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Improving the Catalytic Performance of Cobalt for CO Preferential Oxidation by Stabilizing the Active Phase through Vanadium Promotion

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ABSTRACT: Preferential oxidation of CO (COPrOx) is a catalytic reaction targeting the removal of trace amounts of CO from hydrogen-rich gas mixtures. Non-noble metal catalysts, such as Cu and Co, can be equally active to Pt for the reaction; however, their commercialization is limited by their poor

stability. We have recently shown that CoO is the most active state of cobalt for COPrOx, but under certain reaction conditions, it is readily oxidized to Co_3O_4 and deactivates. Here, we report a simple method to stabilize the Co^{2+} state by vanadium addition. The V promoted cobalt catalyst exhibits considerably higher activity and stability than pure cobalt. The nature of the catalytic active sites during COPrOx was established by operando NAP-XPS and NEXAFS, while the stability of the Co^{2+} state on the surface was verified by in situ NEXAFS at 1 bar pressure. The active phase consists of an ultra-thin cobalt-vanadate surface layer, containing tetrahedral V^{5+} and octahedral Co^{2+} cations, with an electronic and geometric structure that is deviating from the standard mixed bulk oxides. In addition, V addition helps to maintain the population of Co^{2+} species involved in the reaction, inhibiting carbonate species formation that are responsible for the deactivation. The promoting effect of V is discussed in terms of enhancement of CoO redox stability on the surface induced by electronic and structural modifications. These results demonstrate that V-promoted cobalt is a promising COPrOx catalyst and validate the application of in situ spectroscopy to provide the concept for designing better performing catalysts.

KEYWORDS: COPrOx, cobalt oxides, vanadium oxides, mixed oxides, operando spectroscopy, NAP-XPS, NEXAFS

1. INTRODUCTION

Hydrogen, as a clean energy carrier, is the primary fuel for proton-exchange membrane fuel cells (PEMFCs). Although more advanced technologies for hydrogen production are rising, to date, the majority of commercial H_2 is still produced by steam reforming of hydrocarbon resources.^{1,2} H_2 produced by a steam reforming process followed by water-gas shift contains traces of CO_2 , CO, and CH_4 , which are considered as impurities for PEMFCs.³ Among them, CO is the most critical one, since even 10 ppm of CO in the feedstock can deactivate the platinum group metal (PGM) catalysts in a PEMFC anode,^{4,5} limiting the credibility of this

technology.⁵ So far, various technologies have been developed for hydrogen purification.^{6–9} CO preferential oxidation (COPrOx) in H₂-rich gas is considered as one of the most efficient and straightforward methods for CO elimination. Apart from precious metals (e.g., Pt and Au) that are typically used as catalysts, non-noble metal oxides (e.g., Cu and Co oxides), pure or combined with other elements, have shown excellent activity of CO oxidation in the presence of H₂.^{10–14} Among them, cobalt oxide has attracted wide attention due to its high intrinsic activity toward CO oxidation.^{15,16}

Apart from the influences of structure and morphology, surface state has been considered as the dominant factor of the catalytic performance.^{17,18} Typically, COPrOx over reducible metal oxides follows the Mars–van Krevelen reaction mechanism. In particular, initially, CO adsorbs on cationic sites reacting with surface lattice oxygen to form carbonates, which eventually desorb as CO₂. Gas-phase O₂ regenerates lattice oxygen and closes the catalytic cycle.^{15,19–22} DFT calculations predicted that carbonate decomposition is the rate-limiting step of CO oxidation on cobalt oxides.²³ Therefore, although both Co₃O₄ and CoO oxides are active for CO oxidation, formation and desorption of CO₂ are energetically more favorable on CoO as compared to Co₃O₄, hence producing higher reaction rates on CoO.^{23–25} However, our recent study made clear that CoO is metastable in COPrOx reaction conditions and, at certain temperatures, it can be readily oxidized to Co₃O₄, leading to deactivation. The COPrOx reaction temperature seems to be a critical factor of cobalt oxidation since recent studies report that, at higher temperatures, Co₃O₄ is rapidly reduced to metallic Co.^{26–28} Metallic Co is considered inactive for CO oxidation but has the tendency to catalyze methanation and hydrogen combustion reactions.^{28,29} All the above reports converge to the fact that the cobalt oxidation state is extremely dynamic during the COPrOx reaction and the reactivity is closely related to the redox effect of the gas phase. Durability is an indispensable characteristic of a catalyst; thus, stabilizing the optimum surface oxidation state of a cobalt-based COPrOx catalyst is essential.

The redox ability of cobalt, which is related to the stability of a certain oxidation state, can be modulated by several factors. This includes the particle size and morphology^{30–32} and the choice of the catalytic carrier/support.²⁷ The admixture of another metal or oxide, usually referred as a promoter or doping agent, may also be used to influence the redox ability of cobalt.³³ For example, CoO may be stabilized in an oxidative atmosphere by the presence of Pt,^{34,35} but needless to say that its high price limits the application of platinum as a promoter. Given that variable-valence metal ions have been regarded as active modifiers able to tune the chemical bond or surface state of metal oxides, we became interested in vanadium-modified cobalt catalysts. Vanadium can easily change between various oxidation states,³⁶ and it is known to promote CO oxidation³⁷ and Fischer–Tropsch synthesis³⁸ on cobalt. In order to keep the complexity of the catalyst to the minimum possible in order to facilitate the understanding of its function, vanadium was loaded directly onto commercial CoO nanoparticles, without using a catalytic carrier/support. The catalytic results show that vanadium addition significantly improves both COPrOx activity and stability of CoO. Several *ex situ*, *in situ*, and *operando* characterization methods were used to elucidate the effect of V promotion on cobalt. The interaction between Co and V is examined at the molecular level, and detailed information about the nature of the chemical bond on the catalyst surface is provided. To the best of our knowledge, this paper is the first to report about the superior performance of V-promoted catalyst toward the COPrOx reaction and hopefully can act as a new paradigm for future applications of mixed vanadium-cobalt oxides, which are currently actively exploited in electrocatalysis.³⁹

2. EXPERIMENTAL METHODS

2.1. Catalyst Preparation. Commercial highly pure cobalt oxide nanoparticles (CoO nanoparticles, 99.99%, Sigma Aldrich) were used as precursors. V-modified cobalt oxides were synthesized by an incipient wetness impregnation method. CoO nanoparticles (0.9334 g) were post-impregnated in a NH_4VO_3 solution (0.18217 g of NH_4VO_3 (99%, SERLABO) in 0.2 g of hot water at 75 °C) and then manually stirred until the powder of CoO became all wet. The resulting mixture was then dried in air at 120 °C for 12 h and subsequently calcined at 400 °C for 3 h. The nominal atomic ratio of V/Co is kept at 1/8 ($\text{V}_{0.125}\text{Co}$). The surface purity of the catalysts after synthesis was confirmed by X-ray photoelectron spectroscopy (XPS). The ratio of 1:8 between a promoter and cobalt is reported as an optimum content for many promoted Co systems for COPrOx, for example, Ce–Co and Mn–Co systems;^{40,41} for this reason, this ratio was chosen at first to prepare a V–Co catalyst. Since the catalytic results demonstrated an excellent performance and stability of a $\text{V}_{0.125}\text{Co}$ catalyst as compared to pure cobalt, we did not attempt to further optimize this ratio, but we picked this system for a detailed mechanistic study to understand the role of surface vanadium promotion on cobalt.

2.2. Catalytic Tests. COPrOx catalytic tests on CoO and vanadium-modified CoO catalysts were performed in a fully automated continuous-flow fixed-bed reactor (CETRIB SARL, Andlau, France) under atmospheric pressure;⁴² 50 mg of the catalyst was loaded into the quartz tube and pretreated in H_2 (30 mL min⁻¹) at 400 °C for 30 min (heating rate 10 °C min⁻¹), which according to the TPR- H_2 profile (Figure S1) is enough to reduce CoO to metallic Co. Consequently, the sample was cooled down at 50 °C and the gas mixture switched to 1%CO, 1%O₂, and 50%H₂ in He (50 mL min⁻¹). The reactants and products were monitored by a compact gas chromatograph (CGC from Interscience, Belgium) equipped with a thermal conductivity detector (TCD) detector. Water in the outlet of the reactor was filtered by a moisture trap before the introduction of the gases in the GC columns. Prior to each test, the pre-reduced catalyst was reduced in situ by heating at 10 °C min⁻¹ to 400 °C, holding at 400 °C for 30 min, and cooling back down to 30 °C under 100% hydrogen (50 mL min⁻¹ total flow). The residual oxygen content of the gas phase was below 100 ppm. For light-off tests (increase in the reaction temperature), the catalyst was heated under the COPrOx mixture at 50, 100, 150, 200, 250, 300, and 350 °C using a ramp rate of 10 °C min⁻¹ and 30 min dwell at each temperature. For the stability tests (total duration about 6 h), the catalyst was heated in COPrOx at 250 and 300 °C, before cooling down again to 250 °C (within 15 min). The CO conversion (X_{CO}) and the CO selectivity to CO₂ (S_{CO_2}) were calculated based on eqs 1 and 2, respectively:^{43,44}

$$X_{\text{CO}}(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

$$S_{\text{CO}_2}(\%) = \frac{1}{2} \times \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100 \quad (2)$$

In these equations, $[\text{CO}]_{\text{in}}$, $[\text{O}_2]_{\text{in}}$ and $[\text{CO}]_{\text{out}}$, $[\text{O}_2]_{\text{out}}$ are the molar flows of gases at the reactor inlet and outlet, respectively.

2.3. Characterization of Bulk Structure and Morphology. Hydrogen temperature-programmed reduction (TPRH₂) measurements were performed by means of an automated

characterization system (Micromeritics, model AutoChem II), which incorporates a thermal conductivity detector (TCD). The surface area was determined with a Quantachrome Autosorb-6B surface area analyzer using krypton (Kr) as an adsorbate gas. Samples were degassed at 120 °C for about 5 h prior to Kr adsorption at 77 K, and the specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method using 11 data points in the relative pressure (p/p_0) range of 0.05–0.3. The X-ray diffractograms were collected on a Bruker D8 Advance diffractometer, using Cu K α radiation ($\lambda = 0.15418$ nm) between 20 and 90° (2 θ), with a step of 0.02° and a time of 1 s per step. The morphology of spent and fresh catalysts was examined by a Zeiss GeminiSEM 500 SEM microscope combined with energy-dispersive X-ray spectroscopy (EDS). Scanning transmission electron microscopy (STEM) analysis was carried out using a JEOL 2100 FEG S/TEM microscope operated at 200 kV equipped with a spherical aberration corrector on the probe forming lens. The samples were dispersed by ultrasonication in ethanol and deposited on a holey carbon-coated TEM grids. The STEM images were carried out using a spot size of 0.13 nm, a current density of 140 pA, and a camera focal length of 8 cm, corresponding to inner and outer diameters of the annular detector of about 73 and 194 mrad. Elemental analyses of Co, V, and O were carried out with an EDS probe using a silicon drift detector (SDD) with a sensor size of 60 mm².

2.4. Operando Near-Ambient XPS and NEXAFS. The operando synchrotron-based near-ambient pressure X-ray photoelectron (NAP-XPS) and near-edge X-ray absorption fine structure spectroscopies (NEXAFS) were performed at the CAT branch of the EMIL beamlines (Energie Materials In-situ Laboratory Berlin) at the synchrotron radiation facility BESSY II of the Helmholtz Zentrum Berlin.^{45,46} The gas-phase composition was monitored on-line by a differentially pumped quadrupole mass spectrometer (QMS, Pfeiffer PrismaPro), which was connected to the experimental cell through a leak valve. The NEXAFS spectra were recorded in the total electron yield (TEY) mode. The catalysts powders were pressed into pellets and placed on a stainless steel plate, which could be heated at the back side by an IR laser. The pellets were initially pretreated in 0.5 mbar H₂ at 400 °C for 30 min. After the pretreatment, the catalyst was cooled down to room temperature and the reactant gas mixture of 1%CO, 1%O₂, and 50%H₂ in He of 0.5 mbar was introduced via 4 calibrated mass flow controllers (Bronkhorst) at a total mass flow of 30 mL min⁻¹. The catalysts were initially measured at different temperatures by stepwise heating for about 1 h in each temperature (light-off measurements). In addition, fresh catalysts after pre-reduction step were measured by directly heating at 250 °C for about 2 h to resemble the conditions of the steady-state catalytic tests. XPS spectra of Co 2p, V 2p, O 1s, and C 1s as well as NEXAFS Co L3 and V L3-edges were collected during the reaction. The Co 2p spectra were fitted by a linear combination of peak lineshapes recorded on reference materials^{47,48} using the CASA XPS version 2.3.23 software (more details are provided in the Supporting Information). For the quantitative analysis, the photon flux and the photon-energy dependence of the atomic subshell photoionization cross sections⁴⁹ were taken into account. The XPS Co 2p and V 2p peak intensities were simulated using SESSA version 2.1.1 software⁵⁰ for a model consisting of spherical layered particles with 50 nm in diameter.

The V L3-edges were simulated using the charge-transfer multiplet (CTM) approach in order to obtain qualitative information from the absorption spectra.^{51,52} The calculations have been performed using the CTM4XAS5.23 program.⁵³ The tetrahedral symmetry is chosen for the calculations of V⁵⁺ in Co₃V₂O₈⁵⁴ and CoVO_x while the octahedral one for V⁵⁺ in the V₂O₅.⁵⁵ The crystal field value (10Dq) and the charge transfer energy value (Δ) were the main parameters adjusted in the simulation to obtain the best accordance with the experimental

spectra. Other simulation parameters were as follows: (i) for CoVO_x , Slater integrals (F_{dd} , F_{pd} , G_{pd}) = 0.8, spin-orbit splitting parameter $SO = 1$, optical parameters $D_t = D_s = -0.1$ eV, core hole potential U_{pd} and the 3d-3d repulsion energy $U_{pd} = U_{dd} = 0.5$, and the hopping parameters $e_g = 1$ eV and $t_{2g} = 0.7$ eV; (ii) for the V_2O_5 reference, (F_{dd} , F_{pd} , G_{pd}) = 1, $SO = 1.05$, $U_{pd} - U_{dd} = 2.5$, $e_g = 1.2$ eV and $t_{2g} = 0.6$ eV; and (iii) for the $\text{Co}_3\text{V}_2\text{O}_8$ reference, (F_{dd} , F_{pd} , G_{pd}) = 0.75, $SO = 1$, $D_t = D_s = -0.1$ eV, $U_{pd} = 0$, $U_{dd} = 1.2$, $e_g = 1.6$ eV and $t_{2g} = 0$.

2.5. In Situ NEXAFS in 1 bar. In situ NEXAFS experiments at 1 bar were performed at the APE-HE beamline of the Elettra synchrotron radiation facility (Trieste, Italy), exploiting a dedicated setup based on a reaction cell with Si_3N_4 membranes, as described in detail elsewhere.⁵⁶ The NEXAFS signal was detected in TEY mode by probing the drain current from the sample with a picoammeter. The catalyst powder was loaded in the in situ cell, installed in the APE-HE instrument, and interfaced with gas delivery and temperature control systems. Gas flows were realized by calibrated mass flow controllers at 50 mL min^{-1} . The sample was initially pretreated in O_2 at 200°C for 15 min and then cooled to room temperature under He gas flow to remove adventitious carbon. In situ NEXAFS spectra at Co and V L-edges were then recorded (i) under a reducing atmosphere (pure H_2) and (ii) exposing the reduced sample to an oxidizing atmosphere (10% O_2/He) at selected temperatures in the $38\text{--}315^\circ\text{C}$ range. NEXAFS data were acquired after 15 min at each selected temperature point. After the reduction step in H_2 , the sample was cooled down to room temperature in He gas flow prior to the oxidation step in 10% O_2/He . Data treatment, involving energy alignment, background subtraction using an asymmetric least squares fitting routine, and normalization to the total area under the curves, was performed by using the recently developed THORONDOR code.⁵⁷

3. RESULTS

3.1. Catalytic Performance in COPrOx Reaction. Figure 1 compares the CO conversion (X_{CO}) and the selectivity to CO_2 (S_{CO_2}) of pure CoO (hereafter referred to as CoO_x) and V-modified CoO (hereafter referred to as CoVO_x) catalysts. Prior to the reaction, the samples were reduced at 400°C . Our previous study showed that reduced cobalt catalysts are more active in COPrOx than their oxidized counterpart.²³ For both catalysts, X_{CO} increases with the reaction temperature (Figure 1a); however, X_{CO} over CoVO_x is always higher than pure CoO_x . The CO_2 selectivity decreases with temperature for both catalysts (Figure 1b). At low temperatures, CoO_x seems to have a higher S_{CO_2} than CoVO_x , while above 250°C , the trend is reversed. A decrease in S_{CO_2} with temperature is common in COPrOx studies of both noble^{10,58} and transition metals.^{59,60} This is attributed to the higher activation energy of the H_2 oxidation reaction as compared to the CO oxidation reaction.^{14,60,61} Therefore, as the temperature increases, the rate of H_2 oxidation increases faster, leading to a lower CO_2 selectivity. Higher hydrocarbons were not observed in the products, but at high temperatures, methane was detected. Details about methane production can be found in the Supporting Information (see Figure S2 and relevant discussion).

To evaluate their stability, the two catalysts were monitored during COPrOx at 250 and 300°C for about 6 h on stream. Note that these tests succeed the temperature tests of Figure 1a,b using the same samples after a reduction pretreatment to 400°C . As shown in Figure 1c,d, the X_{CO} and S_{CO_2} remained quite stable in the case of CoVO_x , in contrast to CoO_x , which undergoes rapid deactivation especially at the initial test at 250°C . The X_{CO} of CoO_x at 250°C decreased rapidly from 90% to 35% within about 90 min (Figure 1c). The X_{CO} increases

for both catalysts when the temperature increases to 300 °C, but CoVO_x remains almost 30% more active than CoO_x. Finally, when the temperature goes back to 250 °C, there is a slight deactivation of CoVO_x as compared to the X_{CO} initially observed, but this sample continues to be considerably more active than pure CoO_x. The superior performance of CoVO_x also expands in the CO₂ selectivity, which is significantly higher for this sample at both temperatures. Overall, the addition of vanadium into cobalt oxide has significantly enhanced the COPrOx reactivity and CO₂ selectivity. Note that pure vanadium oxide is largely inactive for COPrOx (Figure S3); therefore, the dramatic improvement of reactivity can be only ascribed to a synergetic/promotional effect between cobalt and vanadium.

Figure 1. (a) CO conversion and (b) CO₂ selectivity of CoO_x and CoVO_x catalysts as a function of the COPrOx reaction temperature and (c) CO conversion and (d) CO₂ selectivity as a function of the time-on-stream at two characteristic temperatures. The tests were performed in a fixed bed reactor in 1%CO, 1%O₂, and 50%H₂ in He-balanced flow; 50 mg of catalyst; 50 mL/min of total flow at atmospheric pressure.

3.2. Ex Situ Characterization. 3.2.1. Structure and Morphology. The X-ray diffraction (XRD) patterns of fresh, reduced, and spent CoO_x and CoVO_x catalysts are shown in Figure S4. The characteristic diffraction peaks of pristine CoO_x are clearly observed at $2\theta = 36.54, 42.44, 61.53, 73.82, \text{ and } 77.66^\circ$, which correspond to the crystalline planes of (111), (200), (220), (311), and (222) of the face-centered cubic (fcc) CoO phase.^{62,63} Different diffraction peaks appear in the XRD pattern of the as-prepared CoVO_x, which are well assigned to the crystallographic planes of Co₃O₄ cubic spinel structure (PDF #76-1802 of the JCPDCS). The Co₃O₄ phase formation over CoVO_x is the result of calcination in air at 400 °C according to the preparation protocol of this catalyst. After reduction in H₂, the XRD patterns of both CoO_x and CoVO_x have the same diffraction peaks, which characterize the metallic Co phase. This

proves that, in their bulk, both catalysts are fully reduced during the reduction treatment preceding the COPrOx. The XRD patterns after reaction (spent catalyst) are very similar to those after H₂ treatment, suggesting that metallic Co is preserved in the bulk of the catalysts also under COPrOx. Notably, no additional peaks associated to vanadium compounds are observed in the XRD pattern of the V-modified CoO sample. The absence of the vanadium phase suggests that the vanadium atoms either form an amorphous oxide or are highly dispersed on the surface of cobalt or even interdiffused in the lattice of cobalt oxide.

Figure 2. (Left) SEM micrographs of fresh and spent CoO_x and CoVO_x catalysts and (right) EDS mapping of fresh CoVO_x along with the EDS spectrum recorded from the whole area of the SEM image.

The morphology of fresh and spent catalysts was examined by scanning electron microscopy (SEM). The typical images of fresh and spent samples after 5 h in the COPrOx reaction at 250 °C as well as energy-dispersive X-ray spectroscopy (EDS) micrographs of the fresh CoVO_x are shown in Figure 2. SEM images reveal that both fresh CoO_x and CoVO_x catalysts consist of similar nanoparticles with sizes between 30 and 60 nm. The typical images of spent catalysts demonstrate the agglomeration of the particles, which should be expected for unsupported metal particles after the long-term stability test at 250 °C. The EDS mapping shows that vanadium is distributed all over the entire surface of cobalt, while some homogeneously dispersed particles with a diameter of around 1–2 μm can be also distinguished in the vanadium EDS image. The % at. of V calculated from the EDS spectrum corresponding to this SEM image is 11%, which is in good agreement with the nominal V loading on the catalyst (12.5%).

Figure 3a shows a typical annular bright-field (ABF) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images of the CoVO_x catalyst after 5 h COPrOx at a 250 °C reaction (spent catalyst). Additional STEM images of the spent catalyst, as well as just after reducing pretreatment and before the catalytic tests, can be found in Figures S5a and S5b. The ABF-STEM image shows aggregated CoVO_x nanoparticles with a size of around 50 nm. The presence of darker regions inside the particles is clearly visible in the HAADF-STEM image. Since, in HAADF mode, the contrast is directly related to the atomic number and the material density, one can assume that the darker regions are cavities or voids with a mean size of about 10 nm. Interestingly, as depicted by Figure 3a, the cavities have a round shape. Similar morphologies have been observed also in our previous work on pure cobalt oxides.²³

Aiming at locating V in the catalyst grains, a complementary analysis was carried out using STEM combined with EDS. The STEM-EDS maps of an aggregate with about 60 nm in diameter are presented in Figure 3b. Elemental mapping reveals significant overlap between V and Co, suggesting that V is well distributed all over the Co particles. Although this is the most common arrangement of the catalyst (see Figure S5), sometimes STEM-EDS images with separated Co and V could be also depicted (not shown here). A clearly visible feature in the STEM-EDS image that combines Co and V signals (Figure 3b) is that the V content is increasing at the edge of the particle, suggesting that V is enriched on the surface of the grains. However, the Co signal is extending to the perimeter of the aggregate overlapping with V, which is strong evidence that the two elements are not segregated in the near surface area but most probably they are mixed together. Interestingly, in the XRD patterns of spent CoVO_x shown in Figure S4, there are no features related to vanadium, demonstrating the absence of such phases in the bulk. In accordance to the STEM-EDS analysis, this can be justified by highly distributed vanadium around the cobalt particles and/or the formation of an amorphous vanadium oxide layer.

Figure 3. (a) ABF-STEM and the corresponding HAADF-STEM and (b) STEM-EDS analysis images with elemental mapping (Co and V and merged Co+V). The images were collected over the spent CoVO_x catalyst after a 5 h reaction at 250 °C in a 1 bar COPrOx mixture.

Fine details of the near surface area of the CoVO_x catalyst are given by high-resolution STEM (HR-STEM). Figure 4 presents a characteristic HR-STEM micrograph collected at the external surface of the spent CoVO_x catalyst. Similar micrographs of another catalytic particle can be found in Figure S5c. The separation distances between sets of parallel planes close to the surface (d_{hkl}) were measured in higher magnification images and compared with known d_{hkl} values of cobalt and vanadium oxides. Measurements in several areas well resolved at the

HR-STEM images suggest two d_{hkl} distances of 0.25 and 0.29 nm. These distances match with the (311) and (220) planes, respectively, of Co_3O_4 (JCPDS 03-065-3103) and binary mixed $\text{Co}_3\text{V}_2\text{O}_8$ (JCPDS 00-016-0675), along with the (130) and (013) planes of $\text{Co}_2\text{V}_2\text{O}_7$ (JCPDS 00-029-0519). Monoclinic and orthorhombic V_2O_5 crystal as well as CoO do not fit with the measured d_{hkl} distances and should be excluded. Although HR-STEM cannot be conclusive about the composition of the surface layer, the possibility of a mixed Co–V oxide formation is in line with the surface-sensitive spectroscopic results, as will be discussed later.

Figure 4. High-resolution ABF-STEM and the corresponding FFT filtered images (bottom right) of spent CoVO_x catalysts derived from catalyst areas close to the particle edge. The interplanar spacing is indicated by two parallel lines. The squares indicate the part of the low magnification image from which the high-resolution images are derived.

3.2.2. BET and TPR. The BET specific surface area measurements of reduced and spent CoO_x and CoVO_x catalysts are presented in Table 1. After reduction, pure CoO_x has a significantly lower surface area than CoVO_x , even though CoO particles from the same batch were initially used for the CoVO_x and CoO_x preparation. This demonstrates that sintering and agglomeration of cobalt nanoparticles upon the reducing thermal treatment is moderated by the addition of V, in agreement with SEM images shown in Figure 2. Another interesting observation is that the surface area increases after the reaction, as compared to the reduced catalyst, which, according to the low magnification STEM images shown in Figure S5b, is due to improvement in the dispersion of the catalytic particles.

Temperature-programmed reduction (TPR) was used to investigate the effect of V addition to cobalt oxide reducibility. The TPR profile (Figure S1) of pure CoO_x after calcination in air is characterized by two main features (peaks), which represent a two-stage reduction process $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$, in good agreement with previous reports.^{37,64} The TPR profile of the CoVO_x catalyst shows a number of additional peaks shifted to higher temperatures as compared to CoO_x . Although the attribution of each feature in the TPR profile of CoVO_x is not straightforward since it involves reduction of both V and Co oxide species as well as their interfaces, the higher reduction temperature implies a strong interaction between cobalt and vanadium, resulting in a material that is more difficult to reduce.⁶⁵ The TPR profiles are related to bulk reduction, and therefore it is hard to correlate them with the catalytic performance. The differences in the reducibility of the surfaces of the two catalysts will be defined in more detail based on the operando spectroscopic results presented below.

Table 1. Surface Area of CoO_x and CoVO_x Catalysts Measured by Kr-BET, Just before (Reduction in H₂ for 30 Min at 400 °C) and after the COPrOx Reaction (Spent) at 250 °C for 90 Min

	CoO _x (m ² gr ⁻¹)	CoVO _x (m ² gr ⁻¹)
reduced catalyst (before reaction)	1.39	9.57
spent catalyst (after reaction)	1.79	16.05

Figure 5. Operando NAP-XPS spectra of Co 2p_{3/2} over CoO_x (a) and CoVO_x (b) catalysts recorded at different temperatures during the COPrOx reaction: 1%CO, 1%O₂, and 50%H₂ in He, at 0.5 mbar total pressure. Each spectrum was recorded after about 10 min in the reaction feed. The distribution of cobalt species obtained by Co 2p peak deconvolution is shown in the inset bar graphs. For clarity, all spectra are normalized to the same intensity and offset to the y axis. (c) Co 2p NAP-XPS and (d) Co L₃-edge NEXAFS spectra of CoO_x and CoVO_x catalysts in conditions that favor the formation of the Co²⁺ state, i.e., at 150 °C in the COPrOx mixture. Co 2p and Co L₃-edge spectra are normalized to the same intensity.

3.3. Comparative Operando NAP-XPS and NEXAFS at 0.5 mbar. 3.3.1. The Oxidation State of Cobalt. Several previous reports have demonstrated that the surface oxidation state of cobalt plays a key role for COPrOx reactivity.^{23,66,67} At low temperatures, the COPrOx mixture can oxidize metallic cobalt, whereas at relatively high temperatures, cobalt oxides could be reduced back to metal.^{26,27,68} Thus, depending on the COPrOx reaction conditions, cobalt may easily swap between different oxidation states. Herein, synchrotron-based NAP-XPS and NEXAFS were used to monitor, on a comparative basis, the surface oxidation state

of CoO_x and CoVO_x during the COPrOx reaction. Light-off and time-on-stream experiments were performed following an experimental protocol similar to the catalytic tests shown in Figure 1. Fresh samples, retrieved from the same synthesis batch, were used in each case. Prior to the reaction, the samples were pre-reduced at 400 °C in 0.5 mbar H_2 for 30 min.

Figure 5 shows the evolution of Co $2p_{3/2}$ spectra as a function of COPrOx reaction temperature for CoO_x (Figure 5a) and CoVO_x (Figure 5b) catalysts. Deconvolution of the spectra using reference peaks was used to quantify the various oxidation states of cobalt (see Figure S6 and relevant discussion). At 50 °C, the main Co $2p_{3/2}$ peak of the CoO_x catalyst (Figure 5a) is centered at 780.5 eV with a satellite peak around 786.7 eV characteristic of Co^{2+} species.^{30,31,62,69,70} The shoulder at 778.6 eV is induced by metallic Co,^{62,71–73} indicating that cobalt forms a mixed Co^0/CoO phase in COPrOx, in accordance with our previous findings.²³ As the reaction temperature increases, cobalt is further oxidized into Co_3O_4 (with an average oxidation state $\text{Co}^{2.67+}$) identified by a broad satellite at 789.5 eV clearly indexed at 300 °C.⁷⁰ However, at 350 °C, the low binding energy (BE) peak appears again in the Co $2p_{3/2}$ spectrum, indicating that part of Co_3O_4 is reduced back to metallic Co. This is an intriguing observation showing that the redox effect of COPrOx mixture on cobalt surface is controlled by the reaction temperature.

In the case of CoVO_x (Figure 5b), a mixed $\text{Co}^0/\text{Co}^{2+}$ oxidation state is found at 50 °C, while at 150 °C, the surface is dominated by Co^{2+} , likewise to the CoO_x sample. However, above this temperature, the stability of Co^{2+} species is distinctly different between the two catalysts. In particular, as clearly shown in the bar graphs, over CoVO_x , the Co^{2+} phase is stabilized up to 250 °C, while partial oxidation to $\text{Co}^{2.67+}$ is observed only above 300 °C. Contrary to CoO_x , the sample is not reduced to metallic Co^0 at 350 °C. Notably, Co^{2+} is a dominant CoVO_x surface phase at intermediate reaction temperatures (ca. 250 °C), which are actually of main interest for COPrOx since higher temperatures promote the undesired water and methane formation.^{23,60}

NEXAFS is a powerful technique to study the electronic and geometric structure of materials in an element-specific fashion.⁷⁴ Moreover, contrary to XRD, it is surface-sensitive (probing depth in the order of 5–10 nm with TEY detection)⁵⁵ and can detect both crystalline and amorphous phases.^{75–77} The operando NEXAFS spectra presented in Figure S7 confirm the higher stability of Co^{2+} species over the CoVO_x catalyst observed in NAP-XPS. In addition to that, the characteristic lineshape of octahedrally coordinated Co^{2+} can be clearly distinguished at intermediate temperatures in both samples. This result implies that the octahedral symmetry of Co^{2+} ions does not change by V addition, in contrast to other promoters, e.g., Zn, which tend to stabilize tetrahedral Co^{2+} species.⁷⁸

In an attempt to identify minor differences in the electronic structure of Co^{2+} species in the two cases, we compare in Figure 5c the Co $2p$ spectra of the two catalysts at conditions where the Co^{2+} species dominate. Despite the similar peak profiles, the spectrum of CoVO_x is shifted by about 0.6 eV with respect to CoO_x . This shift is also observed for Co $2p$ spectra recorded at different photon flux conditions and is not due to electrostatic charging, considering the identical position of the C 1s peak of the two samples (see below). In addition, the shift between the spectra is also visible in partially reduced CoO_x and CoVO_x where the sharp photoelectron peak of Co^0 was used as an internal reference (see Figure S8). The Co $2p_{3/2}$ shift to higher binding energies is consistent with earlier studies of cobalt vanadates;^{79–82} however, the magnitude of the energy shift (0.6 eV) observed here is lower than the previous reports.

The Co L3-edges corresponding to the photoelectron peaks (Figure 5d) are characteristic of octahedrally coordinated Co^{2+} species^{34,70,83} as mentioned above. Although the two spectral lineshapes overlap, in the case of CoVO_x , there is a relatively lower intensity of the peak at 777.7 eV and higher at the features around 780.1 and 781.8 eV (pointed out by arrows). Changes in the NEXAFS spectra indicate deviation in the ligand-field-related Co 3d electronic states of the two catalysts, despite the same symmetry. This can be caused by differences in the Co–O bond length, angle, and strength, as well as the interaction of cobalt ions with V heteroatoms.^{84,85} Similar changes in the Co L3-edge of cobalt–halogen compounds have been attributed to the increase in cobalt ion electronegativity.⁸⁴

Figure 6. (a) % CoO in the overall CoO and Co_3O_4 oxide layer quantified from NAP-XPS Co 2p peak deconvolution as a function of time on stream. (b) Characteristic Co L3-edge NEXAFS spectra recorded at various steps in the COPrOx reaction. The spectra of reference CoO and Co_3O_4 oxides are included for comparison. The spectra for both CoO_x and CoVO_x catalysts were recorded at 250 °C in 1%CO, 1%O₂, and 50%H₂ in He, at 0.5 mbar total pressure.

Short-term stability tests were performed at 250 °C in order to explicate the considerable differences in the durability of the two catalysts found in Figure 1c. The evolution of the % CoO, derived by deconvolution of Co 2p peaks, as a function of the time on stream is shown in Figure 6a. Initially, the surface of both catalysts was dominated by Co^{2+} , which decreases with time in favor of $\text{Co}^{2.67+}$ formation. However, significant differences can be observed in the % fraction of Co^{2+} between the two samples. In particular, for CoO_x , the amount of Co^{2+} species rapidly drops to 30% due to $\text{Co}^{2.67+}$ formation, while for CoVO_x , this value falls only up to 78% in the time scale of the experiment. Depth-dependent measurements of the Co 2p peak were used to distinguish the distribution of the two oxides on the CoVO_x surface (the information depth varied between 1.6 and 4.7 nm). As shown in Figure S9, there is no evident

depth dependency between the two Co 2p components, which indicates that Co^{2+} and $\text{Co}^{2.67+}$ phases do not overlap significantly but are arranged separately on the CoVO_x surface. Comparison of the Co L3-edges in Figure 6b confirms the significant differences in the oxidation state of the two catalysts consistently with NAP-XPS. Overall, from the above presented results, it becomes clear that the thermal stability of octahedral Co^{2+} species in COPrOx conditions is improved by V addition.

3.3.2. The Oxidation State and Surface Distribution of Vanadium. To better understand the behavior of the CoVO_x catalyst, it is important to determine the oxidation state and the stability of vanadium. Figure 7a depicts V 2p operando NAP-XPS spectra of CoVO_x at the initial and highest reaction temperatures. A complete list of the spectra for all temperatures can be found in Figure S10a. Vanadium may occur in several oxidation states that can be distinguished in photoemission experiments. As shown in Figure 7a, at 50 °C, the V 2p_{3/2} peak is deconvoluted in two components at 515.8 and 517.1 eV corresponding to V^{4+} and V^{5+} species, respectively, 86–89 while at 350 °C, the V^{5+} peak dominates the spectrum at the expense of the V^{4+} component. Depth-dependent V 2p measurements (not shown) suggested that both vanadium oxidation states co-exist on the surface without evident depth distribution. From the analysis of %V in different oxidation states with reaction temperature (Figure 7b), we observe progressive oxidation of V^{4+} to V^{5+} . The % Co^{2+} included in the same graph is practically stable between 100 and 250 °C, suggesting that the oxidation behavior of the two elements present in CoVO_x is different. This is also supported by the stability experiments, where, after about 30 min on stream, all vanadium was converted to V^{5+} and remained stable onward (Figure 7a).

Figure 7. (a) Operando NAP-XPS V 2p spectra of the CoVO_x catalyst recorded during temperature-dependent and stability COPrOx tests. The spectra are normalized to the same intensity and offset to the y axis. (b) % evolution of V^{5+} and Co^{2+} species with temperature calculated based on V 2p peak deconvolution shown in (a) and Co 2p spectra shown in Figure 5b. (c) Operando V L3-edge NEXAFS spectra of the CoVO_x catalyst (solid black line) recorded at 250 °C during stability COPrOx tests. Reference V L3-edge spectra of V_2O_5 and $\text{Co}_3\text{V}_2\text{O}_8$ (solid blue and red lines, respectively) are included for comparison. Theoretically simulated V L3-edges (dashed lines) for the same V oxidation state (5+) but different crystal field geometries (Td and Oh); 10Dq and Δ values adopted in the simulations are included under each theoretical spectrum. The exp. $\text{Co}_3\text{V}_2\text{O}_8$ V L3-edge spectrum is adapted with permission from ref 54. The exp. V_2O_5 spectrum is taken from ref 91 published by the PCCP Owner Societies.

In Figure 7c, the V L3-edge of CoVO_x recorded at 250 °C during COPrOx stability tests is compared with spectra of $\text{Co}_3\text{V}_2\text{O}_8$ and V_2O_5 reference compounds. The evolution of V L3-edges as a function of the reaction temperature is given in Figure S10b. The reference oxides were selected because of different vanadium coordination geometries with the oxygen ligands: tetrahedral (Td) for $\text{Co}_3\text{V}_2\text{O}_8$ ⁵⁴ and distorted octahedral (Oh) for V_2O_5 ,^{55,90} albeit they are both composed of V^{5+} cations similar to CoVO_x . According to the literature, the various V oxidation states are differentiated by a shift in all discernible spectral features of V L-edge spectra. For example, the NEXAFS peak maximum of V^{5+} in V_2O_5 oxide is centered at around 518.8 eV and is shifted by approximately 1 eV from that of V^{4+} .^{36,77,91–94} The alignment of the peak maximum for all NEXAFS spectra in Figure 7c confirms the XPS results, which show that V^{5+} is the dominant oxidation state of vanadium during COPrOx. The CoVO_x peak profile does not contain the features around 517 and 519.5 eV, resembling more to the $\text{Co}_3\text{V}_2\text{O}_8$ than V_2O_5 reference oxide. This suggests that the majority of V^{5+} in our catalyst is mostly in Td coordination with O^{2-} anions and not as segregated V_2O_5 particles. However, there are some clear differences in the NEXAFS lineshapes between CoVO_x and $\text{Co}_3\text{V}_2\text{O}_8$, with the most prominent being the increased intensity of the former at around 517.5 eV. This cannot be induced by lower vanadium oxidation states since these states should have been also visible in the V 2p spectra, supporting the idea of a distorted V–O symmetry as compared to the vanadate reference oxide.

The spectral shape of the NEXAFS V L3-edge is strongly correlated to the coordination environment and the number of 3d electrons of the metal center.⁵¹ Therefore, it may be used to provide interesting insights into the local geometry around the V^{5+} cation,⁹² as has been shown previously for other transition metal oxides.^{95,96} Theoretical simulation of the V L3-edge using the charge-transfer multiplet (CTM) approach can help to estimate the variations in the V–O interaction that are accountable for the differences in the lineshapes.^{51,52} The two key parameters affecting the shape of the calculated XAS curves are 10Dq (crystal field splitting) and Δ (charge transfer energy). The 10Dq parameter determines the splitting in the crystal field and depends mainly on the metal–ligand distance, in a way that an increase in the value of 10Dq corresponds to a decrease in V–O distance. The charge transfer energy term Δ describes the interaction of V 2p ions with delocalized electrons from the O 2p orbital.³¹ An increase in Δ value corresponds to weaker interaction between V 2p and O 2p orbitals. The theoretically simulated V L3-edges that give the best accordance with the experimental spectra are included in Figure 7c, while the 10Dq and Δ parameters are shown in Table 2. The CoVO_x catalyst has higher 10Dq and lower Δ values as compared to $\text{Co}_3\text{V}_2\text{O}_8$. According to the assignment mentioned above, the distance between V and O ions is shorter and their interaction is stronger in CoVO_x as compared to $\text{Co}_3\text{V}_2\text{O}_8$. Assuming that Co and V ions share

some oxygen atoms in their lattice, shorter V–O bonds induce correspondingly longer Co–O bonds. The net result of this change is that the cobalt 3d electrons are more localized on the cobalt atoms in CoVO_x as compared to Co₃V₂O₈ bulk oxide.⁸⁵

The surface atomic percent (at. %) of V on the CoVO_x surface was determined from the V 2p and Co 2p NAP-XPS peaks. In order to estimate the distribution of vanadium in the outer surface layers, the %V concentration was calculated at different analysis depths using Co 2p and V 2p peaks recorded with increasing photon energies.⁹⁷ The results presented in Figure S11 show that the V concentration decreases with the analysis depth. This indicates that V and Co are not homogeneously mixed in the outermost 5 nm of the catalyst (maximum analysis depth of NAP-XPS) but form a layer structure where V is the shell and CoO is the inner core. More details will be provided based on quantitative simulation of these results shown below.

Table 2. Symmetry, 10Dq (Crystal Field Splitting), and Δ (Charge Transfer Energy) Parameters Found by the Multiplet Calculation to Give the Best Accordance with the Experimental Spectra Shown in Figure 7c

	symmetry	10Dq (eV)	Δ (eV)
V ₂ O ₅	O_h	1.3	3
Co ₃ V ₂ O ₈	T_d	0.7	2.2
CoVO _x	T_d	1	0.5

3.3.3. Evolution of the Adsorbed Species during COPrOx. Operando NAP-XPS provides the necessary chemical and surface specificity to identify adsorbed carbon species during the reaction. In Figure 8, the C 1s spectra at characteristic reaction temperatures are shown together with the evolution of the carbon surface concentration for CoO_x and CoVO_x catalysts. The amount of adsorbed carbon over CoVO_x is constant up to 200 °C, while above this temperature, it shows a decreasing tendency. Carbon evolution over CoO_x is notably different, exhibiting a fast decrease of carbon population up to 200 °C and a steep rising above this temperature, which overwhelms almost four times the carbon observed on CoVO_x.

Deconvolution of the C 1s peak can help to distinguish the nature of adsorbed carbon. As shown in Figure 8, four main carbon species coexist on the two surfaces. Based on previous reports, the peak at 284.5 eV is due to C–H and C–C bonds, while the two peaks at 286.4 and 288.4 eV are attributed to oxygenated carbon species like C–O–C and O–C=O, respectively.²³ These species persist on the surface of CoVO_x catalysts at all reaction temperatures with small variations in their relative population. In the case of CoO_x, the evolution of carbon species is remarkably different, with a new C 1s peak at 289.3 dominating the surface above 250 °C. The binding energy of this peak is characteristic for carbonate (CO₃²⁻) or oxalate ((COO)²⁻) species as has been clearly shown previously.^{98,99}

This attribution is confirmed by the O 1s spectra recorded at 350 °C and shown in Figure 8b. The overall O 1s peak can be deconvoluted in two main oxygen species. The one around 529.6 eV is assigned to the lattice oxygen of the cobalt and vanadium oxides (CoO, Co₃O₄, and VO_x have very similar O 1s binding energies).^{23,100} The high binding energy components are located at 531 eV (CoVO_x) and 531.9 eV (CoO_x) and can be attributed to oxygenated

carbon/hydroxyl species^{101,102} and carbonate/oxalate species,^{98,99} respectively. Kruse and coworkers showed that the binding energy difference between the O 1s and C 1s peaks $\Delta BE(O\ 1s-C\ 1s)$ can be used to distinguish between carbonate and oxalate carbon species. Taking as an internal reference the position of the C–C peak, this difference is found in our case to be 242.1 ± 0.1 eV, which is in good agreement with the value of 242.0 ± 0.2 eV reported for carbonate species.^{98,99}

Figure 8. (a) Operando C 1s NAP-XPS spectra recorded at different COPrOx reaction temperatures over CoO_x (top) and CoVO_x catalysts. The middle graph shows the evolution of the carbon atomic percent (at. %) at the surface (2 nm) as a function of the COPrOx reaction temperature, calculated by the C 1s, Co 2p, and V 2p peaks. (b) Comparison of the O 1s NAP-XPS spectra of the two catalysts recorded at 350 °C in COPrOx. The O 1s peaks are normalized to the same intensity and offset to the y axis.

Carbonates have been proposed both as spectators¹⁰³ and inhibitors²³ for the CO oxidation reaction over cobalt surfaces. This ambiguity is probably related to the specific reaction conditions and/or the chemical nature of carbonate species. Indeed, the absence of H₂ from the reaction mixture in ref 103 is expected to decrease the amount and stability of carbonates as compared to the present study. In addition, an evident difference in the nature of the carbonates between ref 103 and this work is manifested by the considerable shift in the C 1s binding energy (288.2 eV in ref 103, instead of 289.3 eV here). In our recent work,²³ the differences in the reactivity between CoO and Co₃O₄ were attributed to their different capacity to form carbonates under COPrOx reaction conditions. The NAP-XPS analysis evidences that stabilization of the Co²⁺ oxidation state by the V promoter controls the amount of adsorbed carbonates during the reaction, having direct benefits on the reactivity.

3.4. Reducibility of CoVO_x Measured by In Situ NEXAFS at 1 bar. The operando NAP-XPS and NEXAFS results clearly demonstrated that Co²⁺ remains the dominant cobalt oxidation state during COPrOx over CoVO_x, in contrast to the pure CoO_x catalyst, which forms a mixture of Co³⁺, Co²⁺, and Co⁰, at least above 200 °C. This finding provides clear evidence that the high catalytic activity and stability of CoVO_x demonstrated in the catalytic tests (Figure 1) is related to the enhanced redox stability of Co²⁺ states. However, before being able to directly correlate NAP-XPS with fix-bed reactor results, the effect of the pressure gap between the two experiments (0.1 mbar in NAP-XPS vs of 1 bar in catalytic tests) should be considered. The XRD analysis of the spent catalysts showed that their bulk structure was not notably affected by the COPrOx reaction, which contradicts the fast adjustment of the surface oxidation state and composition found in NAP-XPS. Therefore, in order to fulfill the requirements of surface sensitivity and atmospheric pressure operation, a recently developed experimental approach was selected, which allows performing in situ NEXAFS under a controlled gas atmosphere at 1 bar.⁵⁶ Due to technical restrictions, these experiments could not be performed in the COPrOx mixture; therefore, the stability of CoVO_x was investigated under a 1 bar H₂ atmosphere (without CO and O₂ addition) and 10%O₂/He, which are much harsher reducing and oxidizing conditions, respectively, than those the catalyst faces in the COPrOx reaction.

Figure 9. (a) In situ V L₃-edge and (b) Co L₃-edge NEXAFS spectra of CoVO_x catalysts recorded at 1 bar H₂ between 47 and 315 °C. (c) In situ V L₃-edge and (d) Co L₃-edge NEXAFS spectra of CoVO_x catalysts recorded at 1 bar 10%O₂ in He between 38 and 150 °C. All spectra are normalized to the same intensity and offset to the y axis.

Figure 9a and Figure 9b show the V and Co L₃-edges, respectively, of pristine (calcined) CoVO_x upon annealing in H₂. Not surprisingly, just after calcination, the V and Co L₃- edges

correspond to V^{5+} and a mixture of Co^{3+} and Co^{2+} species, respectively. Annealing in H_2 partially reduces both V and Co, but not at the same temperature. V^{5+} readily reduces at least partially to V^{4+} already from 50 °C, and after this temperature, the spectral shape remains similar up to 250 °C. Only at 300 °C, spectral modifications consistent with further partial reduction to V^{3+} are observed, through the appearance of a distinct peak at ca. 516.5 eV. In the case of cobalt, the reduction of Co^{3+} appears above 200 °C, while at 315 °C, the lineshape of Co L3-edge resembles that of Co^{2+} .

The oxidation behavior between vanadium and cobalt in 10% O_2 in He at 1 bar (Figure 9c,d) is also very different. When the pre-reduced catalyst is exposed to O_2 , vanadium is readily oxidized to the V^{5+} state already at 38 °C and remains stable afterwards, while cobalt is much more resistant to oxidation. At the maximum annealing temperature of this experiment (150 °C), only a part of Co^{2+} has been oxidized to Co^{3+} as deduced by the Co L3-edge lineshape. Please note that, in 10% O_2 in He, cobalt is more oxidized as compared to the COPrOx mixture shown in NAP-XPS, which is however expected due to the much higher oxidative effect of a 10% O_2 atmosphere. However, this result clearly shows that cobalt and vanadium do not respond to the same manner in redox environments with the former being much more resistant to oxidation than the latter. Consequently, in situ NEXAFS confirms that the Co^{2+} state might be stable under atmospheric pressure conditions that closely resemble those of the catalytic tests. This is further evidence that the higher activity and stability of $CoVO_x$ should be a direct consequence of the redox stability of surface Co^{2+} species.

4. DISCUSSION

4.1. Surface Arrangement. The analysis of the photoemission, X-ray adsorption, and STEM results evokes that the vast majority of vanadium resides over cobalt particles, and this influences the electronic structure of the two materials. Two possible arrangements can be correlated with these experimental findings: (i) formation of well-dispersed two-dimensional VO_x overlayer over the CoO support (i.e., $VO_x@CoO$) or (ii) the two materials intermix at their interface forming a thin cobalt–vanadium mixed oxide layer (i.e., $Co_xV_yO_z$). The analysis of V L-edge presented above suggests that the V^{5+} species on $CoVO_x$ catalysts are not octahedrally coordinated as expected for V_2O_5 bulk oxide, but tetrahedrally. However, the shape and position of the photoemission and absorption spectra of $CoVO_x$ do not exactly match neither with twodimensional vanadium oxides^{91,104} nor with octahedral cobalt vanadate compounds (e.g., $Co_3V_2O_8$)^{54,85,91,104} and therefore do not allow a direct and unambiguous identification of the arrangement at the interface in our case.

Theoretical simulation of the photoelectron peak intensities was used in order to decide which of the above described arrangements fits better with the experimental data. Figure 10 presents the %V at the surface as a function of the analysis depth calculated based on theoretically simulated Co 2p and V 2p photoemission spectra using SESSA version 2.1.1 software. Three different arrangement models were used for the simulations, assuming a V-containing oxide layer over a CoO core: (i) $V_2O_5@CoO$, (ii) $Co_3V_2O_8@CoO$, and (iii) $Co_6V_2O_{11}@CoO$. In all cases, the sample morphology was 50 nm diameter layered spheres with CoO in the inner core and an overlayer of V_2O_5 , $Co_3V_2O_8$, or $Co_6V_2O_{11}$. The thickness of the overlayer was adjusted in order to fit the experimental %V at the 230 eV KE (dashed line) measurement. After finding this value, the arrangement model was kept identical in the calculations of the other two depths.

Figure 10. Surface % at. V as a function of the photoelectron kinetic energy (or information depth) calculated based on theoretically simulated Co 2p to V 2p spectra using SESSA version 2.1.1 software. Three different arrangement configurations were used in the calculations (see figure annotation). A schematic representation of the layer thickness obtained for each model is included in the figure. The black dashed line indicates the experimental % at. V obtained by NAP-XPS, and results are shown in Figure S11.

From Figure 10, it is clear that the V₂O₅/CoO arrangement has the highest deviation from the experimental results. In addition, the calculated thickness of the V₂O₅ layer (0.29 nm) corresponds to an overall 1.1 at.%V (calculated based on the volume of the particles assumed in the simulation), which is far less than the nominal 12.5 at.%V loading. On the other hand, mixed cobalt–vanadate layers can better simulate the experimental results and provide more realistic at.%V. The best fitting was found by a hypothetical cobalt–vanadate layer rich in cobalt (Co₆V₂O₁₁) with 1.9 nm in thickness, which corresponds to an 8 at.% overall V loading. Therefore, based on the quantitative simulation of the depth profile data, the mixed cobalt–vanadate layer on the surface of CoO is proposed as the most likely surface arrangement of the CoVO_x catalyst under reaction conditions. Taking into account that metallic Co was detected in the XRD (Figure S4), a complex structure consisting of cobalt–vanadate on the surface and metallic cobalt in the bulk should be anticipated as the active state of the CoVO_x catalyst.

4.2. Effect of the V Promoter on the Reactivity of Co Ions. Catalytic tests show that vanadium addition to cobalt oxide results in a material with a higher CO conversion in the COPrOx reaction. There are two general paths in which promoters, V in our case, may influence the reactivity of the active Co phase. The first is related to an electronic modification of the catalytic active sites and the second to structural stabilization that enhances their abundance during the reaction.¹⁰⁵ Our results show that the population of Co²⁺

on the surface of bulk metallic cobalt is a strong function of the working conditions. This fact does not change with V addition, but under identical conditions, CoVO_x has systematically higher abundance of Co^{2+} as compared to CoO_x . Therefore, the primary effect of V on Co might be related to the structural stabilization of Co^{2+} sites and their resistance to Co^{3+} transformation. As we have shown previously, this affects the COPrOx reactivity since Co^{2+} surfaces are less susceptible to carbonate species formation,²³ which is one of the main reasons for cobalt catalyst deactivation (see Figure 11).

Figure 11. Schematic representation showing the proposed arrangement (cross section) of the various cobalt oxidation states over pure (CoO_x) and V-modified (CoVO_x) cobalt nanopowder catalysts in the COPrOx reaction. The difference in the bond distance between the central Co^{2+} (red or dark yellow spheres) and the corner O^{2-} ions (purple spheres) in the Co–O octahedron is also illustrated.

To elucidate the stabilization effect of V on Co^{2+} , we first need to consider the mechanism of CoO oxidation to Co_3O_4 . Combining theory with experiment, Robinson and coworkers¹⁰⁶ showed that CoO oxidation proceeds by Co^{2+} ion diffusion to the outer surface through the oxide lattice and/or the grain boundaries. In this process, the O lattice is not considerably affected and it is expected to remain rigid.¹⁰⁶ Our study provides evidences that Co^{2+} and V^{5+} ions at the CoVO_x surface share, to a large extent, the same lattice oxygen forming a mixed oxide (referred as $\text{Co}_x\text{V}_y\text{O}_z$). The vanadium ions can change between 4+ and 5+ valences more easily than cobalt changes between the 2+ and 3+ ones, as demonstrated in NAP-XPS and the atmospheric pressure NEXFAS experiments. Therefore, since V has higher redox ability as compared to Co, it will be selectively oxidized by O_2 gas acting as a buffer for Co^{2+} oxidation. In addition, V can undergo fast redox cycles by storing and releasing oxygen during a reaction cycle. Obviously, the rate of reduction and reoxidation cycles defines the ultimate vanadium oxidation state in reaction equilibrium. Taking into account that the COPrOx mixture contains only 1% O_2 , this can slow down the kinetics of cobalt oxidation and increase the durability of the catalyst. Similarly, in reducing conditions, V^{5+} will be the first ion to release oxygen and convert to V^{4+} , keeping Co^{2+} stable. An analogous stability mechanism has been previously proposed for the Fe-doped Co_3O_4 catalyst.¹⁰⁷

In addition to the clearly manifested stability of Co^{2+} , the analysis of absorption spectra gave evidences of a less pronounced, but still distinguishable, difference between the two catalysts. Specifically, although V does not change the coordination symmetry of Co^{2+} , it affects the Co^{2+} –O anion distance in the CoVO_x surface oxide lattice as well as the Co^{2+} electronic state. Unfortunately, it was not possible to quantify the electronic charge of cobalt ions in the two catalysts, but analysis of the spectroscopic results can qualitatively explain the electronic effects. As mentioned above, the Co^{2+} electronegativity in CoVO_x is higher as compared to CoO_x , while the bond distance between Co^{2+} and O^{2-} increases (Figure 11). Theoretical models predict that a higher metal electronegativity should be followed by lower interaction with oxygen, thus weaker metal–oxygen bond.¹⁰⁸ This can be related to enhanced oxygen mobility on the surface of the CoVO_x catalyst. The oxidation of CO on cobalt oxide follows a Mars–van Krevelen mechanism,²³ which implies that a higher mobility of lattice oxygen ions will result in higher reaction rates.¹⁰⁹ This hypothesis is directly supported by the fact that CoVO_x has higher activity in the 150–200 °C region (Figure 1), even if NAP-XPS analysis shows that the amount of adsorbed carbon species (Figure 8) is very similar in the two catalysts. Therefore, V addition has a dual function on cobalt, first it helps to stabilize the Co^{2+} phase and to inhibit the carbonate-induced deactivation and second it modifies the electronic state of Co^{2+} , increasing the oxygen mobility and in this way enhancing the reaction kinetics.

One should not overlook the notable enhancement of the surface area caused by vanadium addition on cobalt. Definitely, this increase does not correspond to a proportional increase in the cobalt surface sites since, as shown, the cobalt surface is covered/mixed with vanadium species. However, apparently V promotion helps to maintain the morphology of CoO particles (Figure 2), most probably by limiting surface diffusion and agglomeration of cobalt aggregates. However, in contrast to the cobalt oxidation state, which shows a good correlation with the reactivity, the specific surface area differences between CoO_x and CoVO_x seem not to be so critical under the employed reaction conditions. A first argument supporting this idea comes from the strong deactivation of CoO_x observed in the time-of-stream experiments of Figure 1c. The surface area of the CoO_x catalyst increases after the reaction (Table 1); therefore, the activity decrease observed after 20 min in Figure 1c cannot be due to loss of surface area and should be related to the changes in the cobalt oxidation state revealed by NAP-XPS and NEXAFS. In addition, in the light-off tests (Figure 1a) at 150 °C, the CO conversion of the CoVO_x catalyst is ca. 50% higher (13.9 vs 8.6% for CoO_x), despite the fact that this catalyst has more than 700% higher specific surface area (Table 1). At low temperature and low conversion conditions, diffusion phenomena are not rate-limiting, and therefore the overall reaction rate is controlled by the intrinsic reaction kinetics. Consequently, the dominant role of the surface oxidation state of cobalt on the reactivity remains the most likely explanation of the catalytic results.

5. CONCLUSIONS

The COPrOx activity of cobalt oxide is significantly improved by introduction of vanadium. Several ex situ and operand methods were applied to understand the promotion effect including NAP-XPS and atmospheric NEXAFS at 1 bar. The bulk structure and morphology of V-modified catalysts is not significantly influenced as compared to pure cobalt. However, detailed spectroscopic analysis revealed the formation of a mixed cobalt–vanadate phase on the surface, which does not resemble the known bulk mixed oxides. This phase is formed by tetrahedrally coordinated V^{5+} and octahedral Co^{2+} species. Both electronic and structural effects must be considered to understand cobalt catalyst promotion by vanadium. In

particular, V prevents the oxidation of CoO and provides stable active octahedral Co²⁺ sites for COPrOx, resistant to deactivation through carbonate species formation. In addition to that, we found evidences of modifications in the electronic state of Co²⁺ species induced by V promotion, in the direction that enhances the reaction kinetics. Furthermore, by using NEXAFS at atmospheric pressure, we could show that Co²⁺ species are preserved on the CoVO_x surface at a temperature and pressure relevant to the catalytic tests. Overall, our study shows that one can use insights from operando surface spectroscopy to design and produce better COPrOx catalysts. Taking into account the rising accessibility and availability of these methods, this can be a sustainable strategy for the development of new-generation catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.0c05482>.

TPR-H₂ of calcined CoO_x and CoVO_x catalysts; methane selectivity and catalytic performance of pure vanadium oxide after different pretreatments for COPrOx; ex situ XRD patterns of fresh, reduced, and spent CoO_x and CoVO_x catalysts; additional STEMEDS and HR-STEM images; characteristic examples of Co 2p deconvolution; in situ NEXAFs spectra of Co L3-edge as a function of reaction temperature during COPrOx; NAP-XPS depth-profiling analysis of Co 2p over CoO_x and CoVO_x during COPrOx; and the %at. V as a function of the NAP-XPS analysis depth (PDF)

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Notes

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