Supporting Information

Modulating Defective Oxygen of Co-based Crystals by Calcination Temperature for Improving Catalytic Removal of Propane

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Experimental

Catalyst preparation

(1) Preparation of Co_3O_4 crystals

The specific experimental procedure is as follows: 4.5 mmol $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 mL of deionized water, and then 8 mmol of urea and 0.3 mmol of sodium citrate dihydrate were added under constant stirring, followed by stirring for 1 h. The resulting solution was transferred to a PTFE-lined stainless steel autoclave and heated at 180 °C for 1 h. The obtained pink pellet was centrifuged to pH = 7 and lyophilized for 12 h.

(2) Calcination of Co_3O_4

A series of Co_3O_4 catalysts were prepared by calcining the Co_3O_4 precursor in an air atmosphere, the heating rate was 2 °C·min^{-1}, and the calcination time was 4 h.

Catalyst Characterization

Scanning electron microscopy (SEM) images were taken on a Hitachi S4800 scanning electron microscopy. TEM images were obtained using a FEI F20 with an acceleration voltage of 200 kV. Thermogravimetry and derivative thermogravimetry (TG/DTG) was recorded using a Mettler-Toledo TGA/DSC. The sample was heated to 500 °C at a heating rate of 10 °C·min^{-1}, and the feed gas (air) flow rate was 50 mL·min^{-1}. Fourier Transform infrared spectroscopy (FTIR) spectroscopy was performed on a Thermo Fisher Scientific Nicolet 6700 spectrometer. X-ray diffraction (XRD) patterns were collected by a Rigaku SmartLab 3 Kw instrument with Cu Kα radiation (40 kV, 30 mA). N_2 physisorption was performed on a Micromeritics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific NEXSA instrument. Raman spectra in the range of 100~1500 cm^{-1} were obtained on a confocal microprobe raman spectroscopy (LabRAM HR Evolution, HORIBA Jobin Yvon). O_2 temperature-programmed desorption (O_2-TPD), CO_2 temperature-programmed desorption (CO_2-TPD), and H_2 temperature-programmed reduction (H_2-TPR) were measured using a Xiangen TP-5080 instrument. For TPD, each catalyst was first pretreated under He atmosphere at 180 °C for 30 min to remove moisture. Next, the system was purged with He for 2 h and cooled to room temperature before chemisorption.

After adsorbing O_2 or CO_2 at 50 °C for 30 min, it was heated to 700 °C at a rate of 10 °C·min⁻¹ under He flow. For H_2-TPR, each sample was pretreated at 180 °C for 1 h under an Ar atmosphere, and then heated to 700 °C at a rate of 10 °C·min⁻¹ under a 10% H_2/Ar flow rate.

Catalyst activity test

The catalytic combustion reaction was carried out in a continuous flow microreactor consisting of a quartz tube with an inner diameter of 4 mm and a height of 400 mm. 0.1g of catalyst particles (40-60 mesh) were placed in the quartz tube reactor, and both ends of the catalyst were blocked with quartz wool. A reaction gas containing 1000 ppm propane (air as balance gas) was passed through the reactor at a flow rate of 50 mL·min⁻¹ and the WHSV of 30,000 mL·g_{cat}⁻¹·h⁻¹. Effluent gases were analyzed online using a gas chromatograph (SHIMADZU GC-2014C) equipped with a FID flame ionization detector. Catalytic activity was measured in the range of 50–250 °C. Propane conversion is calculated using Equation 1:

$$X_{C_3H_8} = \frac{[C_3H_8]_{in} - [C_3H_8]_{out}}{[C_3H_8]_{in}} \tag{1}$$

where $[C_3H_8]_{in}$ and $[C_3H_8]_{out}$ represent the import and export concentrations of propane, respectively.

The reaction rate (mmol mg⁻¹ h⁻¹) is calculated according to Equation (2):

$$r_{C_3H_8} = \frac{10^3 \cdot 3600 \cdot X_{C_3H_8} \cdot V_{C_3H_8}}{W_{cat}} \tag{2}$$

where W_{cat} represents the catalyst mass and $V_{C_3H_8}$ represents the gas flow rate of C_3H_8 (mol s⁻¹).

The reaction activation energy (Ea) was calculated by Equation (3):

$$\ln r_{C_3H_8} = -\frac{Ea}{RT} + \ln A \tag{3}$$

where $r_{C_3H_8}$ represents the propane reaction rate, Ea represents the reaction activation energy (kJ mol⁻¹), R represents the gas constant (J mol⁻¹ K⁻¹), and T represents the reaction temperature (K). The stability testing of the catalyst was performed at 180°C.
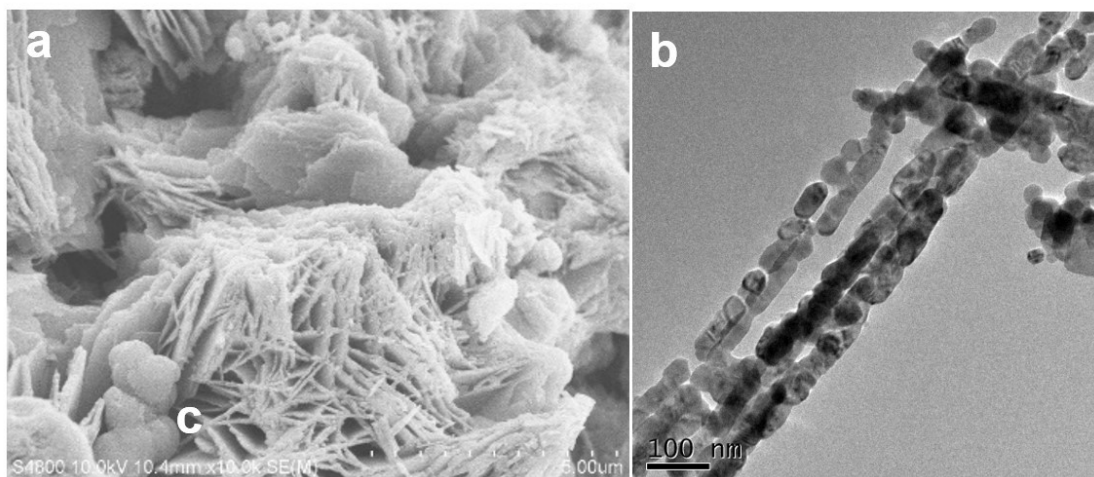
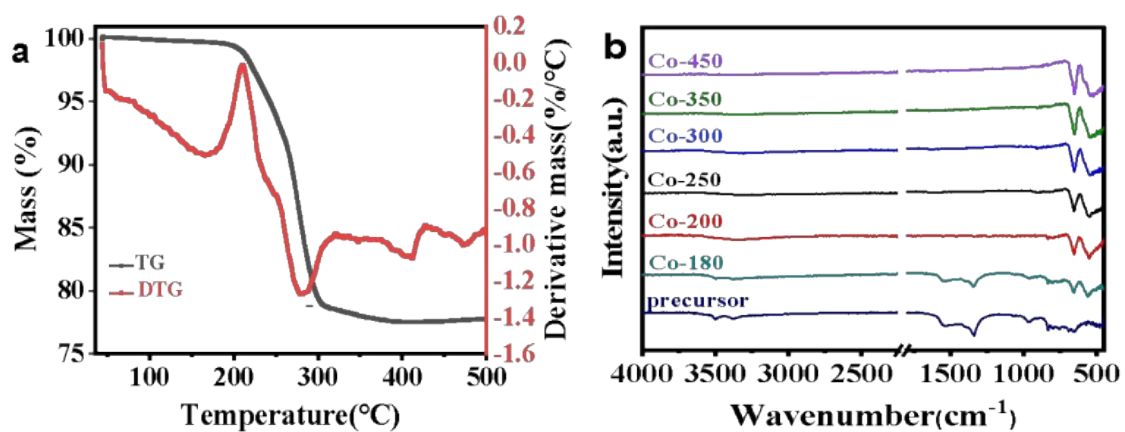Fig. S1 The SEM and low-magnification TEM of Co-450. Scale bars are 5μm and 100 nm.

Fig. S2 (a)TG/DTG profile of the cobalt oxide precursors. (b) FTIR of the Co_3O_4 precursors and the Co_3O_4 catalysts calcinated at different temperatures.
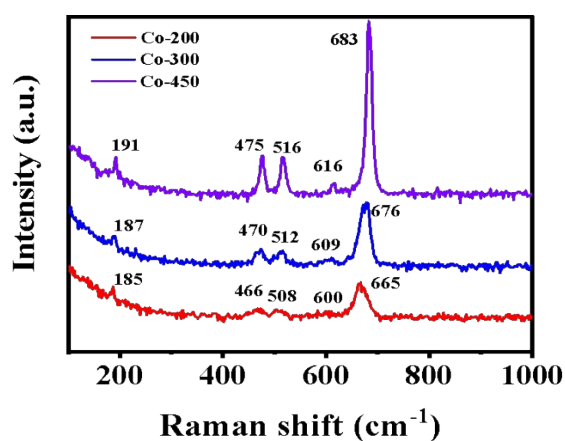

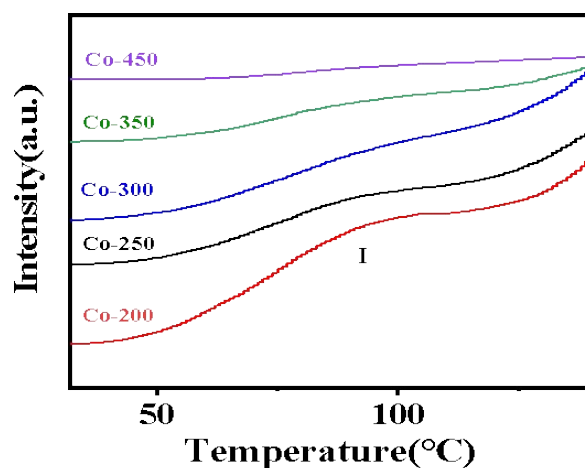Fig. S3 Raman of the Co_3O_4 catalysts calcinated at different temperatures.

Fig. S4 Local magnification of H$_2$-TPR profiles of catalysts calcined at different temperatures.
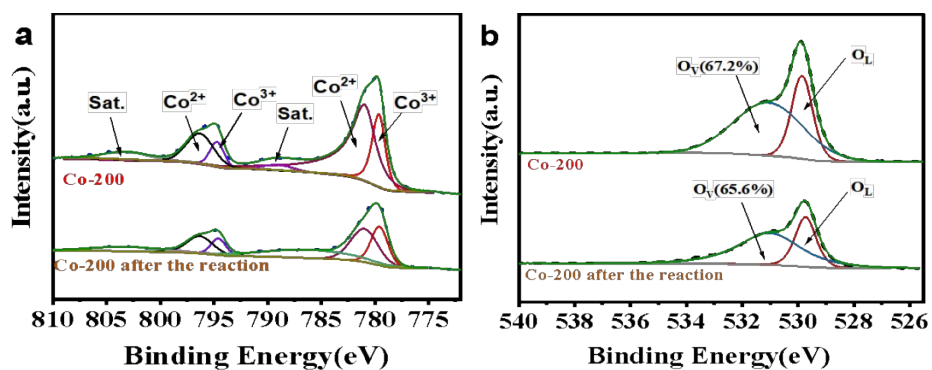

Fig. S5 (a) Co 2p and (b) O 1s XPS spectra of the Co-200 catalysts before and after the reaction.
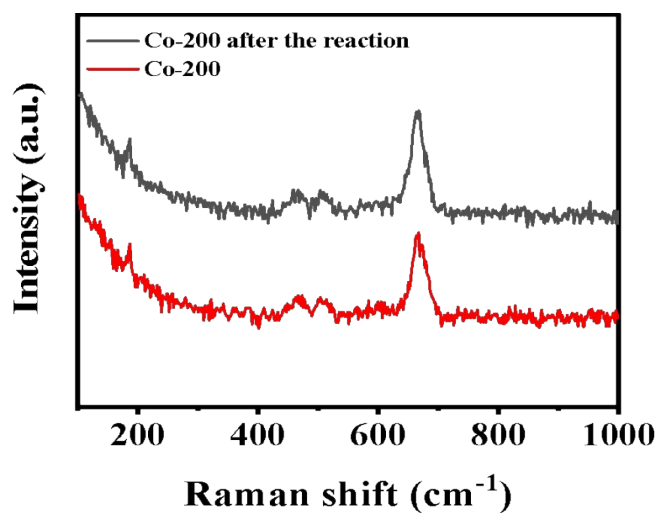

Fig. S6 Raman spectra of the Co-200 catalysts before and after the reaction.

Table S1 SSA and average pore diameter of the Co_3O_4 catalysts.

Samples	SSA (m^2 / g)	Average pore diameter (nm)
Co-200	176.08	2.2
Co-250	219.32	2.3
Co-300	127.29	3.7
Co-350	41.88	8.8
Co-450	21.19	46.7

Table S2. Surface element analysis of the Co_3O_4 catalysts calcined at different temperatures.

Samples	Co^{3+}/Co^{2+}	$O_V(\%)^a$
Co-200	0.35	67.2
Co-300	0.50	54.0
Co-450	0.61	52.6

$*^aO_V(\%)=O_V/(O_V+O_L)$

Table S3 Catalytic activity of the Co_3O_4 catalysts for propane oxidation.

Samples	T_{50} (°C)	T_{90} (°C)
Co-200	147	170
Co-250	161	177
Co-300	167	183
Co-350	179	197
Co-450	194	216

Table S4 Comparison of some catalysts reported in the literature for propane oxidation.

Sample	Reaction conditions	WHSV[a] $(mL·g_{cat}^{-1}·h^{-1})$	T_{50}[b] (ºC)	T_{90}[b] (ºC)	Ref.
Co-200	1000 ppm C_3H_8 + Air	30,000	147	170	This work
Co_3O_4-R	2500 ppm C_3H_8 + Air	30,000	170	195	[1]
Co_3O_4-S	900 ppm C_3H_8 + Air	30,000	203	210	[2]
CoO-Co_3O_4	3000 ppm C_3H_8 + Air	30,000	214	235	[3]
$Co_2Ce_1O_x$	800 ppm C_3H_8 + 10% O_2	90,000	215	249	[4]
Co_3O_4	2500 ppm C_3H_8 + 10% O_2	120,000	225	241	[5]
Co_3O_4/ZSM-5	2000 ppm C_3H_8 + 2%O_2	30,000	235	260	[6]
1.5%Ru/CeO_2	2000 ppm C_3H_8 + 2%O_2	30,000	170	190	[7]
0.5%Pt/BN	2000 ppm C_3H_8 + 2%O_2	80,000	260	340	[8]
5%Ru-Mo/Al_2O_3	800 ppm C_3H_8 + Air	60,000	150	200	[9]
1%Pt/AlF_3	2000 ppm C_3H_8 + 2%O_2	80,000	230	290	[10]

[a] Weight hourly space velocity; [b] Temperatures at which 50% and 90% conversion of propane.

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