

Supporting Information

Correlation between reactivity and oxidation state of cobalt oxide catalysts for CO preferential oxidation

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Supporting information 1

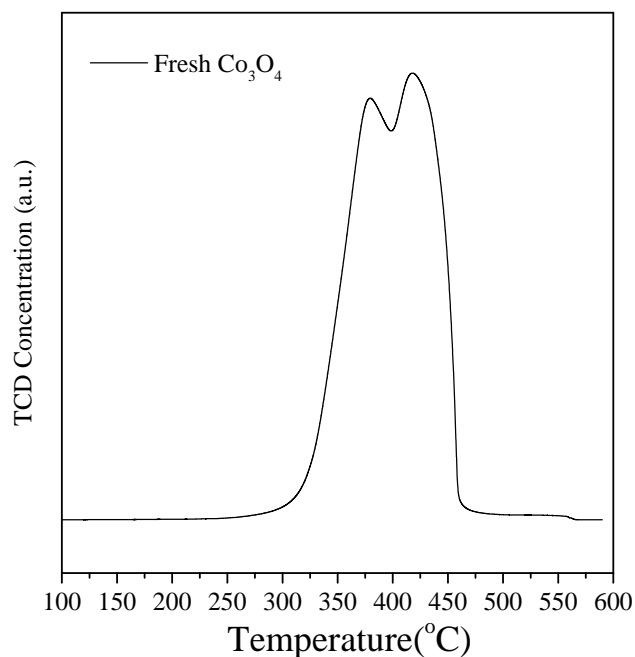


Figure S1. TPR-H₂ profile of the fresh Co₃O₄ sample measured in the temperature range of 100-600 °C. Operating conditions: 50 ml/min H₂ (5 vol. %)/Ar, 5 °C /min. Sample weight, 250 mg.

Supporting information 2

Table S1. The structural properties of cobalt catalysts after different pretreatment

Cobalt Catalysts	Crystallite size (nm)	Kr-BET surface area (m ² /g)
PreH ₂ Co	42.8 ^{CoO}	1.616
PreO ₂ Co	58.9 ^{Co₃O₄}	0.831

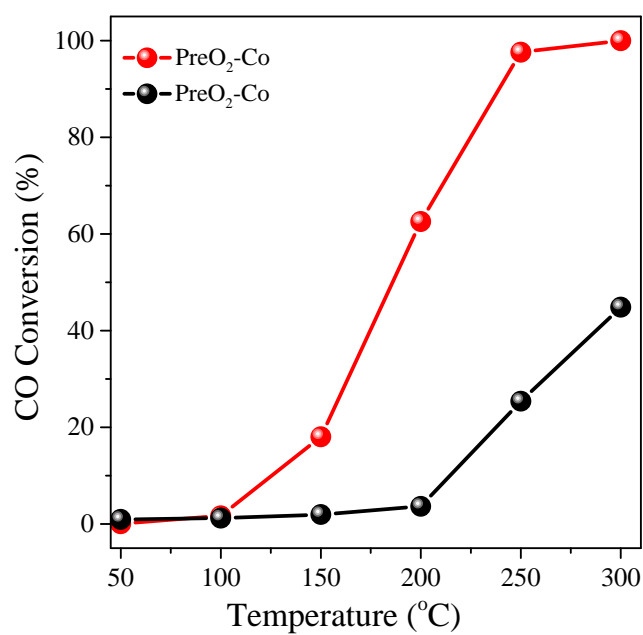


Figure S2. CO conversion for PreO₂-Co and PreH₂-Co as a function of temperature-based gas chromatography (GC) measurements. Experimental Conditions: 1%CO, 2%O₂ and 40% H₂ in He-balanced flow; 0.15 g catalysts; 10ml/min of total flow; atmospheric pressure (1 bar). Every point was recorded after remaining for 30 min at each temperature.

Supporting information 3

The notable difference regarding methane formation above 250 °C between the two samples should be associated to the preference of each sample to form adsorbed hydroxyl groups. Previous reports suggested that the mechanism of methane formation involves the interaction of CO with surface adsorbed OH groups.^{1,2} Both, in situ NAP-XPS (figure 4b) and DRIFTS (figure 6) show that there is a significant higher population of adsorbed OH groups in the case of PreH₂-Co as compared to PreO₂-Co. Therefore, a possible cause of the higher methane production in the case of PreH₂-Co catalyst is related to the higher tendency of this sample to form adsorbed OH groups.

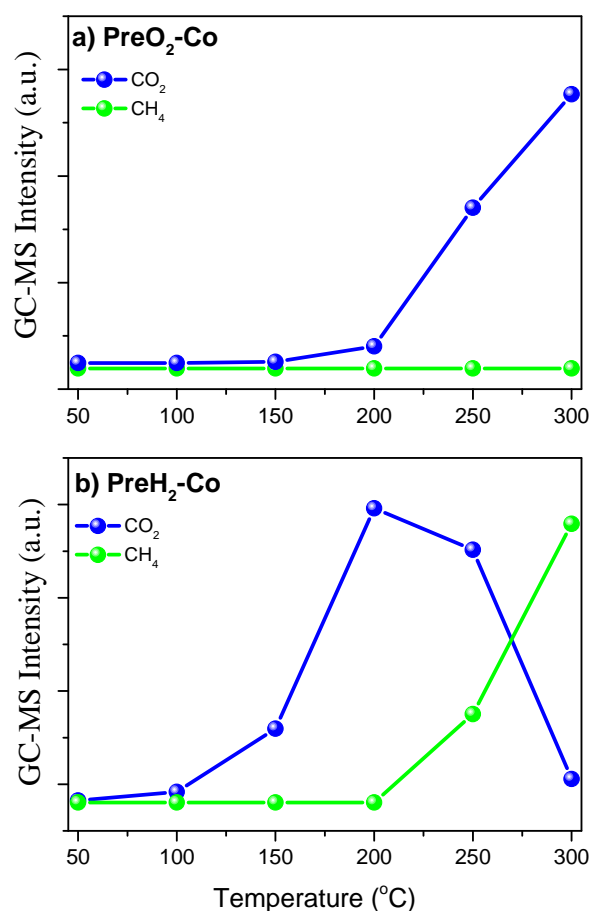


Figure S3. The evolution of CO₂ and CH₄ GC signals of the COPrOx reaction as a function of temperature for (a) PreO₂-Co and (b) PreH₂-Co catalysts. Experimental conditions: 1%CO, 2%O₂ and 40% H₂ in He-balanced flow; 0.15g catalysts; 10ml/min of total flow; atmospheric pressure (1bar) and after remaining for 30 min at each temperature.

Supporting information 4

The X-ray diffraction (XRD) patterns of fresh Co_3O_4 , fresh and spent (used) $\text{PreO}_2\text{-Co}$ (Figure S4) correspond to the Co_3O_4 cubic structure (PDF#76-1802 of the JCPDCS). The strong and sharp Bragg diffraction peaks suggest a high degree of crystallinity, while the absence of secondary phases in the XRD patterns confirms the high phase purity of Co_3O_4 powder. The stability of the XRD patterns indicates that the bulk structure of the $\text{PreO}_2\text{-Co}$ sample is not modified during COPrOx reaction. In case of used $\text{PreH}_2\text{-Co}$, three new diffraction peaks appear at $2\theta = 36.53, 42.41,$ and 61.64 degrees in addition to those of Co_3O_4 spinel. These peaks are assigned to the (111), (200), and (220) planes of the CoO crystal. The XRD patterns before COPrOx on this sample are dominated by the diffraction peaks of metallic Co , while the presence of small peaks due to CoO are related to the re-oxidation of the sample in atmosphere (*ex situ* XRD measurements). The XRD results show that the bulk structure of the $\text{PreH}_2\text{-Co}$ sample remains partially reduced to $\text{CoO/Co}_3\text{O}_4$ mixture during COPrOx reaction, while in case of $\text{PreO}_2\text{-Co}$ the catalysts remains always as Co_3O_4 .

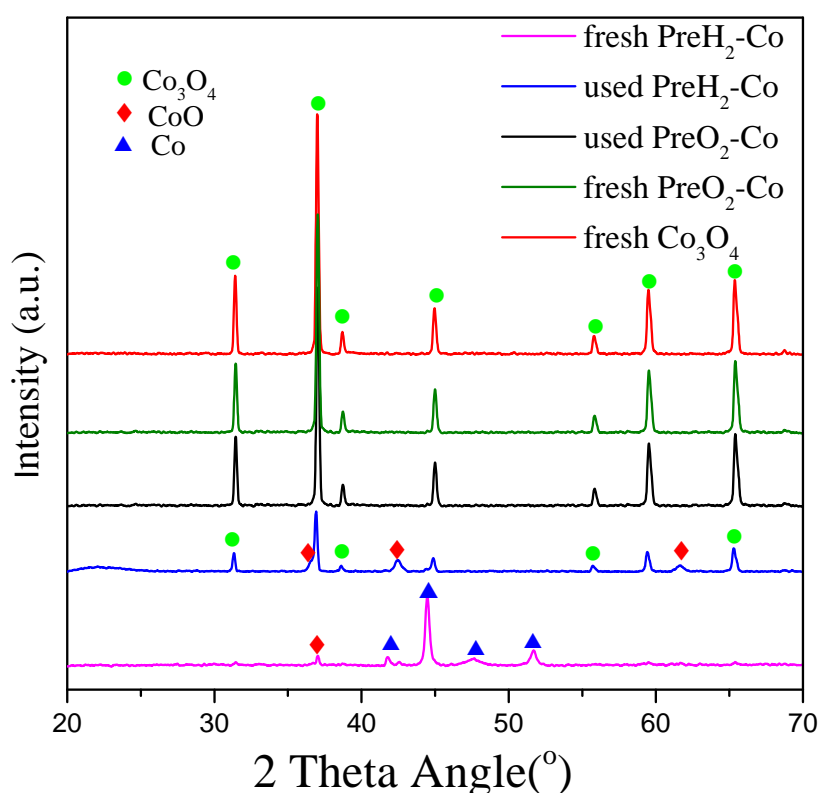


Figure S4. The XRD patterns of fresh cobalt catalyst, as well as $\text{PreO}_2\text{-Co}$ and $\text{PreH}_2\text{-Co}$ catalysts just before (*fresh*) and after (*used*) the COPrOx reaction at 1bar for 2 hours.

Supporting information 5

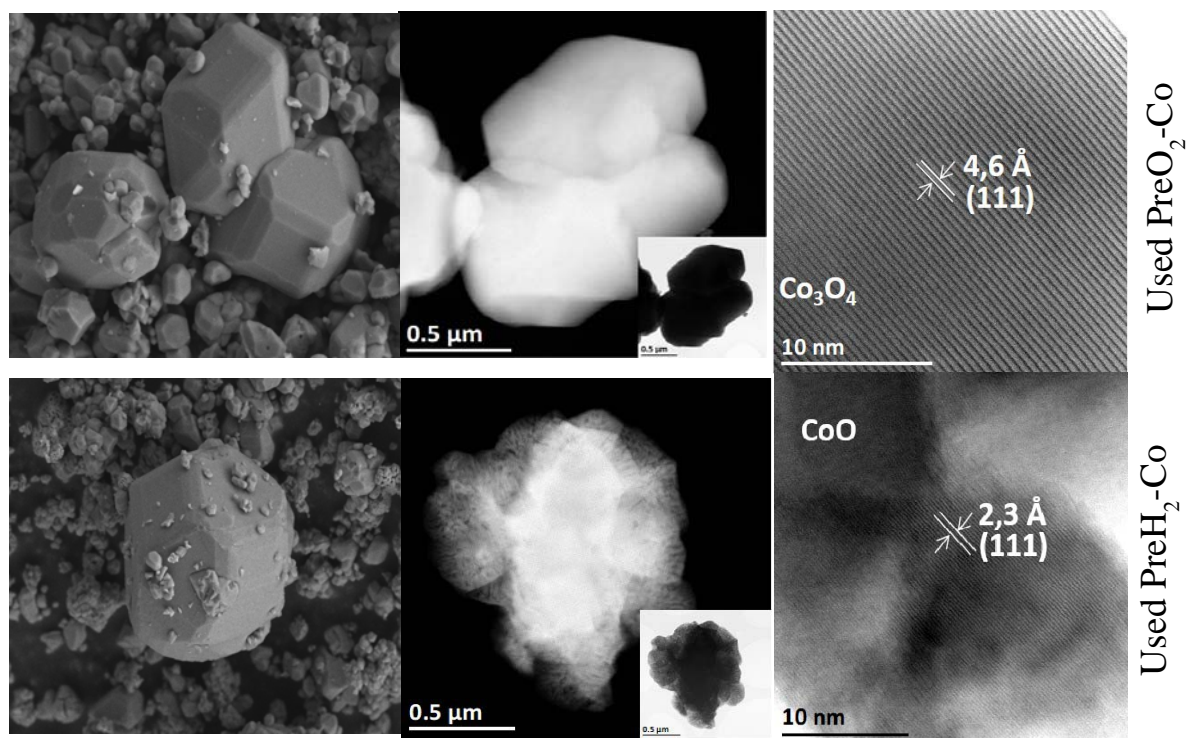


Figure S5. The SEM and HR-TEM images of spent PreO₂-Co(upper) and PreH₂-Co (lower) after COPrOx reaction up to 200 °C for 1 hour

Supporting information 6

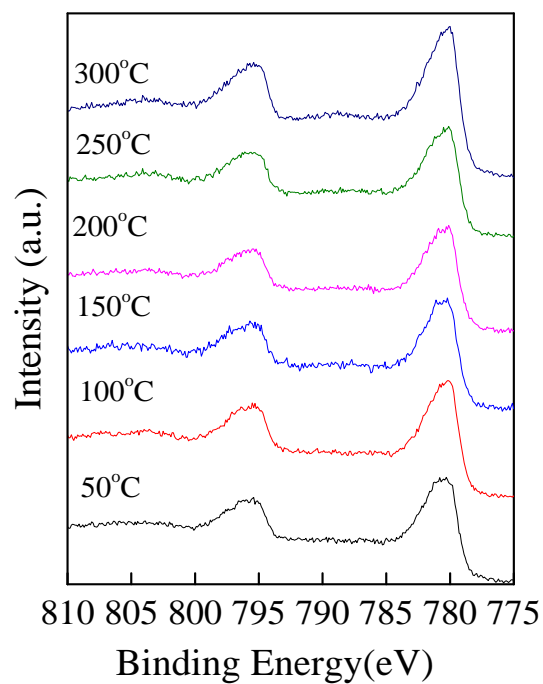


Figure S6. The Co₂p spectra of PreO₂-Co measured in different COPrOx reaction temperatures.

Supporting information 7

The depth distribution of CoO and Co₃O₄ over the first few atomic layers as investigated by non-destructive depth profile measurements. In brief, upon photo-ionization the photoelectron kinetic energy, and thus the information depth (i.d.), is determined by the incident photon energy (hν). The contribution of surface components is less influential in the spectrum as the electron kinetic energy increases.

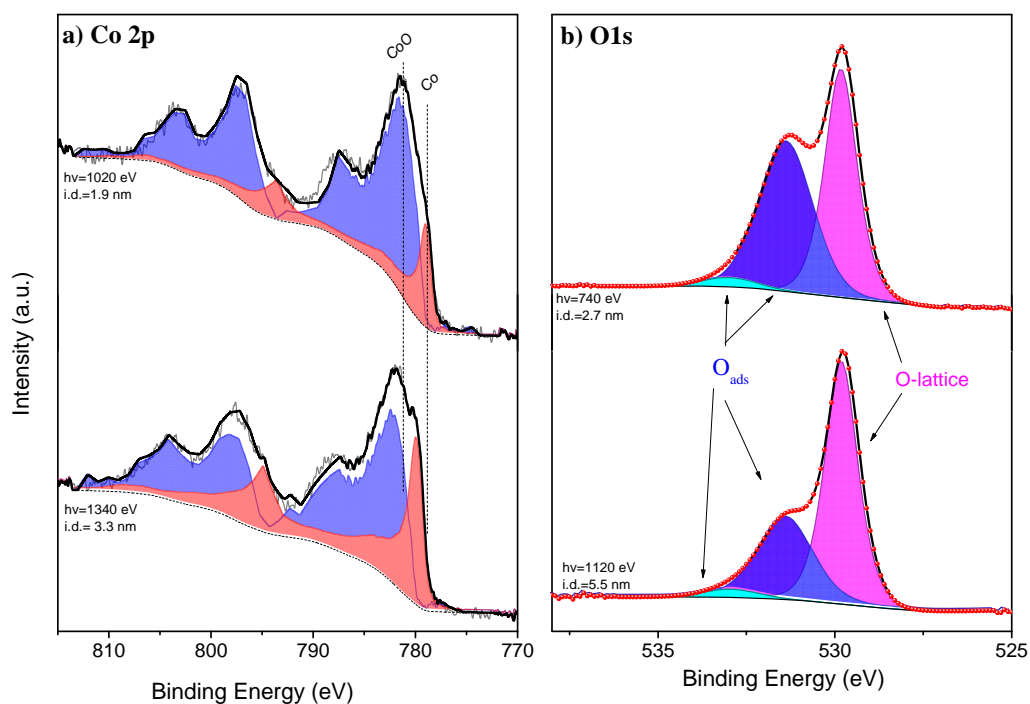


Figure S7. a) The Co 2p peak obtained on PreH₂-Co catalyst in CO-PrOx at 200°C. **b)** The O 1s peak obtained on PreO₂-Co catalyst in CO-PrOx at 250°C. CO-PrOx conditions: 1%CO, 2%O₂ and 97%H₂, 0.5 mbar. Spectra are recorded using two different excitation energies (hν), resulting in two electron kinetic energies (KE) and information depths (i.d.). The mean thickness of CoO estimated by the two spectra in figure S7a is 1.1±0.1 nm.

Supporting information 8

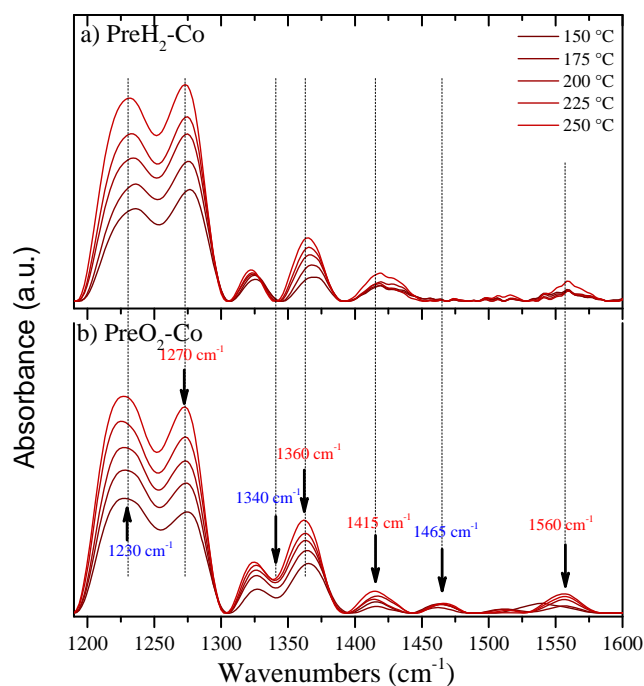


Figure S8. The in situ DRIFTS spectra over PreH₂-Co (a) and PreO₂-Co (b) under COPrOx reaction condition from 150 to 250°C. Conditions: 1%CO, 2%O₂, 40%H₂ in He balance. The broad peak of absorbed water around 1600 cm⁻¹ has been subtracted to facilitate the detection of carbon-based species.

References

- (1) Gunasooriya, G. T. K. K.; van Bavel, A. P.; Kuipers, H. P. C. E.; Saeys, M. Key Role of Surface Hydroxyl Groups in C–O Activation during Fischer–Tropsch Synthesis. *ACS Catal.* **2016**, *6*, 3660–3664.
- (2) Singh, S. A.; Mukherjee, S.; Madras, G. Role of CO₂ Methanation into the Kinetics of Preferential CO Oxidation on Cu/Co₃O₄. *Mol. Catal.* **2019**, *466*, 167–180.