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Supplementary Information

Weakly basic Co/CeO$_x$ catalytic system for one-pot conversion of cellulose to diols: Kungfu on eggs

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Contents

Experimental Section

Reagents

α-Cellulose (particle size = 25 μm), ruthenium trichloride hydrate ($RuCl_3 \cdot xH_2O$) (AR, 35.0–42.0%), and bicyclohexane (AR, > 99%) were purchased from Aladdin Chemical Reagent Co., Ltd., whereas cobaltous nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (AR, > 99%), cerous nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) (AR, > 99%), copper nitrate hexahydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (AR, > 99%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) (AR, > 99%), ZrO_2, TiO_2, La_2O_3, and activated carbon (AC) were purchased from Sinopharm Chemical Reagent Co., Ltd. High-purity H_2 and N_2 gases were provided by Nanjing Special Gas Factory Co. Ltd.

Catalysts Preparation

A series of Co/CeO_x catalysts with different amounts of loaded Co were prepared by precipitation method. To prepare the CeO_2 support, 3.0 g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 300 g of deionized water contained in a 500 mL round-bottom flask. The solution was stirred at 60°C for 1 h, and 0.1 $mol \cdot L^{-1}$ aqueous ammonia was added in a dropwise manner to attain a final pH value of 10. The mixture was then stirred vigorously for another 6 h. Subsequently, the suspension was filtered and washed several times with distilled water until a pH value of 7 was achieved. The separated solid was dried in an oven at 105 °C for 12 h. After drying, the sample was calcined in a furnace whose temperature was programmed to rise from 20 °C to 400 °C at a rate of 3 °C min^{-1} and then stabilize at 400 °C for 4 h.

A total of 1.2 g of the prepared CeO_2 support was added to 100 g of deionized water in a 250 mL round-bottom flask and stirred at 60 °C. A mixture of 415 mg $Co(NO_3)_2 \cdot 6H_2O$ in 5 g deionized water was then added dropwise to the magnetically stirred CeO_2 solution. The resulting mixture was stirred vigorously for 12 h before adding drops of 0.1 $mol \cdot L^{-1}$ aqueous ammonia until a pH value of 10 was achieved, then stirring again for another 6 h. Afterward, the suspension was filtered and repeatedly washed with distilled water to achieve a filtrate pH value of 7. The collected solid was dried in an oven at 105 °C for 12 h, then calcined in a furnace at temperatures increasing from 20 °C to 300 °C at a rate of 1 $°C \cdot min^{-1}$ and stabilizing at 300 °C for another 2 h. To re-calcine the sample, the furnace temperature was further increased to 600 °C (1 °C min^{-1}) at which it was kept for 2 h. The calcined catalysts were reduced in H_2 atmosphere at 600 °C for 2 h with a heating rate of 1 °C min^{-1}, before reaction.

To eliminate the individual differences for catalyst preparation, three different persons prepared the catalyst and tested in cellulose conversion reaction independently. All the catalysts made by different person revealed similar activity, the final yield error was less than 3%.

Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the catalysts were measured by an X'pert (PANalytical) diffractometer, using CuKα radiation at 40 kV and 40 mA, with a 2θ range of 10–70°.

The temperature-programmed reduction (H_2-TPR) was carried out in a home-built reactor system coupled to a gas chromatograph. Before TPR testing, the samples were pretreated in Ar flow at 500 °C for 1 h. The TPR was performed under gas flow conditions of 5% H_2/Ar with flow rates of 40 mL/min and temperatures rising from 40 °C to 800 °C at the rate of 10 °C min^{-1}. A liquid nitrogen/ethanol cooling bath was used to remove moisture from the effluent stream before entering the thermal conductivity detector (TCD).

Experiments of ammonia (NH_3-TPD) and carbon dioxide (CO_2-TPD) temperature-programmed desorption were carried out in the same system used for H_2-TPR tests, under gas flow rates of 40 mL min^{-1}, in order to determine the total acidity of the catalysts. Prior to saturation with pure NH_3 or CO_2, 100 mg of the catalyst sample was heated at 500 °C for 1 h under Ar flow, then cooled to 40 °C. After flushing with Ar for 1 h, NH_3-TPD and CO_2-TPD tests were performed at temperatures rising from 40 °C to 800 °C (heating rate = 10 °C min^{-1}). The desorbed ammonia and carbon dioxide were monitored using on-line gas chromatography equipped with a thermal conductivity detector (TCD).

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken with a JEOL n JEM 2011F apparatus operating at a voltage of 200 kV. Before being transferred into the TEM chamber, the samples were dispersed in ethanol for 30 min, deposited onto a carbon-coated copper grid, and then quickly moved into the vacuum evaporator. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and EDS mapping were obtained with a FEI Tecnai G2 F20 at 200 kV.

X-ray photoelectron spectra (XPS) were recorded by an ESCALAB250 spectrometer (Thermo-VG Scientific, USA) at room temperature and 10^{-8}–10^{-9} Torr pressure using monochromated Al Kα radiation (1486.92 eV). The binding energies (BE) were calibrated relative to the carbon 1s band at 284.6 eV.

The chemical composition of catalysts was identified using the Optima 7300 DV inductively coupled plasma atomic absorption spectroscopy (ICP-AAS) system. The analyses were performed on a PerkinElmer Corporation Analyst 800 instrument. The analyzed samples were prepared by adding 10 mg of catalyst to 4 mL of aqua regia in a 10 mL round-bottom flask, then stirring at 80 °C for 24 h to completely dissolve the metal, followed by dilution to 25 mL.

Catalyst Test

All catalytic reactions investigated in this study were performed in a 25 mL NSC-type reactor purchased from Anhui Kemi Machinery Technology Co., Ltd. The reaction mixture was prepared by adding 100 mg of cellulose to 120 mg of the reduced catalyst and 10 mL of water. The desired temperature and pressure were attained by heating and by flowing H_2 gas into the previously purged reactor (purged four times), respectively. Magnetic stirring was used to ensure the homogeneity of the reaction mixture. At predetermined time intervals, the reaction was stopped by cooling to room temperature, and the products were washed with methanol. Finally, the collected samples were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 5975C), and the components were quantified using both, i) gas chromatograph (Kexiao 1690) with HP-INNOWAX capillary column (30 m*0.250 mm*0.25 μm) and flame ionization detector (FIM), and ii) high-performance liquid chromatography (HPLC, Hitachi L2000) with Sugar 2011 column. The GC detecting conditions were as follows: nitrogen as carrier gas; injection port temperature of 280°C; FID temperature of 280°C; and column temperature of 40° rising up to 250°C at a heating rate of 10°C/min. Bicyclohexane was used as internal standard to quantify the products. Meanwhile, HPLC analyses were conducted at the column temperature of 323 K using water as the mobile phase with a flow rate of 0.5 $mL\cdot min^{-1}$. The injected sample volume was set at 10 μL. Each experiment was repeated three times to ensure reproducibility, and all reported data correspond to the average values with experimental errors less than 1%. The conversion and yield percentages were calculated according to the following equations:

$$Conv.(\%) = \left(1 - \frac{mass\ of\ carbon\ in\ residue\ after\ reaction}{mass\ of\ carbon\ in\ cellulose\ put\ in\ the\ reactor}\right) \times 100\%$$

$$Yield(\%) = \frac{mass\ of\ carbon\ in\ target\ product}{mass\ of\ carbon\ in\ cellulose\ put\ in\ the\ reactor} \times 100\%$$

Table S1. Carbon yields of cellulose conversion to lower diols using a variety of catalysts.

Entry	Catalyst	Carbon yield (%)					
		EL	EG	PL	1,2-PG	Total diols	Total C
1	10% Co/CeO_x	3.5	55.2	4.7	33.9	89.1	97.3
2	10% Ni/CeO_x	9.1	15.7	8.5	13.9	29.6	47.2
3	5% Ru/CeO_x	3.5	9.6	3.1	7.2	16.8	23.4
4	10% Cu/CeO_x	4.4	27.0	4.1	22.6	49.6	58.1
5	10% Co/ZrO_2	6.9	7.0	3.3	6.3	13.3	23.5
6	10% Co/TiO_2	7.8	6.5	3.2	6.4	12.9	23.9
7	10% Co/LaOx	12.5	21.7	4.6	13.8	35.5	52.6
8	10% Co/AC	1.0	8.2	1.0	4.8	13.0	15.0
9	Co particles	1.2	5.1	1.0	3.4	8.5	10.7
10[a]	10% Co/AC + CeO_2	0.4	3.0	0.2	1.4	4.4	5.0
11[b]	10% Co/AC + CeO_x	0.9	6.2	0.5	2.1	8.3	9.7

Reaction conditions: 120 mg of catalyst, 100 mg of cellulose, 10 mL of water as the solvent, 245°C, 3 MPa H_2, 6 h, and 800 rpm. a. Reduced Co/AC and calcined CeO_2; b. Reduced Co/AC and reduced CeO_x. EL: ethanol, PL: propanol, EG: ethylene glycol, and 1,2-PG: 1,2-propylene glycol.

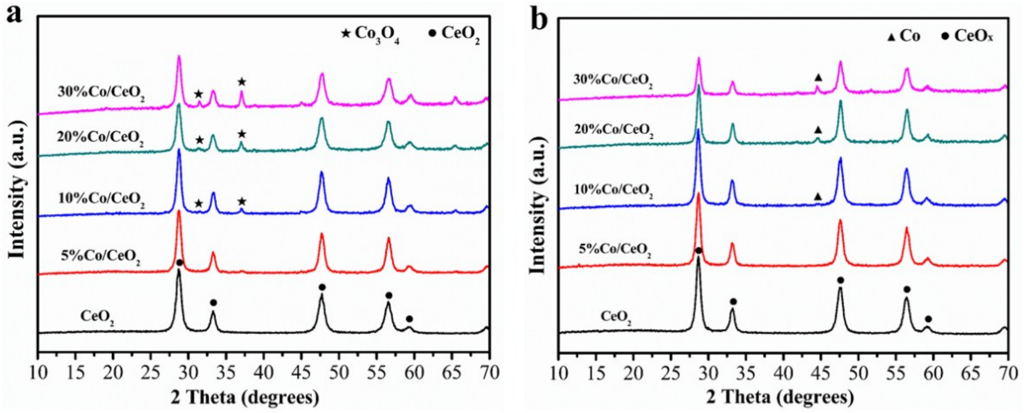


Figure S1. XRD patterns of calcined (a) and reduced (b) CeO_2 and Co/CeO_x catalysts.

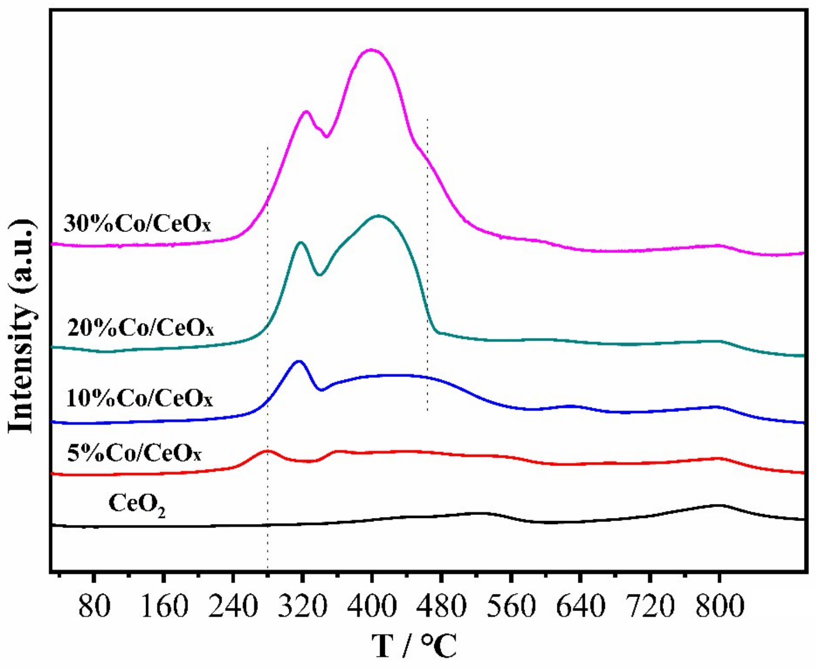


Figure S2. H_2-TPR profiles of Co/CeO_x samples.

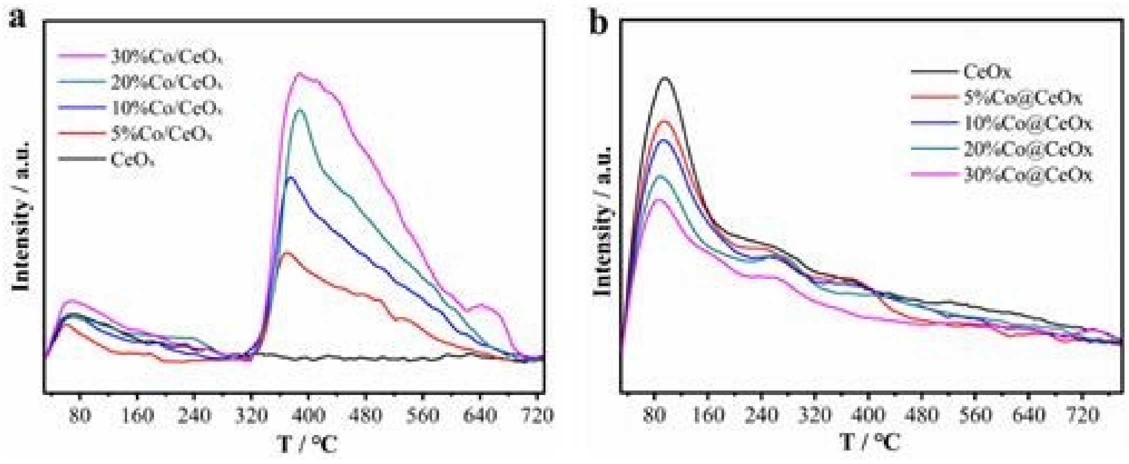
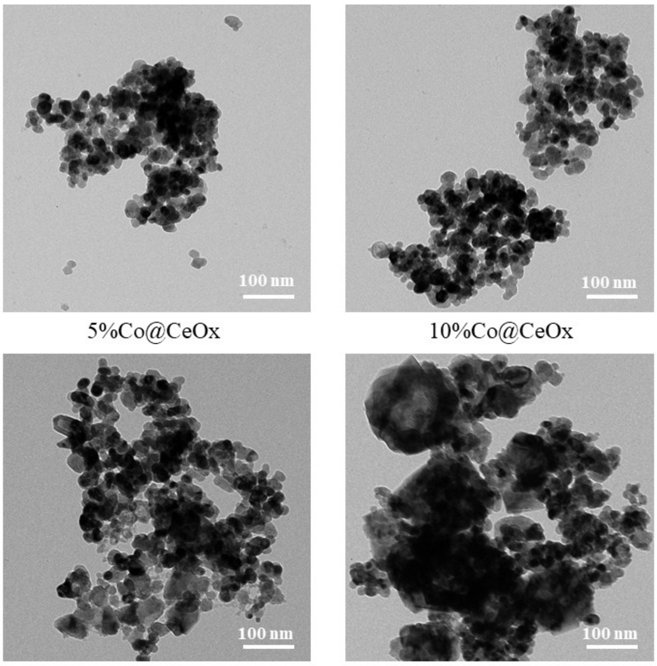


Figure S3. NH_3-TPD (a) and CO_2-TPD (b) curves of CeO_x and various Co/CeO_x catalysts.



5%Co@CeOx 10%Co@CeOx

20%Co@CeOx 30%Co@CeOx

Figure S4. TEM images of Co/CeO_x catalysts.

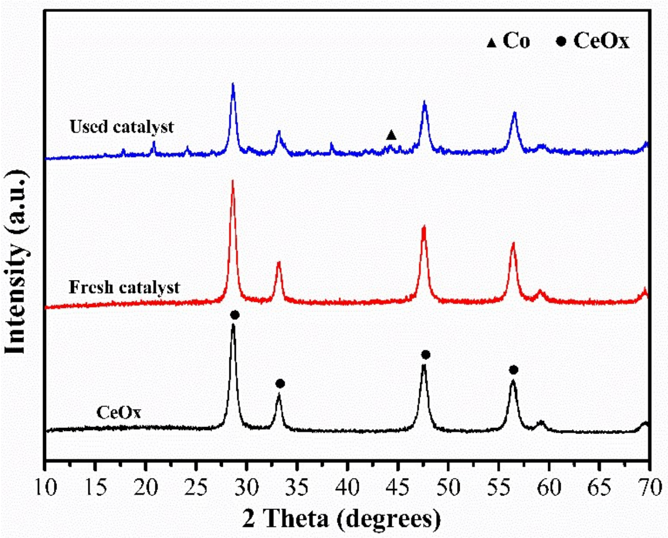


Figure S5. Powder XRD patterns of CeO_x, as well as fresh and used 10% Co/CeO_x.

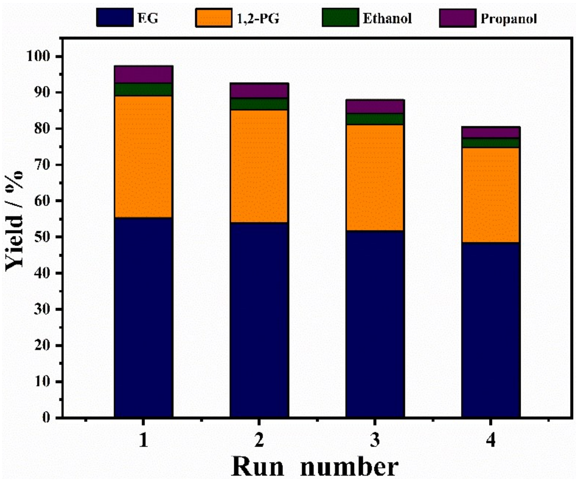


Figure S6. The recycling experiments for the catalytic conversion of cellulose to lower diols over 10%Co/CeO_x catalyst. Reaction conditions: 120 mg of catalyst, 100 mg of cellulose, 10 mL of water as solvent, 245 °C, 3 MPa H_2, 6 h, and 800 rpm. EG: ethylene glycol, 1,2-PG: 1,2-propylene glycol.

According to Figure S5 and S6, the deactivation could be due to a little aggregation of Co nanoclusters. Compared to previous literatures, the Co/CeO_x catalyst revealed much better stability than traditional W or Sn catalysts.

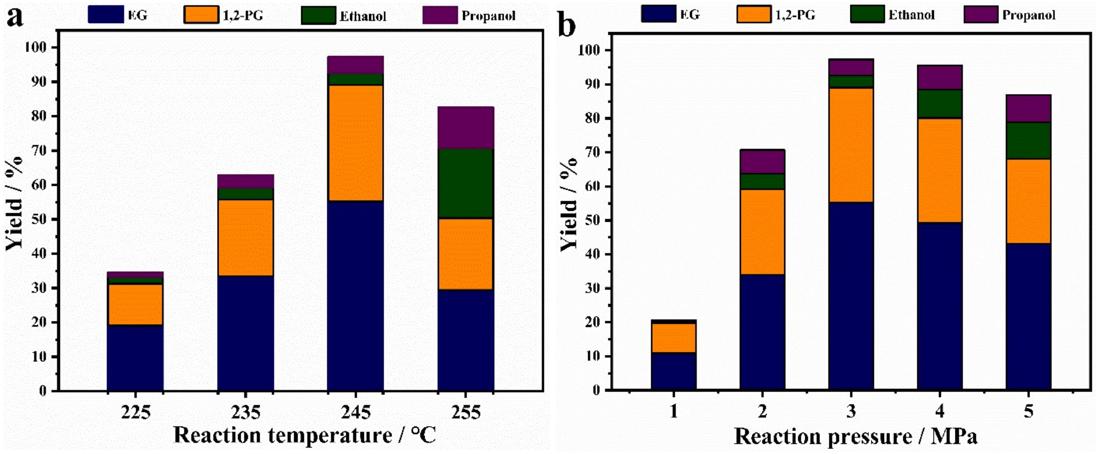


Figure S7. (a) Effect of reaction temperature on the carbon yields of cellulose conversion. (b) Effect of reaction hydrogen pressure on the carbon yields of cellulose conversion. Reaction conditions: 120 mg of 10% Co/CeO_x catalyst, 100 mg of cellulose, 10 mL of water as solvent, 3 MPa H_2, 6 h, and 800 rpm. (b) Effect of reaction hydrogen pressure. Reaction conditions: 120 mg of 10% Co/CeO_x catalyst, 100 mg of cellulose, 10 mL of water as solvent, 245 °C, 6 h, and 800 rpm. EG: ethylene glycol, and 1,2-PG: 1,2-propylene glycol.