Supporting information

Catalytic Transfer Hydrogenation of Oleic Acid into Octadecanol over Magnetic Recoverable Cobalt Catalysts

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Experimental Section

Materials and reagents

Oleic acid (99%), stearic acid (98%), octadecanol (98%), heptadecane (99%), octadecane(98%) were purchased from TCI, Japan. Isopropyl stearate (95%), metallic Co (AR), CoO (AR), Co_3O_4 (AR), stearyl stearate (98%) were purchased from Shanghai Macklin Biochemical Co. Ltd., China. $Co(NO_3)_2 \cdot 6H_2O$ (AR), $Fe(NO_3)_3 \cdot 9H_2O$ (AR), $Cu(NO_3)_2 \cdot 3H_2O$ (AR), $Ni(NO_3)_2 \cdot 6H_2O$ (AR), Na_2CO_3 (AR), NaOH (AR), isopropanol (AR), acetone (AR) was obtained from Sinopharm Chemical Reagent Co. Ltd., China. All the above chemicals were used as received without further purification.

Catalyst characterization

Powder X-ray diffraction (XRD) was carried out with Ni-filtered Cu Kα (λ=0.154 nm) operating at 40 kV and 30 mA on a PANalytical Empyrean 200895 diffractometer. X-ray photoelectron spectra (XPS) were collected on a Thermo Scientific ESCALab 250Xi using a 200 W monochromatic Al Kα radiation (hν=1486.6 eV). XPS measurement was carried out without exposure to air during the sample transfer. The binding energies for different spectrum were calibrated according to the C 1s line at 284.8 eV. Transmission electron microscopy (TEM) images were obtained on a field emission transmission electron microscope at 200 kV (TEM, TF 20, FEI Electron Optics Company, USA). The temperature-programmed reduction (TPR) was performed on FineSorb-3010 equipped with a thermal conductivity detector (TCD). In a typical

test, a certain amount of catalyst was pretreated at 120 °C for 60 min in an Ar flow of 20 mL/min and then cooled down to 60 °C. Subsequently, the sample was heated to 800 °C with the heating rate of 10 °C/min under 10% H_2/Ar (15 mL/min).

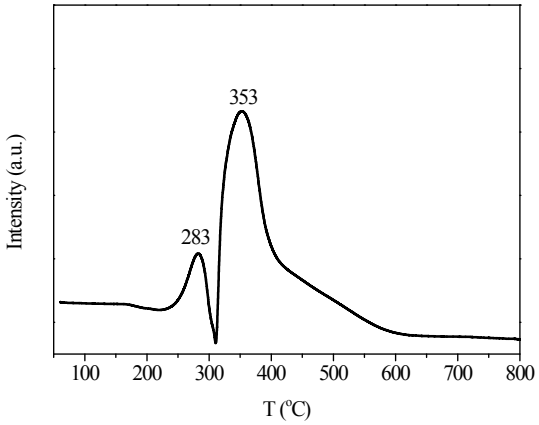

Fig. S1 H_2-TPR profile of the Co-O catalyst.

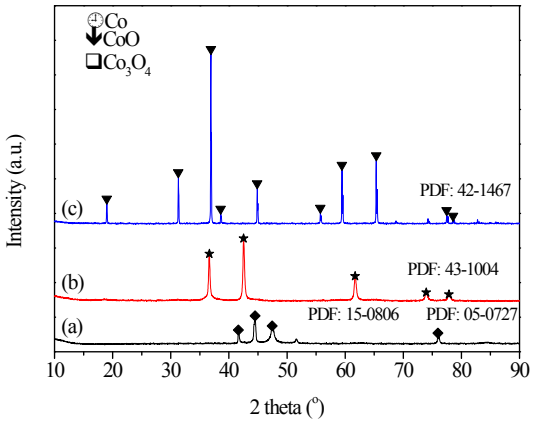

Fig. S2 XRD patterns of (a) commercial metallic cobalt, (b) commercial CoO and (c) commercial Co_3O_4.

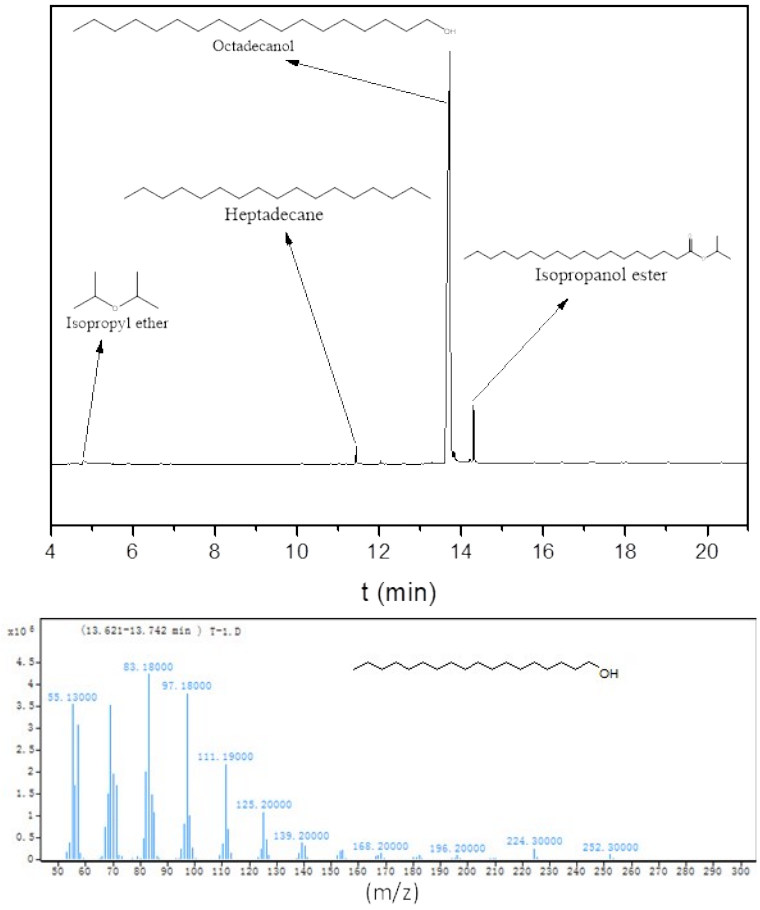

Fig. S3 GC-MS profiles of reaction mixture.

Reaction conditions: oleic acid (70 mg), Co-350 (10 mg), isopropanol (7 mL), 200 °C, 4 h.

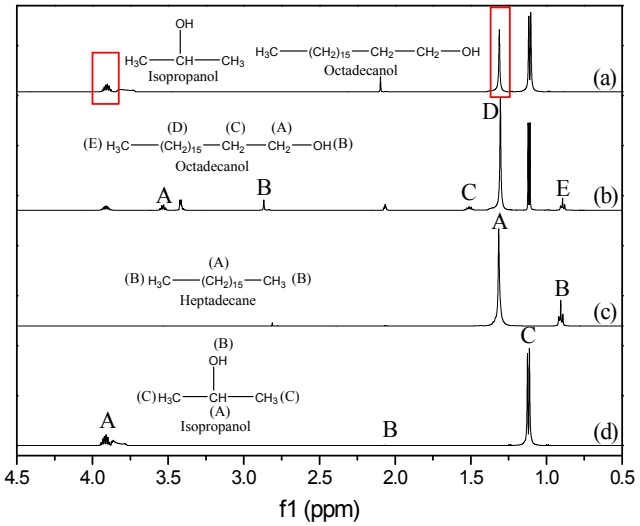

Fig. S4 ^{1}H-NMR spectra of (a) reaction solution, (b) octadecanol, (c) heptadecane and (d) isopropanol.

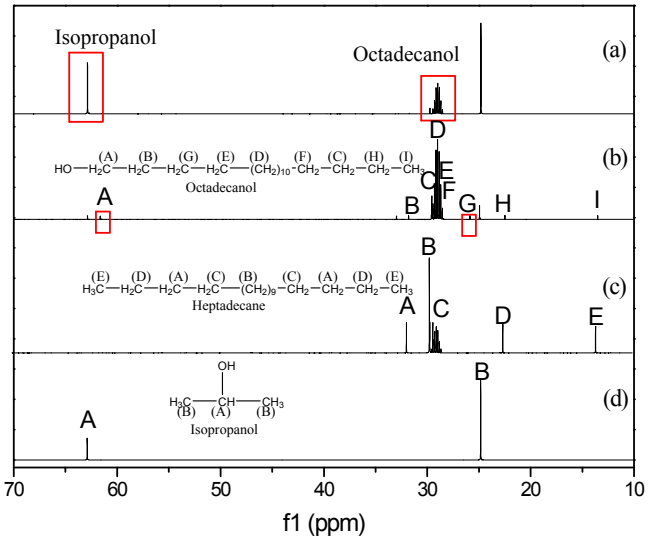

Fig. S5 ^{13}C-NMR spectra of (a) reaction solution, (b) octadecanol, (c) heptadecane and (d) isopropanol.

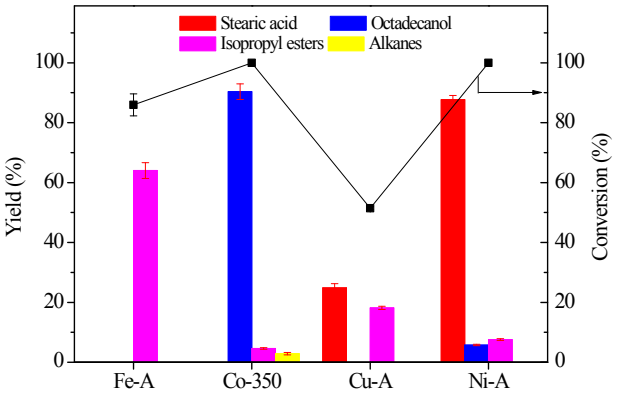

Fig. S6 Effect of metals to CTH of oleic acid.
Reaction conditions: oleic acid (70 mg), catalyst (10 mg), isopropanol (7 mL), 200 °C, 4 h.

Table S1 Representative works for the production of fatty alcohol without external hydrogen.

catalyst	Reaction conditions	Substrate	Product	Conv./%	Selec./%	Ref.
$Cu/ZnO/Al_2O_3$	242 °C, 30 mmol methanol + 4 mmol water, 2 mmol substrate, 50 mg catalyst, 20 h.	methyl laurate	lauryl alcohol	91.8	96.7	[1]
Cu/Al_2O_3	330 °C, 50 mg methanol + 0.5 mL water, 50 mg substrate, 15 mg catalyst, 3 h.	lauric acid	lauryl alcohol	98.9	99.0	[2]

Cu/MgO	330 °C, 50 mg methanol + 0.5 mL water, 50 mg substrate, 15 mg catalyst, 3 h.	lauric acid	lauryl alcohol	96.9	99.0	[2]
Cu/ZrO_2	330 °C, 50 mg methanol + 0.5 mL water, 50 mg substrate, 15 mg catalyst, 3 h.	lauric acid	lauryl alcohol	94.5	98.3	[2]
Ru-Sn-Mo-C	270 °C, 40 mL tetradecane + 56 mmol water, 28 mmol Fe, 4 mmol substrate, 43 mg catalyst, 0.1 MPa N_2, 24 h.	lauric acid	lauryl alcohol	98.0	59.2	[3]
Ni	300 °C, 2.28 mL water, 5 mmol Zn, 0.2 mmol substrate, 1 mmol catalyst, 2 h.	palmitic acid	hexadecanol	100	81.4	[4]
Cu/SiO_2	240 °C, 40 mL methanol, 0.3 g substrate, 0.2 g catalyst, 2 MPa N_2, 4 h.	methyl laurate	lauryl alcohol	85	100	[5]
Co-350	200 °C, 7 mL isopropanol, 70 mg substrate, 10 mg catalyst, 4 h	oleic acid	octadecanol	100	91.9	This study

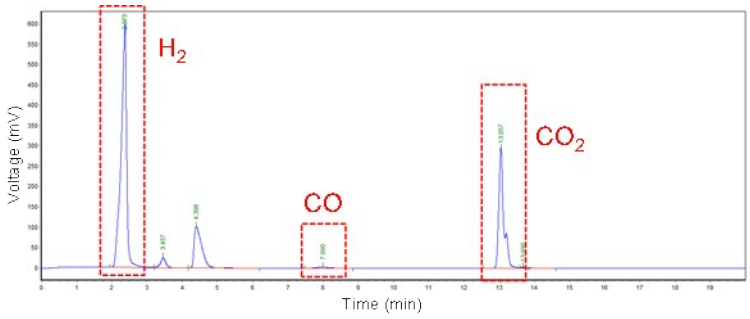

Fig. S7 GC-TCD analysis of gaseous phase.

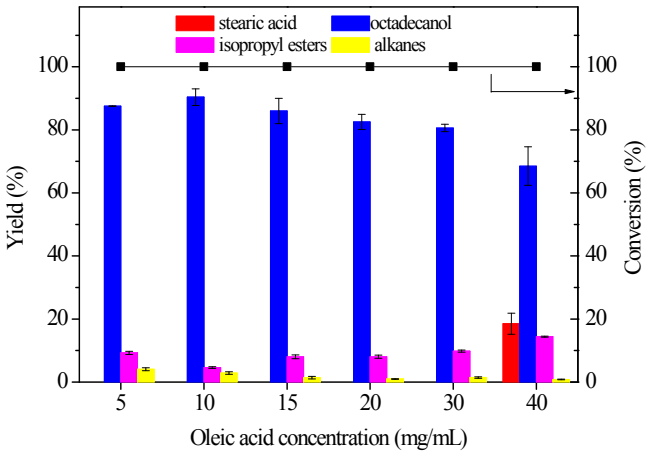

Fig. S8 Effect of substrate concentration to the CTH of oleic acid.
Reaction conditions: oleic acid, catalyst (10 mg), isopropanol (7 mL), 200 °C, 4 h.

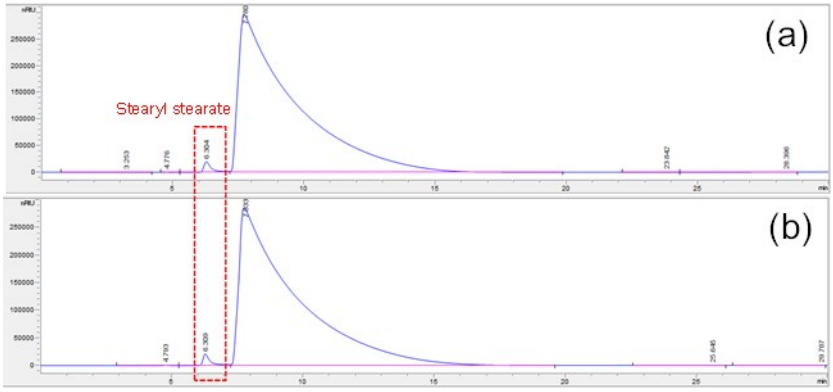

Fig. S9 HPLC profiles of (a) standard solution of stearyl stearate and (b) reaction mixture at 1h.

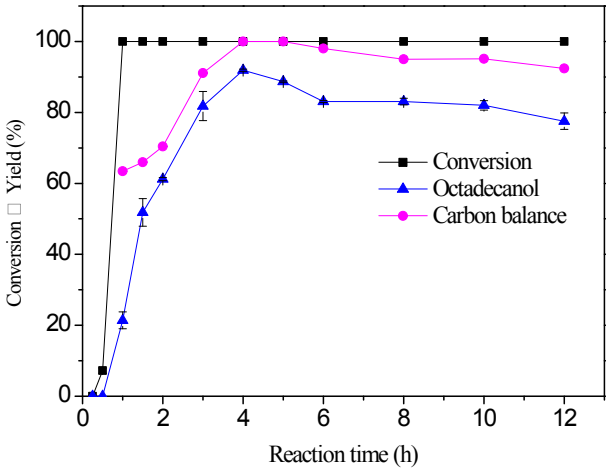

Fig. S10 Carbon balance plot for the reaction profile presented in Fig. 8. Carbon balance does not include stearyl stearate.

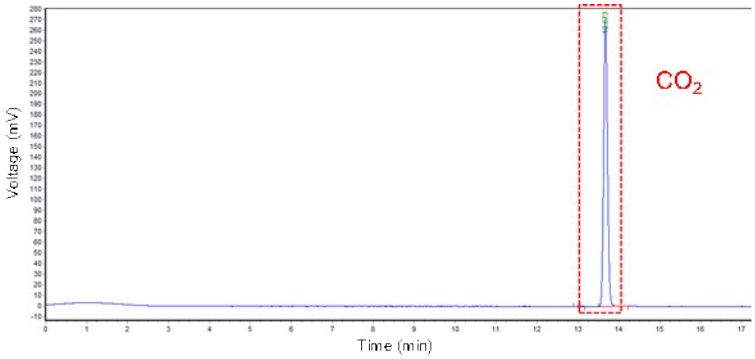

Fig. S11 GC-FID analysis of gaseous phase.

Table S2 Scale-up experiment for CTH of oleic acid over Co-350.

Entry	Catalysts	Conv. /%	Yield/%			
			Stearic acid	Octadecanol	Alkanes	Isopropyl esters
1[a]	Co-350	100	n.d	80.1	1.0	17.7
2[b]	Co-350	100	n.d	83.6	n.d	14.3

[a] Reaction conditions: Oleic acid (0.5 g), catalyst (70 mg), isopropanol (50 mL), 200 °C, 4 h. [b] Oleic acid (1.0 g), catalyst (140 mg), isopropanol (100 mL), 200 °C, 4h.

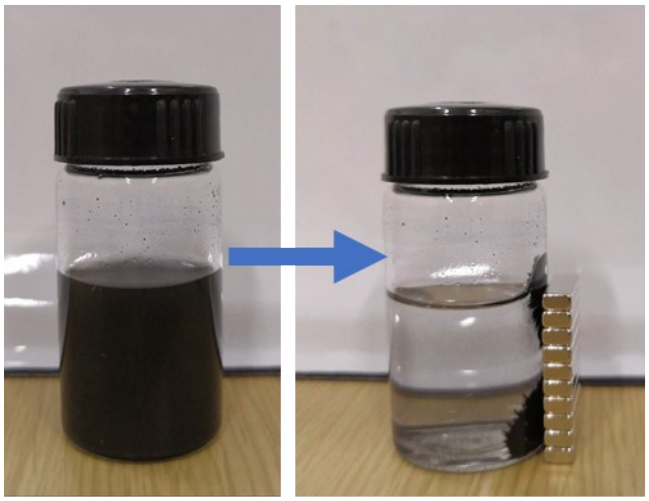

Fig. S12 Photographs of magnetic recovery of Co-350 catalyst.

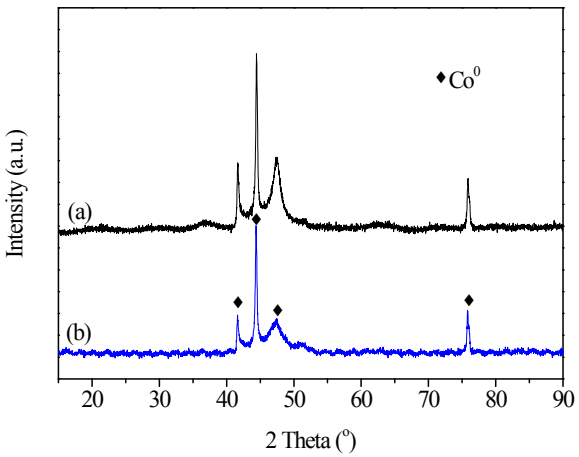

Fig. S13 XRD patterns of (a) fresh and (b) reused Co-350 catalysts.

References

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