Supporting information

Photothermal catalytic CO_2 oxidative propane dehydrogenation over an oxygen-vacancy-rich perovskite-type $CeNiO_3$ catalyst

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1. Experimental

2.1 Materials

$Ce(NO_3)_3 \cdot 6H_2O$ (99.5%), $Ni(NO_3)_2 \cdot 6H_2O$ (99.9%), and $C_6H_8O_7$ (99.5%) were provided by Aladdin Industrial Co., Ltd. The experimental gases were sourced from Xi'an TEDA Cryogenic Equipment Co., Ltd. All chemicals were used directly without any purification.

2.2 Preparation of catalysts

The $CeNiO_3$ catalyst was synthesized via a citric acid-assisted sol-gel route, and the main procedures are given in **Fig. 1a**. Stoichiometric quantities of $Ni(NO_3)_2 \cdot 6H_2O$ (1.45g) and $Ce(NO_3)_3 \cdot 6H_2O$ (2.17 g), corresponding to a Ni/Ce molar ratio of 1:1, were dissolved in 20 mL of deionized water. An appropriate amount of anhydrous citric acid and ethanol was then added to the solution as chelating agents. After stirring until a homogeneous solution was obtained, the mixture was continuously agitated in an 80 °C oil bath to facilitate gel formation. The precursor gel was dried in an oven at 100 °C for 12 h, yielding a green, porous mesh-like material. This dried product was ground into a fine powder in an agate mortar and subsequently subjected to a two-step thermal treatment: pre-calcination in a muffle furnace at 450 °C for 2 h, followed by annealing at 650 °C for an additional 2 h. For comparative purposes, pure CeO_2 and NiO catalysts were also prepared following the identical procedure. **Fig. S1** shows the photographs of $CeNiO_3$, CeO_2, and NiO samples.

2.3 Catalyst characterization and photoelectric properties tests

XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ=0.154 nm). Data were collected in the 2θ range of 5° to 80° at a scanning rate of 5°/min.

N_2 physisorption measurements were conducted on a Micromeritics ASAP 2460 analyzer at -196 °C. The catalyst was pre-treated by degassing at 120 °C for 12 h under vacuum to remove moisture and other adsorbates.

The morphology and size of the catalyst were characterized using a Tecnai G2 F20 TEM operating at 200 kV. For testing, a small amount of powder sample was dispersed in ethanol, sonicated for 30 min, and then dropped onto silicon wafers and copper grids using a pipette. The samples were dried before testing.

XPS was performed on a Thermo ESCALAB 250XI equipped with 300 W Al Kα radiation (HV =1486.6 eV) and a hemispherical energy analyzer. The binding energy was referenced to the C 1s peak

at 284.6 eV. Surface concentrations of C, O, Ni, and Ce were determined by integrating the areas of the O 1s, Ni 2p, and Ce 3d peaks using XPS peak software.

EPR testing was conducted on a Bruker A300 instrument to determine the VOs (O_V) of the catalyst.

The ultraviolet-visible (UV-Vis) absorption characteristics of the samples were characterized using a Cary 5000 UV-Vis spectrophotometer (Agilent, USA) across the wavelength range of 200-800 nm.

EIS testing was performed on a CHI660 electrochemical workstation (CH instrument, Shanghai Chenhua Instrument Co., Ltd., China). For testing, a mixture of the sample (15 mg) and Nafion (5%, 0.05 mL) in 1 mL of isopropanol was sonicated for 30 min. The mixture was then evenly dispersed on conductive glass (1.0 cm × 1.0 cm). EIS testing was conducted in a 0.5 mol/L Na_2SO_4 electrolyte. The photocurrent time test followed the same procedure but used a 300 W xenon lamp as the light source.

Prior to CO_2-TPD measurements, the catalyst was pretreated in an He flow (30 mL/min) at 300 °C for 30 min to remove adsorbed moisture. After cooling to 50 °C under He, the catalyst was saturated with CO_2 for 60 min, followed by purging with He to eliminate any physisorbed CO_2. The TPD profile was then recorded under He flow while heating from 50 to 700 °C at a constant rate of 10 °C/min by using a TCD detector.

In-situ DRIFTS measurements were performed to detect and characterize potential surface intermediates on the $CeNiO_3$ catalyst under thermal catalytic reaction conditions (temperature range 150-300 °C). Spectra were collected using an MCT detector. Prior to measurement, the catalyst was pre-treated with Ar at 200 °C for 120 minutes and then naturally cooled to room temperature.

2.4 Catalyst evaluation in photothermal catalytic CO_2-ODHP

The photo-thermal catalytic CO_2 oxidative dehydrogenation of propane (CO_2-ODHP) was performed in a customized reactor (180 mL) equipped with an internal quartz liner and a top sapphire window. Typically, 30 mg of the catalyst was uniformly dispersed within the quartz liner, which was then placed inside the reactor. After sealing, the reactor was evacuated to remove residual air and subsequently charged with the reaction gas mixture (30 mL C_3H_8 and 150 mL CO_2).

The reaction was initiated by simultaneously switching on a xenon lamp and heating the reactor with an external electric furnace to the target temperature of 300 °C. The gaseous products were analyzed using an online gas chromatograph (GC). Hydrocarbons, including CH_4, C_2H_6, C_2H_4, C_3H_8,

C_3H_6, and C_4H_{10} (primarily *n*-butane), were separated using an Agilent capillary column (0.53 mm × 50 m, 15.0 μm film thickness) and detected by a flame ionization detector (FID). Permanent gas CO_2 was analyzed using a thermal conductivity detector (TCD) equipped with a combination of Porapak Q, GDX-502, and 5A molecular sieve packed columns.

2.5 Calculation of solar to chemical energy conversion efficiency (η_{SCC}):

Given the present reaction network is complicated, and the solar-to-chemical conversion efficiency (SCC) was analyzed by assuming the reactants follows the reaction of $CO_2 + C_3H_8 \rightarrow CO + C_3H_6 + H_2O$. The SCC was experimentally determined using a reaction vessel loaded with 30 mg of the $CeNiO_3$ catalyst. The light intensity was measured using a PL-MW2000 optical power meter. After 1 hour of illumination, the reaction products were collected and quantified via gas chromatography. The SCC was then calculated according to the following formula [1]:

$$SCC = \frac{\Delta_r G \times n_{C_3H_6}}{t_{ir} \times S_{ir} \times I} \times 100\%$$

where $\Delta_r G$ is the free energy change for the reaction (68.3 kJ mol^{-1}); $n_{C_3H_6}$ is the amount of generated; t_{ir} is the irradiation times, S_{ir} is the irradiation area, S_{ir} = 4.90 cm^2; I is the overall irradiation intensity, I = the intensity of irradiation light ($W \cdot cm^{-2}$) = 0.32 W/(3.14*1^2) = 0.1019 $W \cdot cm^{-2}$.

Table S1. Specific surface area, pore size, pore volume, and Ce^{3+} surface concentration of the $CeNiO_3$, CeO_2, and NiO catalysts

Entry	Catalysts	S_{BET} ($cm^2 \cdot g^{-1}$)	V_{Total} ($cm^3 \cdot g^{-1}$)	D_p (nm)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$
1	$CeNiO_3$	47	0.15	12.13	0.42
2	$CeNiO_3$[2]	30	0.06	9.21	0.26
3	CeO_2	18	0.06	11.61	0.37
4	NiO	6	0.02	15.59	/

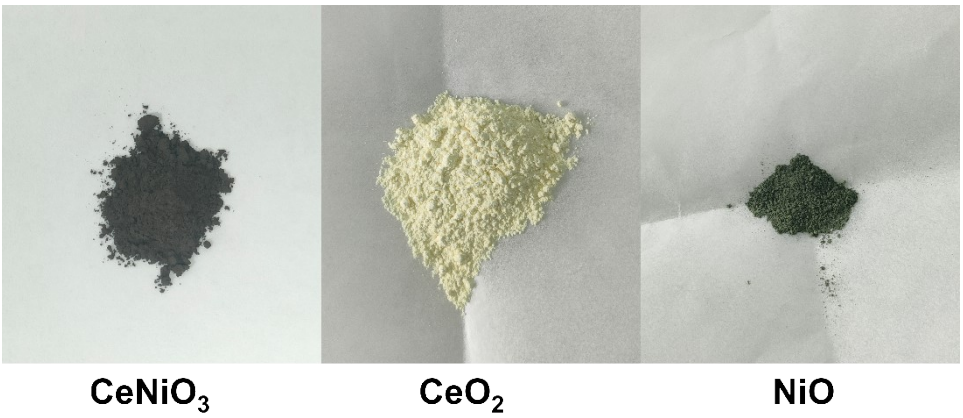

Fig. S1 Photographs of $CeNiO_3$, CeO_2, and NiO samples.

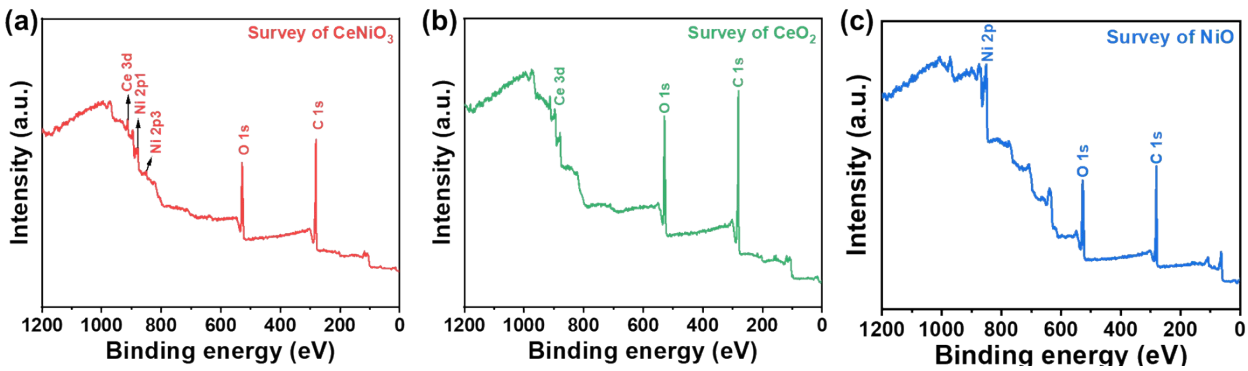

Fig. S2 Full spectrum analysis of different catalysts, including the full spectrum of the $CeNiO_3$ catalyst (a), the CeO_2 catalyst (b), and the NiO catalyst (c)

Table S2. Concentration of surface oxygen species over different catalysts

Entry	Catalysts	O 1s (%)		
		Oxygen vacancies	Lattice oxygen	O-H
1	CeO_2	35.42	39.68	24.90
2	NiO	34.21	44.04	21.75
3	$CeNiO_3$	39.97	26.01	34.02
4	$CeNiO_3$（reaction）	38.52	29.73	31.75

Table S3. Photothermal catalytic CO_2-ODHP over different catalysts

Catalysts	T (°C)	Gas ratio	Activity (μmol·g_{cat}^{-1}·h^{-1})		Ref.
			C_3H_6	CO	
Co-Mn/MCM-41	250	C_3H_8/CO_2 = 1/5	225.7	272.0	[3]
BiOI	270	C_3H_8/CO_2 = 1/5	282.6	525.2	[4]
40 wt% BiOI/AC	300	C_3H_8/CO_2 = 1/5	432.1	427.5	[5]
Pt-GaN/STO	300	C_3H_8/CO_2 = 1/5	396.7	503.0	[6]
$CeNiO_3$	300	C_3H_8/CO_2 = 1/5	1229.7	876.9	This Work

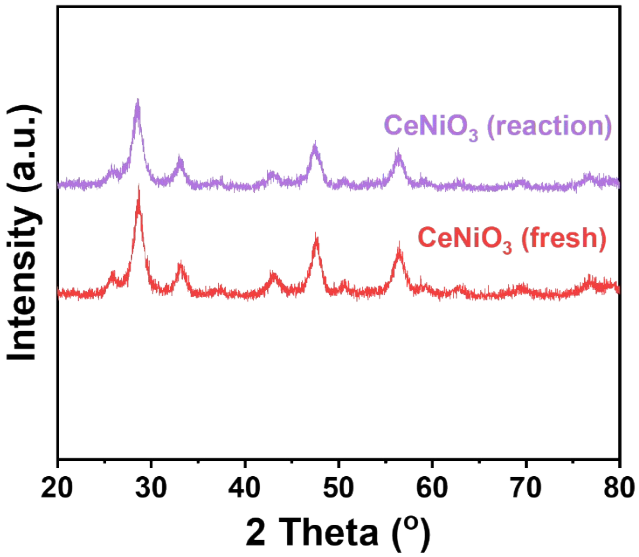

Fig. S3 XRD spectra of different catalysts and $CeNiO_3$ catalyst after reaction

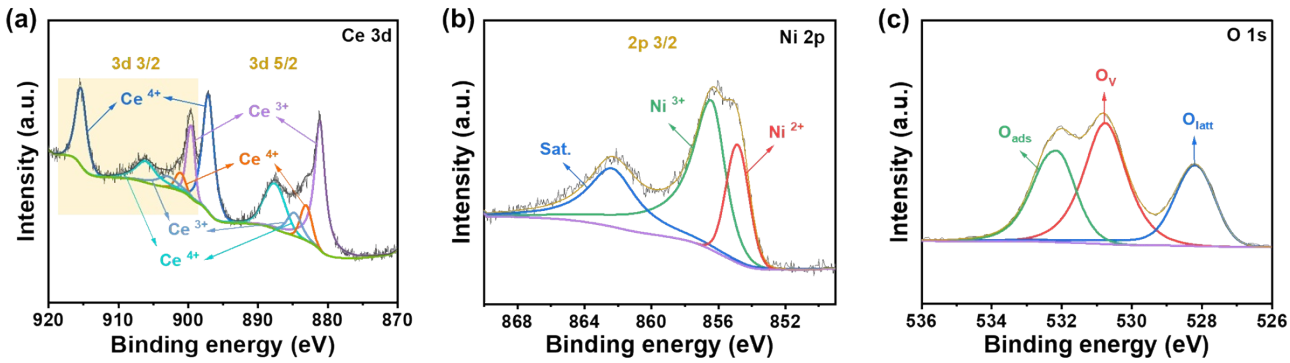

Fig. S4 The XPS spectrum after the reaction of the $CeNiO_3$, Ce 3d (a), Ni 2p (b), and O 1s (c)

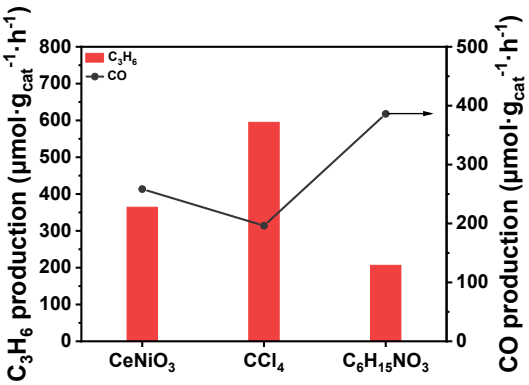

Fig. S5 Comparative experimental results of adding carbon tetrachloride and triethanolamine. Reaction conditions: total volume 180 mL, C_3H_8/CO_2 volume ratio 1/5, 200 °C, catalyst 30 mg, 1 h, 300 W xenon lamp.

References

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