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New insights into the role of active copper species in CuO/Cryptomelane catalysts for the CO-PROX reaction

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Graphical Abstract

Highlights

- Synergistic CuO – cryptomelane effect confers outstanding catalytic properties to Cu/CR catalyst with a higher molecular affinity to CO and O₂.
- The enhanced reducibility in Cu/CR catalyst favors Cu⁺ interfacial sites, active in CO oxidation.
- Oxygen vacancy refilling occurs mainly in bulky CuO particles aided by the support.

- The correct balance between CuO and Cu⁺ sites in the 7% Cu/CR catalyst turns into the optimum CO-PROX catalytic performance.

Abstract

Nominally different Cu contents have been loaded on synthetic Cryptomelane oxide and the resulting CuO/Cryptomelane catalysts have been tested in the CO-PROX reaction. Catalytic activity was assessed in terms of the tunable synergistic interaction between copper and cryptomelane. This work entails the use of conventional characterization techniques such as XRD, Raman, FE-SEM, XPS with complementary DFT simulation. Additionally, it is reported for the first time, in-situ Work Function measurements of CO and O₂ interaction in CuO/Cryptomelane catalysts. Results reveal the strong influence of the interfacial properties on CuO/Cryptomelane reducibility, where Cu⁺ species are formed by means of redox interplay between Cu⁺²/Cu⁺ and Mn³⁺/Mn⁴⁺. The optimal performance is achieved by the efficient participation of two active species: (1) Cu⁺ from an intimate MnO_x contact, providing the active sites for CO oxidation; and (2) surface Cu⁺ species stabilized in CuO bulky particles for the efficient O₂ refilling.

Keywords: copper-based catalyst; CO-PROX; cryptomelane; H₂ purification; work function

1. Introduction

The Preferential CO Oxidation (CO-PROX) reaction is the selective oxidation of residual CO in strongly reducing H₂-rich flows with the final target to ensure safe utilization of H₂ streams. To this aim, it is required an appropriate catalyst capable to keep high activity and selectivity in the low temperature range of CO-PROX operation [1–4]. After decades of research, the most successful and promising results are provided by the copper oxide – cerium oxide systems [5–9]. Apart from the excellent activity, because of their moderate price, large stability and acceptable CO₂ and H₂O compatibility, copper oxide – cerium oxide catalysts have demonstrated to be perfectly suitable for long time operation in real conditions of CO-PROX reaction [10–14].

In addition, it is well-known that cryptomelane redox properties can be tuned by means of the introduction of different framework dopants such as Fe [15,16], Ce [17–19], Ni [20–22], Co [19,21,23–26], Ag [27,28], V [29–31] or Cu [32–37]. From the above, in general the best results have been achieved with Cu^{2+} doping, effect attributed to: (1) the higher electronegativity of Cu, which weakens in a large extent the Mn–O bond in Mn–O–Cu bridges, resulting in the mobility and reactivity of the active oxygen species; and (2) the versatile insertion of Cu substituting Mn^{2+} , fitting into CuO_6 octahedra, or tunnel K^+ cations, which increases Mn average oxidation state and provokes crystal structure distortion and formation of defects [15,32,38–40]. As a result, Cu-modified cryptomelane materials are more active catalytic systems when compared to bare cryptomelane, though thermally less stable and more prone to framework collapse.

Interestingly, another approach to improve catalytic performance is to disperse CuO particles on the external facets of cryptomelane structure, seeking the formation of a binary catalytic system composed of CuO supported on cryptomelane (CuO/Cryptomelane) [41–43], in analogy to the well-reported CuO/Ceria catalysts, where special interfacial redox properties by means of synergistic effect result in an excellent performance [44,45]. However, despite CuO may be forming as a segregated phase, in our previous publication we proved that CuO/cryptomelane catalysts also showed lower stability over reducing – oxidizing cycling conditions than bare cryptomelane, whereas the catalytic activity in CO-PROX reaction was improved by large [42]. The poorer stability was evidenced by the loss in the cryptomelane tunneled structure and the formation of a spinel-type Mn_3O_4 material based on XRD analyses of the spent samples, in agreement with the studies of Nicolas-Tolentino et al [36]. However, the nature of such complex deactivation process is not clearly defined, and the activity of the different Cu entities existing in the CuO/Cryptomelane catalyst has not been disentangled yet.

Besides, although CuO/Cryptomelane has demonstrated an outstanding catalytic activity in CO-PROX reaction, mechanistic studies provided so far are truly limited since the black-colored cryptomelane character hinders the infrared spectroscopic operando analyses. In this scenario, we propose an alternative methodology to study CO-PROX mechanism over CuO/Cryptomelane catalysts based on in-situ Work Function (WF) measurement experiments [46], which is a powerful tool and novel approach for this purpose, not reported yet to the best of our knowledge.

Hence, the aim of this work is to provide relevant insights into CuO/Cryptomelane catalysts description and performance, with the main focus on: (1) discern the different Cu-rich species present in the catalyst and establish the correlation between CuO – CR interaction and CuO dispersion; (2) resolve CO-PROX mechanism operating on this particular and promising material.

Experimental Section

1.1. Catalyst synthesis

Synthetic cryptomelane was prepared using the previously described reflux method [47,48]. To this end, 11 g of manganese(II) acetate (Aldrich) was dissolved in 40 g of distilled water and the pH of the solution was fixed at 5 using glacial acetic acid. Then, it was heated and maintained at the boiling temperature under reflux for 30 min. After that, a solution of 6.5 g of potassium permanganate (Aldrich) dissolved in 150 ml of distilled water was added, and the mixture was kept under reflux with vigorous stirring for 24 h. The solid was filtered, washed with distilled water until neutral pH and dried at 120°C overnight. Finally, it was calcined at 450°C for 2 h to obtain bare cryptomelane (CR). Afterwards, a battery of CuO/Cryptomelane (Cu/CR) catalysts were prepared by incipient

wetness impregnation of cryptomelane with a copper(II) nitrate trihydrate (Sigma Aldrich) water solution. The impregnated solid was dried at 110°C overnight and calcined at 400°C for 5 h using a heating ramp of 5°C/min. Thus, the series of CuO/Cryptomelane catalysts: 4% Cu/CR, 7% Cu/CR and 11% Cu/CR was obtained.

1.2. Catalyst characterization.

The chemical composition of the samples was determined by means of XRF using an Energy-Dispersive XRF spectrometer (Thermo Scientific, ARL QUANT'X) with X-rays of 4-50 kV (1 mm beam size) from a Rh anode. For quantitative analysis, metallic standards were used for calibration and data was obtained from the UniQuant software.

X-ray diffractograms in the 2θ range between 10° and 80° were recorded in a Bruker D8-Advance diffractometer using Cu K α radiation ($\lambda = 1.540598$ Å). Crystallite size of CR was determined with the Scherrer equation using the (211) peak.

Field Emission Scanning Electron Microscope (FE-SEM) analysis was performed using a Merlin VP Compact microscope (Zeiss), working at low voltages (from 0.02 kV to 30 kV). Textural characterization was carried out by means of N₂ adsorption at -196°C in an automatic adsorption instrument Autosorb-6, by Quantachrome. Prior to adsorption measurements the catalysts were degassed at 250 °C for 4 h in order to remove any adsorbed impurities. Surface area was calculated by using the BET equation (SBET), micropore volume (< 2 nm) with the Dubinin-Radushkevich equation (DR).

Experiments of temperature programmed reduction with H₂ (H₂-TPR) were performed using a Micromeritics Pulse ChemiSorb 2705 device. 40 mg of catalyst were placed in a U-shaped reactor and the temperature was increased from room temperature up to 900°C with a heating rate of 10°C/min in 20 ml/min of 5% H₂ in Ar. For quantitative analysis a CuO reference provided by the manufacturer was used.

The Cu2p, O1s, C1s, K2p and Mn2p region analysis in the fresh catalysts were characterised by X-ray photoelectron spectroscopy (XPS) measurements performed using a K-Alpha spectrometer (Thermo-Scientific) with a high-resolution monochromator. The binding energy was adjusted using the C1s transition, appearing at 284.6 eV, providing measures accurate to ± 0.2 eV. Complementary Auger spectroscopy analysis was conducted to resolve Cu oxidation states.

Since cryptomelane is known to emit potassium at elevated temperatures [49,50], potassium thermal desorption was investigated by measuring the potassium atom flux from pelletized samples (100 mg, 13 mm diameter) heated in a vacuum chamber. Due to the low ionization potential of potassium ($I = 4.3$ eV) from solid surfaces potassium is typically thermally emitted in the form of atoms and ions. The samples were biased with a positive potential of +5 V to prevent the thermal emission of electrons during a heating program up to ~ 500 °C. For each temperature the resultant positive current was averaged over 10 independent data points and measure with the use of Keithley 6512 digital electrometer.

Work function measurements were carried out by means of a Kelvin Probe (KP) apparatus (KP6500, McAllister Technical Services) ruled by the dynamic condenser method. Since work function is the most sensitive parameter describing surface electronic properties of the materials, this tool gained large interest and the operation of KP apparatus and work function measurements have been thoroughly addressed by many research papers and review papers [51–54]. On the other hand, provided that physisorption and chemisorption change this sensitive property, work function measurement with KP is a very convenient non-invasive tool to follow the interaction of the reactant gases with a targeted catalyst. In particular, KP enables the determination of the contact potential difference (CPD) between a work electrode, in electrical contact with the investigated layer from a

pelletized sample, and a reference electrode provided by the manufacturer. The work function values are obtained from a simple relation $CPD = \Phi_{ref} - \Phi_{sample}$; where $\Phi_{ref} = 4.3$ eV as specified for the standard stainless-steel plate electrode used as reference, which is the KP tip. The measurements were recorded under a fixed gradient of the peak-to-peak versus backing potential of 0.2 V, vibration frequency of 120 Hz, and 40 a.u amplitude. 60 independent points using two backing potentials were accounted for the average of the final CPD values, as Figure S1 represents in a basic scheme.

In-situ WF measurements for cryptomelane-based catalysts were conducted at 200 and 300°C after a thermal treatment up to 450 °C in vacuum conditions. The atmosphere was switched among vacuum (below 10^{-6} atm), O₂ (Air Products, 99.9998%) and 5% CO/He at two different chamber pressures: $3.5 \cdot 10^{-5}$ and $8.0 \cdot 10^{-5}$ atm.

DFT calculations were conducted by means of the CP2K package in its 4.1 version using the QUICKSTEP module [55]. Dispersion corrected (D3)[56] GGA-PBE[57] exchange correlation functional under periodic boundary conditions (PBS) were used for all simulations. CO and H₂ molecules were positioned close the surface of Cu(111), Cu₂O(111) and CuO(111) slabs of 320 atoms, 180 atoms and 160 atoms respectively and the systems were allowed to relax. Adsorption energies of CO and H₂ molecules were calculated by using Equations (1) and (2), respectively:

$$E_{CO,ads} = E_{slab + CO,ads} - (E_{slab} + E_{CO(g)}) \quad (\text{Equation 1})$$

$$E_{H2,ads} = E_{slab + H2,ads} - (E_{slab} + E_{H2(g)}) \quad (\text{Equation 2})$$

Additional information on computational details can be found in the Supplementary Material document.

1.3. CO-PROX activity tests.

To perform CO-PROX experiments, 150 mg of CuO/Cryptomelane was placed in a U-shaped reactor with 16 mm inner diameter and the gas mixture of 2 % CO, 2 % O₂, 30 %

H₂ and He balance was fed to the reactor. The O₂ excess with regard to CO was $\lambda = 2$ (being $\lambda = 1$ for stoichiometric CO-O₂ conditions). The catalytic tests were performed using a heating rate of 2°C/min from 25 to 250°C and a total gas flow rate of 100 ml/min that was set by means of Mass Flow Controllers (Bronkhorst). The exhaust gases were analysed using a gas chromatograph (HP model 6890 Plus Series) equipped with two columns: Porapak Q 80/100 for CO₂ and H₂O separation and Molecular Sieve 13X for O₂ and CO separation, coupled to a TCD detector.

3. Results and discussion

3.1. Catalysts characterization

Results from textural, crystallographic and chemical characterization for bare cryptomelane (CR) and the prepared CuO/Cryptomelane (Cu/CR) catalysts are summarized in Table 1, while presented in detail in the enclosed Supplementary Material. Thus, BET surface areas calculated from N₂ physisorption isotherms (Figure S2), decrease with the Cu loading in the Cu/CR catalyst series, though differences between 7% and 11% Cu/CR are negligible. On the contrary, the micropore volume (V_{DR}) is lowered up to the same extent in Cu/CR samples with regards to CR, with independence of Cu loading. Since N₂ physisorption technique is limited at providing information in the ultra-micropore range (< 0.7 nm), as in the case of cryptomelane tunnel size (0.65 nm diameter), the calculated V_{DR} does not consider intra-channel space [58], so partial tunnel insertion cannot be ruled out. Thus, textural characterization over Cu/CR catalysts indicate that CuO is mainly deposited on the cryptomelane surface causing blocking of the macro/meso-pore ranges, in qualitative agreement with N₂ isotherms (Figure S2a) and DFT-calculated pore size distribution (Figure S2b).

XRD characterization (Figure S3) showed a pattern for all the catalysts consisting of the characteristic diffraction peaks of cryptomelane (JCPDS no. 29-1020). The presence of CuO tenorite phase (JCPDS no. 80-1268) is only detected in 11% Cu/CR catalyst, which suggests that in 4% Cu/CR and 7% Cu/CR, samples with lower Cu loadings, CuO might be finely dispersed since its crystallite size is below the threshold detection limit of the XRD apparatus. On the other hand, the determination of crystallite sizes and lattice parameters of the cryptomelane-based catalysts [59,60] reveal that cryptomelane crystalline features remain essentially unchanged upon Cu loading (Table S1).

FE-SEM analyses were conducted in order to determine the dispersion of CuO particles within the Cu/CR catalysts series (Figure 1a-c). Representative images of the fresh samples show the characteristic needle-shaped micro-structure of cryptomelane, exhibiting nano-rods from a varying length in the range of 100-500 nm [61,62], as it is elsewhere reported when following the reflux method for cryptomelane synthesis [47]. Among the Cu/CR catalysts, no significant differences are found, which confirms the stability and integrity of bare cryptomelane support after Cu loading procedure. It is important to highlight that despite the huge efforts invested, it was unfeasible to discern CuO presence among the tangled cryptomelane nano-rods provided the negligible contrast existing between Cu- and Mn-rich phases. Furthermore, despite imprecise particles might be spotted in the images, punctual EDX chemical analysis confirmed these correspond with heterogeneities from cryptomelane rather than CuO. In this regard, it can be tentatively inferred that CuO particles may be embedded in between the spaces left upon the array of cryptomelane nano-rods. This particular arrangement would be a consequence of the low wettability of the hydrophobic cryptomelane surface by the Cu precursor aqueous solution during impregnation procedure [63]. On the other hand, attempts to elucidate CuO dispersion by Cu-selective oxidative chemisorption of N₂O did

not provide conclusive evidences either, since cryptomelane support was prone to chemisorb N_2O , too. Therefore, unfortunately, we were not able to determine CuO distribution by means of straightforward techniques, so the CuO dispersion degree in the Cu/CR catalyst series had to be estimated by means of indirect outputs, as described in the following.

First, considering the atomic Cu/Mn bulk ratios calculated by XRF analyses, this parameter shows a proportional linear trend upon Cu loading. On the contrary, analogue atomic ratios provided by XPS analysis, which is a surface technique, showed Cu enrichment, which suggests the preferential location of CuO particles on the crystal surface of the Cu/CR catalysts. Furthermore, among the Cu/CR catalysts, surface Cu content is not monotonically coupled to Cu nominal values. This discrepancy, which is much higher for 11% Cu/CR could be tentatively interpreted as a consequence of either the formation of larger CuO particles when increasing Cu loading, or their worse distribution, roughly identified by XPS as a lowering in the Cu content.

In conclusion, Cu loading is not importantly altering the basic MnO_x framework structure of cryptomelane, as it was expected for an impregnation procedure. The decrease in BET surface should be attributed to the formation of CuO particles mainly deposited on the surface of cryptomelane that partially block the porosity. With the higher Cu content, it is inferred a larger CuO particle size, which forms a detectable crystalline phase in 11% Cu/CR, but not in 4% Cu/CR nor in 7% Cu/CR catalysts.

3.2. Catalytic CO-PROX reaction tests

Bare CR, bulk CuO and the Cu/CR catalysts were tested in CO-PROX reaction activity experiments and results are presented in Figure 2.

The beneficial effect of Cu loading into cryptomelane in the Cu/CR catalysts performance with regards to bare CR and CuO samples is clear and evidenced by a dramatic lowering

in the temperature range over CO conversion profiles (Figure 2a), roughly shifted *ca.* 100°C lower for Cu/CR catalysts. Conversely, differences are moderate among the series of Cu/CR catalysts, which reach the maximum CO conversion (~90 %) in a narrow temperature range, following the trend 7% Cu/CR > 11% Cu/CR > 4% Cu/CR. Nevertheless, in terms of CO selectivity (Figure 2b), 7% Cu/CR and 11% Cu/CR catalysts present the best behavior with region of complete CO selectivity at low temperatures and the typical selectivity decay up to (~40 %), by the competitive H₂ oxidation on-set. Such selectivity value is acceptable to guarantee a good CO-PROX catalytic performance, provided the experimental conditions of $\lambda=2$ for O₂ [64]. In this regard, considering in global perspective the state-of-the-art of CO-PROX reaction, the prepared Cu/CR catalysts demonstrate promising opportunities and their utilization holds multiple environmental advantages with regards, for instance, to the high-performance CuO/CeO₂ systems, reported to be more active in equivalent conditions [65–67].

Therefore, 7% Cu is assessed as the optimum loading in Cu/CR catalysts, but in close similarity to the 4 and 11%. In order to get further insights, H₂-TPR and XPS analyses were conducted to determine the redox properties of the different Cu/CR catalysts.

3.3. CuO – CR redox interaction study

Figure 3 displays the H₂-temperature programmed reduction profiles of the tested catalysts, showing that their different susceptibility for H₂ reduction is affected by the interaction of CR and CuO phases.

In the case of cryptomelane phase, manganese species achieve the final oxidation state of +2 under the reduction treatment [21,68,69]. For pure cryptomelane, CR profile presents three main reduction events assigned to the redox processes: (i) MnO₂ → Mn₂O₃; (ii) Mn₂O₃ → Mn₃O₄; and (iii) Mn₃O₄ → MnO, seen in broad peaks centred at 300, 335 and 350°C, respectively [32,70]. The introduction of 4% Cu produces little changes in the

average reduction of cryptomelane framework, presenting an overlapping of the manganese reduction processes occurring in the same temperature range as in bare CR. Nevertheless, an extra peak at 150°C assigned to finely dispersed CuO species is detected in the reduction profile. Since reduction of pure bulk CuO occurs above 300°C according to the H₂-TPR profile of CuO sample, also shown in Figure 3, this anticipated CuO reduction evidences a Cu – Mn synergistic effect by means of the formation of labile Cu²⁺ - O- Mn^{y+} entities [43,71,72]. As a consequence, the anticipated partial MnO₂ reduction is gradually taking place, too, as evidenced by the permanent sloping signal above 150°C after the reduction event attributed to CuO species. In contrast, the effect of Cu is much more evident in the 7 and 11% Cu/CR catalysts by shifting the maxima towards lower temperatures of the overall cryptomelane reduction processes (from 350 to 330°C). This shifting proves the superior Cu – Mn interaction in 7% Cu/CR and 11% Cu/CR catalysts, and the effective promotion of Mn⁴⁺/Mn³⁺ redox interplay. The reduction peak attributed to the anticipated reduction of CuO disperse particles is also observed, which shows in the 7% Cu/CR catalyst the greatest area and definition. Whereas, in 11% Cu/CR it is discerned a hindered CuO reduction, probably ascribed to a more limited Cu – Mn contact in agreement with the hypothesized presence of larger CuO particles. Thus, on average, the 7% Cu/CR catalyst exhibits an optimum synergistic effect towards Cu and Mn promoted reduction, relying on the significant broadening of the H₂-reduction profile and the presence of an anticipated manganese reduction peak centred at 250°C.

On the other hand, the quantitative analyses of H₂-TPR profiles indicate that Cu/CR catalysts are, on average, more reduced than bare CR, although differences are moderate. Interestingly, the degree of apparent reduction holds inverse trend to the increase in Cu loading, which suggests that the lower Cu content, it is stronger the promotion of reduced states (Cu⁺ and Mn³⁺) in the resting state of the catalyst.

The Cu2p XPS and CuLMM Auger spectra for CuO and Cu/CR catalysts are presented in Figures 4a-b, showing the Cu2p region peak fitting. Hence, Cu2p_{3/2} peak is composed of two main contributions. Namely: (i) at lower binding energy (931.5 – 932.0 eV), attributed to reduced (undistinguishable Cu⁺ and Cu⁰) copper species; and (ii) a higher binding energy contribution (933.6 – 933.8 eV), attributed to oxidized (Cu²⁺) species. Analogue deconvolution of Cu2p_{1/2} is presented with the proportional parameters according to spin-orbit coupling. On the other hand, Cu²⁺ characteristic satellite peaks are observed in all cases, though overlapped under intense MnLMM Auger lines.

The analysis data of the deconvoluted Cu2p regions in correlation with Auger peaks is compiled in Table 2. According to Cu Auger spectra, main contribution of surface Cu species observed in all Cu/CR catalysts is defined by an intermediate electronic state between +2 and +1, as tabulated values indicate in Table S2. Nevertheless, among the Cu/CR catalysts series, Cu⁺ species display different overall contribution, following the trend 4% Cu/CR > 7% Cu/CR > 11% Cu/CR, which is in agreement with H₂-TPR analyses. In this scenario, the abundance of Cu⁺ contribution is tentatively ascribed as a sign of the degree of copper oxide – cryptomelane interaction, which promotes Cu reducibility by means of Cu²⁺ – O – Mn^{v+} labile bridges. Therefore, according to XPS and Auger analyses, 4% Cu/CR catalyst presents the highest percentage of reducible copper, which would be consistent with a lower CuO particle size [73].

Because of the complexity of Mn2p XPS region (not shown), split in multiple spin-orbit components, the resolution of Mn average oxidation state (AOS) was not achieved. Regarding O1s region (Figure S4a), no significant differences in the labile, or loosely bound oxygen are observed for the Cu/CR and CR catalysts, despite their different reducibilities as proven in H₂-TPR features, and in contrast with other authors who reported a greater population of such active oxygen species when Cu is inserted in the

cryptomelane framework [32,74]. Nevertheless, it is evidenced a clear decrease of adsorbed oxygen species in Cu/CR samples with regard to CR, fitting with the decrease of % C, and specially, with the carbonate-type species displayed in C1s spectra, referred to as O-C=O and O-C-O contributions (Figure S4b). In fact, the % C decrease in Cu/CR samples with respect to CR, might be result of a reported side-effect of impregnation with the acid copper precursor solution, which would dissolve inherent structural and surface carbonates from bare support [75].

In a complementary study, work function measurements of the CR and Cu/CR catalysts and a CuO reference were conducted, and the results are presented in Figure 5a. The compiled data is consistent and shows close values for bare cryptomelane (CR) and copper oxide(II), which hinders to establish a simple correlation among the series of Cu/CR prepared catalysts. Nevertheless, it is clearly observed a decrease in work function for 7% Cu/CR catalyst, even when compared to both pure phases CuO and CR, which is an evidence of electrodonor properties in this sample because of a promoted Cu-Mn interaction. Thus, a lower work function value could be roughly associated to the higher facility towards reduction of the material and in this case 7% Cu/CR presents the strongest effect, in-line with the H₂-TPR results. The lower WF of a material indicates higher electron availability, which leads to a higher reactivity of such catalysts in the reactions where electron transfer from the catalyst surface to reacting molecule plays a key role [76].

Nevertheless, taking into account the conditions of the measurements, and the prior state of samples after calcination in air, the presence of chemisorbed carbonates, hydroxyls and surface groups is important and its effect in work function values should not be ruled out. This surface chemistry affects the electrical properties by the formation of diffuse surface dipoles and electron density transference, which is evidenced by a work function lowering

[77,78]. Thus, the behavior observed with regard to work function is representative of the abundance of oxygen surface species, which are present at the beginning of the CO-PROX activity experiments, as well. These oxygen containing groups (carbonates, bicarbonates, formates and hydroxyls) are not only spectators, but also take part in the CO-PROX mechanism suggested elsewhere [79]. Therefore, for 7% Cu/CR catalyst, which presents the lowest work function value, it can be inferred that the maximum degree of electronic surface distortion with atmospheric components occurs, matching its better catalytic performance. In this regard, Figure 5b shows the work function decrease of Cu/CR catalysts compared to bare cryptomelane and its correlation with the reaction rate at low CO conversion by means of the characteristic temperature for 200 $\mu\text{mol CO/s}\cdot\text{g}$ in CO-PROX experiment. The trend is clear, showing that reaction rate is accelerated with the lowering of the catalyst work function, establishing eventually a plateau below 0.1 eV of decrease. Thus, according to CuO – CR interaction quantified by means of work function decrease, 7% Cu/CR catalyst presents the strongest synergistic effect towards reduction and oxygen groups chemisorption, which should be related to the presence of randomly dispersed CuO particles.

3.4. Role of K in CuO – CR interaction

One key factor for the understanding of the great activity of cryptomelane-based catalysts is the role of potassium in the electronic promotion of copper and manganese towards reduction and oxygen donor capacity. In this regard, specific analysis techniques have been performed in order to establish appropriate determination of such properties. First of all, XPS analysis of K2p_{3/2} photoemission region presented in Figure S5, confirms there are no significant differences among potassium electronic states in the prepared catalysts, as deviations in peak maxima are below XPS sensitivity threshold (0.2 eV), in peaks

centred, on average, at ca. 291.5 eV, which are values reported for cryptomelane [80]. Comparing with ionic potassium compounds, which present a sharp peak centred at 292.9 eV [81], such particularly low BE results are an evidence of potassium electronic enrichment by MnO_x donation in the narrow confinement inside cryptomelane tunnels. Thus, as this BE shifting is present in all CR and Cu/CR catalysts, it can be concluded that K electronic density is not dependent on copper content, showing that most probably copper and potassium are not directly interacting electronically. Additionally, the stability of potassium species was studied by thermal desorption tests, measuring the potassium atom flux from the samples heated in a vacuum chamber (Figure S6). Potassium thermal desorption measurements reveal that the process takes place over 400 °C, thus at temperatures much higher than the CO-PROX catalytic activity. The linear part in the Arrhenius' plot corresponds to typical activation barriers for desorption of 2.1 eV without significant differences for CR and 7% Cu/CR catalysts. It means that the structure of cryptomelane, and thus the state of potassium, is not altered by the addition of copper oxide particles.

In conclusion, potassium species play essentially a structural role in Cu/CR catalysts, stabilizing cryptomelane tunnels via electronic interaction with MnO_6 octahedra. Conversely there is not an electronic promotion or activation of the dispersed copper oxide particles upon K interaction, which is not an unexpected conclusion since potassium remains inside the tunnels, whereas CuO should be located at the periphery covering the external surface of cryptomelane. Therefore, since K – CuO interaction is scarce and occurs only by means of MnO_x intermediation, the particular contribution of K species in the catalytic activity should be equivalent for CR and Cu/CR catalysts, for which is not further considered in the present discussion.

3.5. Study of CO/H₂ interaction with Cu/CR catalysts

As previously stated, CO-PROX operando IR spectroscopic studies are not able to provide valuable information regarding mechanistic aspects of the process for cryptomelane-based catalysts given the dark-colored nature of cryptomelane and its strong IR radiation absorption. Therefore, it is truly complex to obtain mechanistic data when compared to other studied catalysts, such as ceria-based ones, for which several models and mechanisms have been constructed by thorough in situ or operando spectroscopic studies of well-known interpretation [45,79].

In order to get analogue mechanistic information for cryptomelane-based catalysts, instrumental and methodological alternatives must be considered. In the present work, two complementary techniques have been employed to sustain a proposal of mechanism for CO-PROX reaction over cryptomelane-type catalysts: (1) DFT molecular modeling; and (2) in-situ work function measurements. With regards to DFT simulation, our particular approach to the mechanistic studies is based on CO and H₂ gas molecules interaction with the catalyst surface, by means of (1) energy of adsorption; and (2) electronic surface changes upon chemisorption.

First of all, it must be taken into account that CO-PROX reaction consists of two processes taking place in a competitive mechanism over dispersed copper entities: (i) CO oxidation, and (ii) H₂ oxidation. As described in the literature for Cu-based catalysts on reducible oxides such as ceria or MnO_x, copper species change their oxidation state, from Cu²⁺ as initial state to Cu⁺/Cu⁰ mixture [10,45,79], as the reaction is taking place involving catalyst oxygen following a Mars van Krevelen (MVK) mechanism [68,82]. For copper-based catalysts, CO oxidation takes place selectively at low temperatures, and then, by rising temperature along experiment course, selectivity profile drops by the onset of H₂ oxidation reaction. It has been firmly claimed that this selectivity fall is coupled with Cu changing oxidation state, for which it has been postulated that Cu²⁺/Cu⁺ species,

initially present, are responsible for CO oxidation, and latter appearing Cu^+/Cu^0 species are active sites for H_2 oxidation [45,79]. According to this hypothesis, copper entities are active sites for both reactions taking place, and the role of the support is to stabilize its redox state during the reaction by oxygen transfer and accommodation. Therefore, the chosen support has a strong effect on the catalytic activity on the copper-based catalysts. In order to check this theory, simple DFT calculations for the energy of adsorption of CO and H_2 gas molecules onto copper substrates in different oxidation states were conducted. Thus, the aim of this study is to discern the adsorption affinities of CO and H_2 at the different copper-based structures, representative of the catalyst state during reaction course. Figure 6a-f shows the most favorable adsorption position of CO and H_2 gas molecules onto copper-based slabs, considering dissociative or non-dissociative adsorption at different surface sites. The highest computed adsorption energies for each case is represented in Figure 7.

By the assumption that adsorption of gas molecules on the surface of the active sites is the first key step for catalytic reaction to occur, the difference between the energetics of these processes can be tentatively related to the CO-PROX selectivity for each copper-based surface. Therefore, by simple subtraction, it can be established that Cu^+ surface presents the highest energy difference for CO and H_2 adsorption, so the best selectivity is achieved when copper is partially reduced.

When it comes to the whole data comparison, Figure 7 shows that for Cu^{2+} , initial state of the catalyst, the adsorption of H_2 presents quite low energy, whereas CO is significantly higher. In this case, CO-PROX reaction is based on a truly selective CO oxidation. Such activity is enlarged when Cu^{2+} is partially reduced to Cu^+ , as energy of adsorption rises from -1.30 to -2.10 eV. In the same way, the surface doubles the affinity for H_2 adsorption, going from -0.31 eV for Cu^{2+} to -0.68 eV for the Cu^+ surface. This change can be related

with the onset of H₂ oxidation reaction and therefore a loss in selectivity loss from the maximum values. Finally, when Cu⁺ is reduced to Cu⁰, the difference between adsorption energies of CO and H₂ notably decreases, which is may be the cause of poor selectivity and a strong competition.

Despite the fact that the description of adsorption energetics profile matches that of experimental data, it must be taken into account that not all adsorption interactions are necessarily translated into chemical reaction, as a high percentage of adsorptive processes are not efficient and eventually lead to desorption in an adsorption-desorption pseudo-equilibrium situation. However, the energy of adsorption can be an indicator of average reaction process taking place as the relative population of CO and H₂ coverage is affected, and then, the probability of reaction. Furthermore, the higher coverage of CO and H₂ is blocking the adsorption of their counterpart, as competitive adsorption is assumed according to this model.

Finally, in order to check reactivity of Cu – Mn interfaces, *in-situ* work function measurements in an evacuated chamber with further addition of O₂ or CO gases were conducted to check WF changes in those atmospheres. WF is a highly sensitive surface reactivity descriptor and a useful measurable parameter, as it is claimed that surfaces undergo work function changes upon interaction with selected gases according to different sensing/reaction schemes [46,83]. In the case of semiconducting materials, the strength of interaction is directly reflected in WF change, assigned to the depletion/restitution of electrons from the conduction band (CB). The effect can be discussed in terms of the interaction of probe molecules with the surface: (i) O₂, by O-ionosorption (Equation (3)); and (ii) CO, by surface reduction (Equation (4), as particular cases for CO sensing materials. The description of these processes can be done according to the following scheme, where S represents surface sites [46,84,85]:

Equations (3) and (4) suggest that atmospheric oxygen thermally dissociates at the semiconducting sensor surface and is adsorbed as atomic ions by trapping conduction electrons. On the other hand, reducing gases, such as CO can undergo catalytic oxidation removing the ad-oxygen and releasing the captured electron back into the CB. Process from Equation (3) leads to a work function rise as oxygen concentration yields surface negative charge, enlarging surface barrier and depletion degree. Whereas process ruled by Equation (4) is generally observed as a weaker interaction consuming partially adsorbed/surface oxygen and releasing some captured electrons in the CB, providing a slight work function lowering, since CB electrons do not influence directly into work function of the material, but its conductivity.

Therefore, WF measurements under O₂ and CO atmospheres at temperatures at which the catalysts present activity towards CO oxidation, can provide valuable information about catalyst – adsorbate interaction. In order to conduct these analyses, the measurement chamber was heated to 200°C and the studied gasses were added to increase the total pressure in two steps, using: (1) bare cryptomelane; (2) 7% CuO/cryptomelane; and (3) pure CuO; which are representative for MnO_x surface; Cu – Mn interface and CuO surface; respectively. Figure 8 compiles these results.

Figure 8 evidence important differences in the behavior of the tested samples, as well as between interacting probe molecules. When it comes to O₂ interaction, WF rises with O₂ concentration in the chamber, as previously explained, according to the theoretical model. In all cases, this interaction is mainly non-reversible, as vacuum measurement after O₂ contact does not bring back original work function values. Comparing between samples, 7% Cu/CR and CuO show a sharp work function change upon O₂ interaction, while CR

shows much poorer response. These results reveal that the copper-rich phase is active for O_2 ionosorption and lattice oxygen vacancy replacement, but not MnO_x . However, CuO – CR contact phases occurring at 7% Cu/CR catalyst maximizes O_2 interaction, and therefore, oxygen restitution during reaction. It has to be taken into account that prior to analysis, samples were pretreated at 450°C for 30 min in vacuum, which generally produce structural oxygen release and partial reduction, from CuO to CuO_x and MnO_x to MnO_{x-1} . Thus, the great ability of CuO to undergo easy reduction when compared to MnO_x makes it more susceptible to accept oxygen species from the gas phase, which is observed by a large work function change response. However, it occurs at a higher extent in the case of 7% Cu/CR sample, where a synergistic effect is clearly promoting oxygen restoration in the catalyst. In a possible mechanism, partially reduced CuO_x particles would act as O_2 caption sites, facilitating then, by a spillover effect at the interface, their transport towards MnO_x , and releasing again CuO_x sites for newcoming O_2 molecules. Thus, changes are more significant in Cu/CR as MnO_x takes part as oxygen receptor as well, increasing average oxygen capacity. Besides, given the promoted reduction of MnO_x and CuO in 7% Cu/CR catalyst, it is rational to expect higher extent in vacancy formation, leading to a higher oxygen uptake, and then, a larger work function change. Regarding Figure 8b, a negative change in work function is observed by the effect of CO – surface interaction, assigned to the release of an electron into the CB as a product of CO oxidation, and removal of surface oxygen dipoles. Taking into account that the temperature of measurement is 200°C in chamber (~150°C on sample surface), this modification should necessarily be related to the catalyst activity in CO oxidation at such range of temperatures: 7% Cu/CR (~90% conv. CO) >> CR (~10% conv. CO) > CuO (~2% conv. CO). Despite the fact that the changes are much weaker when compared to O_2 measurements, the trend observed is clear, showing that for 7% Cu/CR the interaction

is the strongest, whereas for reference CuO the electron affinity is not modified. Another important fact which is observable on Figure 8b is the non-reversible CO electronic effect, observed by a maintenance or even slight increase in work function modification after chamber evacuation back to vacuum, which is rather expected as the effect is related to chemical reaction and not merely an adsorption process.

Finally, as complementary characterization using Kelvin Probe instrument, in situ work function measurement experiments with switching O₂ / CO atmospheres were conducted on 7% Cu/CR catalyst, results of which are presented in Figure 9.

The conducted gas switching experiments reveal that the presence of O₂ prevails over CO due to stronger interaction with the surface of the catalysts in the initial uptake, even though the pressure gap between O₂ and CO steps has been compensated by a longer CO exposure. Independent of whether O₂ or CO is supplied first, according to Figure 9a,b on average their introduction conduces to an increase of +0.13 eV, and decrease of -0.02 eV, respectively, in a quite good cyclability. Additionally, turning back to vacuum does not recover in any case work function values from the beginning, probing the non-reversible effect of such gas-surface interaction as described above. Whereas O₂ is refilling vacancies and abstracting electrons from CB, CO is providing electrons to CB and removing lattice O²⁻, back and forth in an imbalanced cycle with superior O₂ interaction. So as a final remark, lattice oxygen must be necessarily involved in CO oxidation mechanism, which confirms MVK mechanism.

4. General discussion

The deposition of Cu by impregnation on cryptomelane support does not change neither textural, crystalline nor chemical features of bare cryptomelane (CR) in the CuO/Cryptomelane (Cu/CR) catalysts. General characterization performed on the Cu/CR

and CR catalysts suggests that CuO is mainly distributed on cryptomelane surface in different dispersion degrees depending on Cu content, which eventually determines the synergistic interfacial interactions existing between CuO and CR phases. Such synergistic interactions are evidenced by the promoted reducibility of the constituent CuO and MnO_x phases in Cu/CR catalysts as a result of the formation of Cu-O-Mn bridges which partially delocalize electron density in Mn-O bonds and bring about a large increase of lattice oxygen mobility [27,32,42]. As a result, it has been demonstrated a very large increase in the CO-PROX catalytic activity for Cu/CR catalysts with regard to pure CuO and CR catalysts, provided that CO-PROX reaction occurs via MVK mechanism with the participation of catalyst oxygen. Therefore, the different CuO distribution and presumed variable CuO particle sizes along the Cu/CR catalyst series allow to tune those interfacial properties that eventually affect to the catalytic performance on the CO-PROX reaction cycles.

Among the Cu/CR catalysts, 7% Cu/CR has been found to be the optimum with the strongest Cu – Mn interaction according to H₂-TPR analysis and work function measurements. Conversely, in 4% Cu/CR catalyst, Cu and Mn species exhibit a more reduced state, probably due to the formation of smaller CuO particles that remain in intimate interaction with MnO_x matrix and promote the redox interplay: $\text{Cu}^+ + \text{Mn}^{4+} \leftrightarrow \text{Cu}^{+2} + \text{Mn}^{3+}$. Thus, the conducted complementary studies based on DFT calculations and *in-situ* work function measurements have allowed to draw the following main conclusions regarding CO-PROX reaction mechanism:

- (1) Cu⁺ states formed upon the enhanced reducibility in Cu/CR catalysts show the predicted maximum selective CO chemisorption compared to that of H₂, so the average result is an improvement in CO oxidation activity in CO-PROX reaction.

- (2) The massive reduction of Cu^+ towards Cu^0 leads to a detrimental effect into CO oxidation activity as H_2 oxidation gains in the competitive reaction environment of CO-PROX.
- (3) To achieve an optimum performance in Cu/CR catalysts the cryptomelane support should not only promote the formation, but also the stabilization of Cu species in the intermediate Cu^+ state, so O_2 restitution processes in equilibrium with lattice oxygen abstraction upon reaction course must be addressed as well.
- (4) According to *in-situ* work function measurements, Cu/CR shows higher interaction with both CO and O_2 gas molecules than bare CuO and CR samples. In addition, the interaction with O_2 is particularly low for bare CR whereas it is highly promoted in CuO.
- (5) In an optimum balance, the presence of bulky CuO sites should facilitate O_2 uptake in the course of CO-PROX reaction, as well as enough Cu^+ sites should preserve good catalytic performance.
- (6) The 7% Cu/CR catalyst, with inferred medium-sized CuO particles and intermediate dispersion, results optimum since it equilibrates partially stable Cu^+ species by means of the strong Cu – Mn synergistic interaction with bulky CuO sites that altogether display good CO oxidation activity and facile O_2 restitution.
- (7) For the 4% Cu/CR catalyst, with a presumed lower CuO particle size, Cu^+ formation is very facilitated, but the lack of sufficient of CuO-rich environment to efficiently undertake O_2 restitution lowers Cu^+ stability and CO selectivity consequently falls.
- (8) 11% Cu/CR catalyst, with segregated CuO phase, presents a large extension of CuO sites prone to reconstitute catalyst oxygen, but their limited Cu – Mn contact hinders Cu^+ formation.

5. Conclusions

Synergistic CuO – CR interaction confers outstanding catalytic properties to Cu/CR catalysts. Such improvement is due to the promotion and stabilization of partially reduced highly active Cu^+ states during CO-PROX reaction in the binary CuO/cryptomelane systems.

The optimum composition for the best catalytic performance was 7% Cu in cryptomelane (7% Cu/CR catalyst), despite 4% Cu/CR sample showed the strongest $\text{Cu}^{2+}/\text{Cu}^+$ - $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox interaction and the CuO highest dispersion. Combining DFT calculations and *in-situ* work function measurements has allowed to conclude that Cu^+ sites, active for the selective CO oxidation, need to be surrounded by a bulky CuO environment to facilitate lattice oxygen restoration as CO-PROX reaction takes place via MVK mechanism. Thus, medium-sized particles in 7% Cu/CR catalyst are the most convenient, holding the optimum compromise between both type of active copper sites.

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Figure Captions

Figure 1. Representative FE-SEM images of (a) 4% Cu/CR; (b) 7% Cu/CR; and (c) 11% Cu/CR.

Figure 2. (a) CO conversion; and (b) CO selectivity profiles in CO-PROX activity tests conducted with the prepared catalysts. 150 mg, 2 °C/min, 100 ml/min 2% CO, 2% O₂, 30% H₂ balance He.

Figure 3. H₂-Temperature Programmed Reduction profiles of CR, Cu/CR and CuO catalysts.

Figure 4a. Deconvoluted XPS Cu 2p_{3/2} photoemission region. **4b.** Cu L₃M_{4,5}M_{4,5} Auger spectra of CuO and Cu/CR prepared catalysts

Figure 5. a) Work Function (Φ) measurements of CR, Cu/CR prepared samples and CuO reference (100% Cu in X-axis) in air and room temperature conditions. b) Temperature for 200 μ mol CO/s·g of reaction rate plotted against Work Function differences ($\Delta\Phi = \Phi_{\text{Cu/CR}} - \Phi_{\text{CR}}$) by the effect of copper loading.

Figure 6. (a,b) CuO(111), (c,d) Cu₂O(111) and (e,f) Cu(111) surface slabs in the most favourable interaction with (a,c,e) CO; (b,d,f) H₂.

Figure 7. Energy of adsorption (eV) for CO and H₂ gas molecules onto slabs of CuO, Cu₂O and Cu, respectively.

Figure 8. WF differences ($\Delta\Phi = \Phi_{\text{p,i}} - \Phi_{\text{vac}}$) measured at 200°C by the effect of (a) O₂; (b) CO, on clean pretreated surfaces (500°C, 30 min vacuum) of cryptomelane (CR), 7% CuO/cryptomelane (7% Cu/CR) and pure CuO.

Figure 9. Work Function differences ($\Delta\Phi = \Phi_{\text{p,i}} - \Phi_{\text{vac}}$) measured at 200 °C over 7% Cu/CR catalyst by the effect of switching atmospheres (i) p O₂: 8E-5 mbar; (ii) p CO: 4E-6 mbar, following the sequence: (a) O₂-CO-O₂; (b) CO-O₂-CO.

Figure 1

Figure 2

Figure 3

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Figure 5

Figure 6

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Figure 7

Figure 8

Figure 9

Tables

Table 1. Compiled results of characterization by N₂ adsorption, XRF (bulk) and XPS (surface) quantification.

Catalyst	S _{BET} [m ² /g]	V _{DR} [cm ³ /g]	^(a) w.% Cu	^(a) Cu/Mn	^(b) Cu/M
CR	72	0.041	-	0.000	0.000
4% Cu/CR	63	0.034	3.7	0.036	0.403
7% Cu/CR	56	0.034	7.2	0.073	0.677
11% Cu/CR	55	0.033	11.2	0.118	0.830

^(a)From XRF characterization; ^(b)From XPS analysis.

Table 2. Redox characterization results from CR and Cu/CR catalysts collected by means of: **(a)** quantitative H₂-TPR experiments; and **(b)** Cu2p XPS and CuLMM Auger spectra.

Catalyst	a	b		
	mmol H ₂ /g _{cat}	α' (eV)[*]	% Cu ⁺ + % Cu ⁰	% Cu ²⁺
CR	12.8	NA	NA	NA
4% Cu/CR	11.4	1850.7	39	61
7% Cu/CR	11.8	1851.1	29	71
11% Cu/CR	12.6	1851.2	22	78

[*]Modified Auger parameter (α').