Supporting Information: Ultralow-Temperature CO Oxidation on In₂O₃-Co₃O₄ Catalyst: A Strategy to Tune CO Adsorption Strength and Oxygen Activation Simultaneously

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The details of Experiment:

The Co₃O₄ and 25 wt.% In₂O₃-Co₃O₄ samples were prepared by precipitation and coprecipitation method, respectively. The cobalt acetate (Co(CH₃COO)₂•4H₂O) and indium chloride (InCl₃) were used as precursor salts, and sodium carbonate (Na₂CO₃) was used as precipitant. After filtering, the solid powder obtained was dried at 65 °C overnight and calcined at 350 °C for 4 h in air. The preparation process was similar to the reference [S1]. The activity of catalyst for CO oxidation was evaluated in a fixed-bed reactor, and 200 mg catalyst (40~60 mesh) was used and the flow rate of feed gas was 50 ml/min containing 1 vol.% CO, 20 vol.% O₂ and N₂ balanced..

The bulk Co_3O_4 was modelled by a conventional cubic unit cell containing 32 O and 24 Co using Monkhorst Pack k-point grids of $4 \times 4 \times 4$ for sampling its Brillion zone. In-doped bulk Co_3O_4 was modelled by replacing 3 of 24 Co³⁺ with In³⁺ due to the detailed experiments that In: Co was nearly 1:7. All spin-polarized density functional theory calculations under periodic boundary conditions were performed with Perdew–Burke–Ernzerh (PBE) exchangecorrelation functional using projector-augmented-wave (PAW) pseudopotentials implemented in VASP [S2, S3]. Hubbard-U correction method (DFT+U) was carried out to improve the description of highly correlated Co 3d orbitals with the value of U set to 2, which had been confirmed by previous work [S4, S5]. The energy cutoff of 400 eV for plane-wave expansion was demonstrated sufficient to achieve the convergence of the calc ulated properties.

The characterization of catalysts

The powder X-ray diffraction pattern (XRD) of sample was obtained with Rigaku D/max 2550 VB/PC diffractometer using a Cu K α radiation ($\lambda = 1.54056$ Å). The X-ray tube was

operated at 40 kV and 100 mA. The intensity data was collected at room temperature in a 2θ range from 10 to 70 ° with a scan rate of 6 °/min.

The temperature-programmed surface reduction of CO (CO-TPSR) was performed in a quartz reactor under a flow of 5 vol.% CO/N₂ (50 ml/min) over 200 mg catalyst using a heating rate of 10 °C/min from -80 °C to room temperature. Before CO-TPSR experiment, the samples were pretreated using 20 vol.% O₂/N₂ (50 ml/min) mixed gas at 350 °C for 40 min.

The temperature-programmed reduction of H₂ (H₂-TPR) was performed with a temperature-programming system. 50 mg of the catalyst was heated in the flow of 5 vol.% H₂/N₂ (20 ml/min) at a heating rate of 10 °C/min from -80 °C to room temperature. The amount of H₂ consumption during the process of reduction was measured by thermal conductivity detector (TCD). Before H₂-TPR experiment, the samples were pretreated by 20 vol.% O₂/N₂ (50 ml/min) mixed gas at 350 °C for 40 min.

The X-ray photoelectron spectroscopy (XPS) was investigated in an AXIS-Ultra-DLD spectrometer (Kratos Analytical) using a mono-chromated Al K α X-ray source (1486.6 eV). The samples of Co₃O₄ and 25 wt.% In₂O₃-Co₃O₄ were mounted onto the double-sided adhesive tape on the sample holder. The XPS spectra of the selected elements were measured with the constant analyzer pass energy of 80.0 eV. All binding energies (BEs) were referred to the adventitious C 1s peak (BE=284.8 eV). The peaks were fitted according to the Ref [S6].

Laser Raman spectra (LRS) of samples were collected at ambient condition on an Renishaw spectrometer. A laser beam (λ = 514 nm) was used for an excitation. The laser beam intensity and the spectrum slit width were 2 mW and 3.5 cm⁻¹, respectively.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of CO adsorbed on the catalyst was measured on a Nicolet Nexus 6700 spectrometer equipped with a MCT detector and low-temperature sample cell which was fitted with ZnSe windows. The samples were firstly pretreated at 350 °C for 40 min by the mixed gas of 20 vol.% O₂ and N₂ balanced; after the samples were cooled to -100 °C, the mixed gas of 1 vol.% CO and N₂ balanced was used instead of the mixed gas of O₂/N₂. The DRIFT spectra obtained were collected in Kubelka-Munk unit with a resolution of 4 cm⁻¹ and 64 scans. *In-situ* DRIFT spectra during the CO oxidation at -70 °C over the catalyst at different reaction time were obtained in the flow of 1 vol.% CO, 20 vol.% O_2 and N_2 balanced. The pretreatment of the sample was the same as the method above.

TOF values were calculated based on the BET surface area. The reaction rate was measured at -75° C under reaction condition of 2 vol.% CO, 10 vol.% O₂, N₂ balance with SV=600,000 ml/g•h. The BET surface areas were measured by nitrogen adsorption at liquid nitrogen temperature by using a surface area and porosity analyzer (Quantachrome NOVA 4000e apparatus). Before measurement, the samples were degassed at 180 °C for 6 h in vacuum.

The activity of catalyst for CO oxidation was tested in a fixed-bed reactor at atmospheric pressure and 200 mg catalyst (40~60 mesh) was used. The feed gas containing 1 vol.% CO, 20 vol.% and N₂ balanced, passed through the catalytic bed at a flow rate of 50 ml/min. The concentrations of CO and CO₂ in the outlet stream were measured by an on-line gas chromatograph (Fuli 9790 equipped with hydrogen flame ionization detector). Before the experiments, the catalyst was pre-treated at 350 °C for 40 min in 20 vol. % O₂/N₂ (50 ml/min). The dry feed gas was obtained by passing the feed gas through cooled trap.

Table S1. The catalytic activity of pure Co_3O_4 and 25 wt.% In_2O_3 - Co_3O_4 under the different reaction conditions.

Sample	Reaction condition	LTCC* / °C
25 wt.% In ₂ O ₃ -Co ₃ O ₄	0.5 vol.% CO + 20 vol.% O ₂ + N ₂	-115
25 wt.% In ₂ O ₃ -Co ₃ O ₄	1 vol.% CO + 20 vol.% O ₂ + N ₂	-105
25 wt.% In ₂ O ₃ -Co ₃ O ₄	1 vol.% CO + 30 vol.% $O_2 + N_2$	-115
Pure Co ₃ O ₄	1 vol.% CO + 20 vol.% O ₂ + N ₂	-40

* The lowest temperature of complete conversion (LTCC)



Fig. S1. The Raman spectra of pure Co₃O₄(a) and 25 wt.% In₂O₃-Co₃O₄(b).

For the pure Co₃O₄, there were five Raman-activated modes [S7-S9]. The peak at 688 cm⁻¹ was attributed to the characteristics of the octahedral sites (CoO₆) (assigned as A_{1g}). The Raman peaks with medium intensity located at 481 and 524 cm⁻¹ had the E_g and F_{2g}^2 symmetry, respectively. The weak peak located at 617 cm⁻¹ had the F_{2g}^3 symmetry. The peak at 191 cm⁻¹ was attributed to the characteristics of the tetrahedral sites (CoO₄) having the F_{2g}^1 symmetry.



Fig. S2. The bulk structure of the In-doped Co₃O₄. The calculated lattice constant (*a*) of Indoped Co₃O₄ was 8.210 Å, and that of pure Co₃O₄ was 8.110 Å.



Fig. S3. The Co 2p XPS spectra of 25 wt.% In₂O₃-Co₃O₄ and pure Co₃O₄.



Fig. S4. The DRIFT spectra of CO adsorption over 25 wt.% In_2O_3 -Co₃O₄ and Co₃O₄ at -100 °C.



Fig. S5. The adsorption structures of CO over In-doped Co₃O₄ (100)-B.

The Co_3O_4 (100) surface has two types of terminations. One is terminated by twocoordination Co^{2+} in the first layer and in the second layer five-coordination Co^{3+} and threecoordination lattice oxygen that binds with two Co^{3+} and one Co^{2+} (denoted as Co_3O_4 -(100)-A). Another one exposes exclusively the five-coordination Co^{3+} cation and two types of lattice oxygen which bind with three Co^{3+} , two Co^{3+} and one Co^{2+} (denoted as Co_3O_4 -(100)- B)). The Co_3O_4 -(100)-B is energetically favored according to ref [S10]. Thus, this termination was used to study the CO oxidation.



Fig. S6. The Low-temperature H₂-TPR profiles of 25 wt.% In_2O_3 -Co₃O₄ (a) and pure Co₃O₄ (b).



Fig. S7 The accumulation of surface carbonate species on the surface of 25InCo and Co₃O₄: total amount of unidentate carbonates and bicarbonate species (a: Co₃O₄ and c: 25InCo); amount of unidentate carbonates (b: Co₃O₄ and d: 25InCo). The amounts of surface carbonate

species against reaction time were obtained by calculating the area of three peaks (shown in Fig. 7 in the main article) located at 1220, 1413 and 1630 cm⁻¹. The calculation procedure was based on reference [S11]. The bands at 1220 and 1413cm⁻¹ were ascribed to the formation of unidentate carbonates by the interaction between carbonate dioxide and the basic sites (coordinatively unsaturated oxygen anions), and the peak at 1630 cm⁻¹ could be attributed to bicarbonate species [S12-14].

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