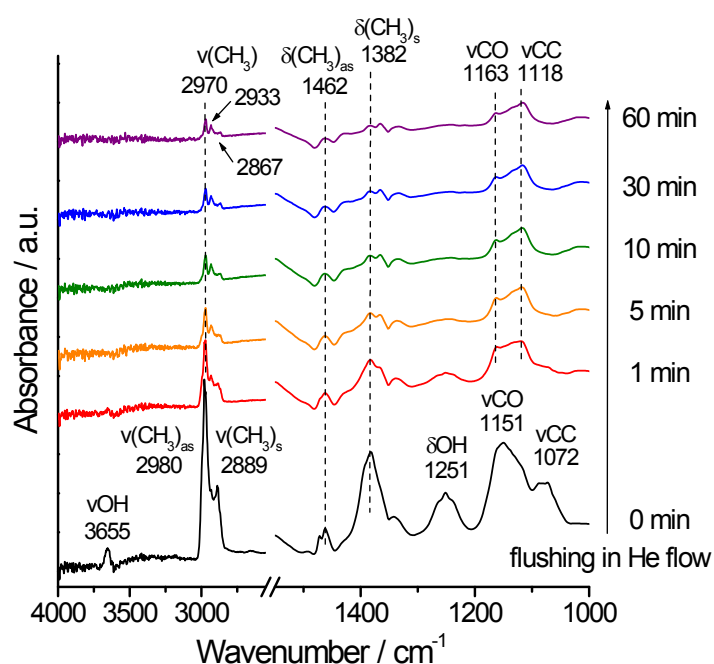
**Fig. S2** CO<sub>2</sub>-temperature programmed desorption profiles of oxide supports. The number of basic sites was quantified based on TCD signals from 50 to 600 °C. The peaks seen at around 113 and 215 °C are attributable to CO<sub>2</sub> adsorbed on weak and medium basic sites, respectively.



**Fig. S3** TEM image of 4%Ru(OH)<sub>x</sub>/TiO<sub>2</sub>(A) catalyst.

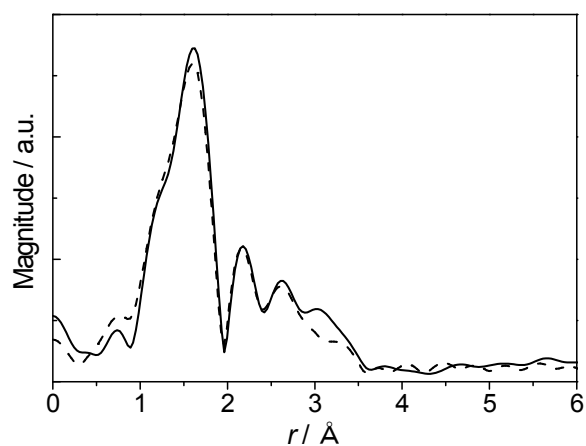


**Fig. S4** Reaction kinetics in (A) the CTH reaction of methyl levulinate (ML) with various alcohols as hydrogen donors and 0.8 mol% Ru catalyst, (B) the CTH reaction of levulinate esters and levulinic acid with 2-propanol and 0.8 mol% Ru catalyst and (C) the CTH reaction of levulinate esters and levulinic acid with 2-propanol and 4.0 mol% Ru catalyst. Reaction conditions: catalyst ( $4\%Ru(OH)_x/TiO_2(A)$ ), substrate (1 mmol), alcohol (5 mL),  $90\text{ }^\circ\text{C}$ , Ar.



**Fig. S5** In situ FTIR difference spectra of the adsorption complexes formed by the adsorption of 2-propanol on  $4\%Ru(OH)_x/TiO_2(A)$  as a function of flushing time in He flow at  $90\text{ }^\circ\text{C}$ . The sample was preheated at  $90\text{ }^\circ\text{C}$  in He flow for 1 h and exposed to a flow of 25 mbar 2-propanol vapor in He at  $90\text{ }^\circ\text{C}$  for 1 h.

The IR spectrum taken at 0 min showed diagnostic absorption bands of free 2-propanol molecules:  $\nu\text{OH}$ ,  $3655\text{ cm}^{-1}$ ;  $\nu(\text{CH}_3)_{\text{as}}$ ,  $2980\text{ cm}^{-1}$ ;  $\nu(\text{CH}_3)_{\text{s}}$ ,  $2889\text{ cm}^{-1}$ ;  $\delta(\text{CH}_3)_{\text{as}}$ ,  $1462\text{ cm}^{-1}$ ;  $\delta(\text{CH}_3)_{\text{s}}$ ,  $1382\text{ cm}^{-1}$ ;  $\delta\text{OH}$ ,  $1251\text{ cm}^{-1}$ ;  $\nu\text{CO}$ ,  $1151\text{ cm}^{-1}$ ;  $\nu\text{CC}$ ,  $1072\text{ cm}^{-1}$  (M. I. Zaki, M. A. Hasan and L. Pasupulety, *Langmuir*, 2001, **17**, 4025). The disappearance of the absorption bands at  $3655$  and  $1251\text{ cm}^{-1}$  after He flushing indicates the desorption of 2-propanol molecules weakly adsorbed on the surface. After He flushing, some absorption bands associated with the adsorption complexes formed by 2-propanol adsorption were observed; the absorption bands assignable to the C–H stretching vibration modes were seen at  $2970$ ,  $2933$ , and  $2867\text{ cm}^{-1}$ , which slightly shifted to lower wavenumbers compared to those of free 2-propanol molecule. These bands together with bands at around  $1163$  and  $1118\text{ cm}^{-1}$  (assignable to C–O/C–C coupled stretching) are characteristic of isopropoxyl groups (M. I. Zaki and N. Sheppard, *J. Catal.* 1983, **80**, 114), which slightly shifted to higher wavenumbers compared to those of free 2-propanol molecule. These results indicate that deprotonation of 2-propanol to form metal-bound 2-propoxide species occurs at  $90\text{ }^\circ\text{C}$  on  $4\%\text{Ru}(\text{OH})_x/\text{TiO}_2(\text{A})$  surface.



**Fig. S6** Ru K-edge radial distribution functions of  $4\%\text{Ru}(\text{OH})_x/\text{TiO}_2(\text{A})$  catalyst before (solid line) and after (dashed line) the catalytic use in alcohol at  $90\text{ }^\circ\text{C}$ . The radial structure function was obtained by fourier transformation of  $k^3$ -weighted normalized EXAFS data over the range  $3.0 < k(\text{Å}^{-1}) < 11.0$ . The peaks observed at around  $r=1.6$  and  $2.7\text{ Å}$  correspond to Ru–O and Ru··Ru bonds, respectively.