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Size-Dependent Effects of Cu⁰ Nanoparticles on Electronic Properties and Ethanol Dehydrogenation Catalysis via Cu⁺-O-Cu⁺ Species

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ABSTRACT

Copper (Cu) nanoparticles, widely utilized as catalysts in industrial applications, exhibit intriguing behavior in structure-sensitive reactions like ethanol dehydrogenation. Contrary to expectations, the catalytic activity does not consistently increase as the size of Cu nanoparticles decreases. In Cu catalysts, the particle size significantly effects the Cu^0/Cu^+ ratio on the nanoparticle surface. Decreasing the size of Cu nanoparticles promotes their oxidation, leading to the formation of Cu^+ and O^{2-} species. This alteration subsequently influences the structural and electronic properties of the catalytic Cu sites. Through Cu nanoparticle calculations, the presence of an O ad-atom was identified to modify the electron density at the Cu site, thereby altering the ethanol adsorption energy and impacting the overall catalytic activity. The increase in O coverage, due to size effects, resulted in a notable decrease in the heat of adsorption on Cu nanoparticles (by approximately 20 kJ mol^{-1}). The observed high ΔE_{ads} indicates that more ethanol molecules could reach the transition state for the reaction, subsequently augmenting turnover rates (TOF) and reducing the apparent activation energy (E_{aap}) concerning Cu particle size.

KEYWORDS: Cu/SiO₂ catalysts, ethanol dehydrogenation, Cu-CuO sites on Cu nanoparticles, in situ characterization.

1. Introduction

Encompassing the Sustainable Development Goals set by the United Nations, which target interconnected themes addressing climate change and its catastrophic impacts (such as ecosystem destruction, heatwaves, droughts, and floods) a pressing imperative persists: the development of sustainable technologies to mitigate potential environmental disasters.[1, 2] This has led to an increasing emphasis on converting renewable and low-carbon emission raw materials, exemplified by ethanol derived from plant sources like sugar cane, lignocellulosic biomass, and microalgae, into valuable industrial products.[3, 4] These sources aid in maintaining a carbon balance closer to neutrality, as any potential CO₂ emissions can be reabsorbed by plants through photosynthesis. [5]

Supported Cu nanoparticles are widely used as industrial catalysts.[6-10] Cu- and Au-based catalysts are used in specific reactions where the C-C and C-O bonds must be protected, such as in the dehydrogenation/hydrogenation of acids, alcohols, and esters. Although the dehydrogenation of ethanol into acetaldehyde can serve as a model reaction to investigate the relationship between structural and electronic properties and activity, this reaction also holds significant industrial interest as an alternative method for producing acetaldehyde from renewable raw materials.[11-16]

Computational and experimental studies have demonstrated that the catalytic properties are generally correlated with the electronic and geometric properties of the catalysts.[6, 17-20] It is commonly considered that the metal surface coordination number suffices to model the surface structure and electronic properties, as well as the binding energies of the reaction intermediates.[21] However, most metals have a high affinity for oxygen, meaning that the presence of oxygen in the actual catalysts modifies the surface properties and, consequently, the catalytic performance.[22]

The interaction of metal (M) nanoparticles with oxygen at the interface with the support can modify the catalytic properties due to the following effects: (i) the strong M-O bond could anchor the metal nanoparticle to the support;[7] (ii) highly active sites for oxidation are generated at the metal-support interface, a region likely to contain oxygen (M-O-Support);[23-25] (iii) in some cases, an oxide support can activate reactants or promote a relevant step of the reaction, in which the intermediates migrate through the M-O interface.[26-28] This effect, typically observed in larger domains in biphasic systems, results in a bifunctional catalyst; (iv) the presence of oxygen on the metal nanoparticle surface could modify the geometry of the active metal site, changing its electronic properties, as observed for $\text{Cu}^0/\text{Al}_2\text{O}_3$. [22, 29] This effect occurs at small M-O domains on the surfaces of the metal nanoparticles. In this case, there is a coexistence of metal and metal oxide; in the case of copper, an equilibrium between Cu^+ and Cu^0 is established. Even when prepared under oxygen-free conditions, Cu nanoparticles interact with the oxygen from the support (SiO_2 , for instance); [30] (v) Pt group and Au nanoparticles supported on reducible metal oxides can also cause a local reduction in support,[31] which can lead to a modification in the geometry and electronic properties of the metal site itself or in the appearance of distinct active sites.[23] This effect is known as a strong metal-support interaction (SMSI).[32]

These different forms of M-O interaction depend on the nature of the metal, the size of the metal particles, the support, the pretreatment conditions, and the reaction conditions. The influence of particle size on catalytic activity has not been fully elucidated, particularly when considering the M-O interactions. This is especially important for structure-sensitive reactions catalyzed by Cu-based catalysts, where the effect of Cu nanoparticle size does not always follow the expected trend of catalytic activity increasing with decreasing metal particle size.[6, 22, 24, 33, 34] For

instance, in methanol synthesis, the catalytic activity decreases for Cu particles smaller than approximately 8 nm, which is attributed to the Cu site configurations (such as step-edge sites), and the poorer reactant accommodation exhibited by smaller particles.[25]

In the case of Cu catalysts, changes in particle size affect the Cu^0/Cu^+ ratio on the nanoparticle surface.[17] Furthermore, the M-O interaction is crucial for determining the electronic and catalytic properties of the neighboring metal sites. Indeed, the catalytic properties may be governed either by the Cu-O interaction or by the morphology and coordination of the metal sites.[35] The remaining challenge is to understand the role of the interface and the M-O interaction on the Cu surface structure and, consequently, in the catalytic activity.

Thus, the aim of this study is to explore the influence of copper nanoparticle size, supported on silica, and its interaction with oxygen on the surface properties, active sites, and catalytic activity. This investigation entails linking molecular insights derived from computational simulations with data obtained under controlled kinetic conditions during the non-oxidative dehydrogenation of ethanol.

2. Experimental

2.1 Preparation of silica gel support (SiO_2)

25.00 g of Tetraethyl Orthosilicate (99.99%, Sigma-Aldrich) was diluted in 75.00 mL of Ethanol (99.90%, JT BAKER). Next, 6.25 mL of HNO_3 (65%, Synth) was added, stirring the mixture for 20 min. Subsequently, 25.00 mL of NH_4OH (27%, Synth) was added, and the stirring continued for 20 min. Another 25.00 mL of ethanol was added, and the resulting mixture underwent filtration and washing. The solid obtained was dried overnight at 80°C . The silica gel was thermally treated using medicinal air at 500°C for 5 h, with a heating rate of $3^\circ\text{C}/\text{min}$.

2.2 Preparation of Copper supported on SiO₂ or CAB-O-SIL® (Cab)

Copper catalysts were synthesized with different Cu/Si wt.% ratios (xCuSi, where x could be: 2.5, 5, 10, and 20 wt.%) and Cu/CAB-O-SIL® wt.% ratios (xCuCab, where x could be: 5, 10 and 20 wt.%) using ammonia-evaporation method. For that, different amounts of Cu(NO₃)₂·2.5H₂O $\geq 98\%$ (Aldrich) were solubilized in deionized water (30.00 mL for SiO₂ and 70.00 mL for CAB-O-SIL®). It was dropped NH₄OH 27% (Synth) until the pH reaches 10.00. So, the mixture was stirred for 30 min. After, it was added 2.00 g of SiO₂ or CAB-O-SIL®. Then, the mixture was heated at 70 °C in a heat bath with a condenser for 6.5 h, when the pH reached about 8.5. Afterward, the solution was filtered/washed and dried at 80 °C overnight. After, the samples were thermally treated in medicinal air flow at 400 °C for 5 h with a heating rate of 3 °C/min.

2.3 Characterization

The reduction profile (TPR-H₂) of the samples (80.00 mg) was determined using a Micromeritics Autochem 2920. Initially, the samples were pretreated at a rate of 10 °C/min until reaching 150 °C (for 30 min) in a flow of 30 mL/min of N₂. Subsequently, the samples were cooled to 40 °C, and the gas was switched to a mixture of 30 mL/min of 10% H₂/N₂. The reduction process began by heating the samples at 10 °C/min until 900 °C, and the consumption of H₂ was recorded using a thermal conductivity detector. Additionally, the Micromeritics Autochem 2920 enables the determination of copper dispersion, $Cu_{N_2O}^0$, through N₂O chemisorption (TPR-N₂O) using the following steps: (1) pretreatment similar to the TPR-H₂ method described previously; (2) reduction to Cu⁰ - using 30 mL/min of 10% H₂/N₂ at 10 °C/min until 300 °C for 1 h. The hydrogen consumption during this step is denoted as A_1 and represents the total moles of Cu⁰, Cu_T^0 ; (3) cooling

step - the samples were cooled in 10% H₂/N₂ until reaching 40 °C; (4) oxidation of Cu⁰ to Cu⁺ - the gas was changed to 10 mL/min of 10%N₂O/He for 10 min; (5) reduction of Cu⁺ to Cu⁰ - the gas was switched back to 30 mL/min of 10%H₂/N₂, and the samples were heated at 10 °C/min until 600 °C. This step resulted in a second hydrogen consumption, denoted as A₂, representing the Cu⁰ on the surface, Cu_S^0 .

$$Cu_{N_2O}^0 = \frac{Cu_S^0}{Cu_T^0} = 100 \times \frac{2A_2}{A_1} \quad (1)$$

The Cu site studies were conducted using FTIR (Fourier Transform Infrared Spectroscopy) with a Thermo Nicolet iS50 equipped with a Transmittance Harrick cell and MCT detector. Initially, the samples underwent reduction with a flow of 20 mL/min of H₂ at a heating rate of 10 °C/min until reaching 300 °C, maintained for 1 h. Subsequently, the catalyst was cooled using a flow of 20 mL/min of He until it reached 25 °C. At this point, the gas was switched to 2 mL/min of CO for the CO adsorption process, conducted over 50 min. During this process, absorbance spectra were collected every 5 min using 64 scans and a resolution of 4 cm⁻¹. Following the CO adsorption step, the gas was changed back to 20 mL/min of He, initiating the desorption process which lasted for approximately 1 h. Spectra were collected at intervals of 5 min during the desorption phase as well.

X-ray absorption experiments were conducted at the XAFS2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas/SP), utilizing Cu K-edge (8979 eV) in Transmission Mode. Initially, the samples (60 mg) were mixed with boron nitride (60 mg) to create a pellet, which was then positioned inside a tubular furnace aligned with the path of photons. The samples underwent reduction using a flow of 100 mL/min of 5%H₂/He until reaching 300 °C for 1 h.

During the heating ramp, XANES data was collected, and during the maintenance at 300 °C, EXAFS data was acquired. Additionally, EXAFS data was collected from Cu, Cu₂O and CuO foils for comparative analysis and amplitude calculation. The XANES Linear Combination Fitting was performed using the *Athena XAS Data Processing of Demeter 0.9.24* package. Parameter estimation was carried out using *Artemis EXAFS Data Analysis* within the same package. The process involved the utilization of the first coordination shell range for Cu⁰ and Cu⁺ species, with $\Delta k = 2.682\text{--}12 \text{ \AA}^{-1}$ and $\Delta r = 1.24\text{--}3.0 \text{ \AA}$. After initial estimations, the Debye-Waller (σ^2) and ΔE parameters were fixed in the fitting process. Paths for Cu⁰ and Cu₂O were simulated until statistically significant results were obtained. The amplitudes used were Cu $S_0^2 = 0.9$ and Cu₂O $S_0^2 = 0.7$, with the fitting calculated employing k^2 weighting.

X-ray photoelectron spectroscopy measurements were conducted using the SPECSLAB II (Phoibos-Hsa 3500 150, 9 channels) apparatus at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas/SP). An Al K α (1486.6 eV) source was employed for the measurements. The catalysts, weighing 90 mg without dilution, underwent reduction at a rate of 10 °C/min until reaching 300 °C using a mixture of 5% H₂/He for 1 h. Subsequently, the catalysts were cooled under vacuum and loaded into the measuring chamber. Spectra were acquired for Cu 2p, Cu Auger, O 1s, Si 2p, and C 1s. The data were processed using *Casa 2.3.19* Software, utilizing Si 2p as a reference pattern for sample calibration (103.7 eV).

The copper particle size in the Cu/SiO₂ catalysts was determined using a JEOL 2100F at the Brazilian Center for Research in Energy and Materials in Campinas/SP/Brazil. The Bright Field detector in STEM mode and Gatan CCD in TEM mode were utilized for this analysis. The samples underwent an initial reduction process in 20 mL/min of H₂ at a rate of 10 °C/min until

reaching 300 °C, maintained for 1 h. Additionally, the Cu/Cab samples underwent similar treatment but were placed on copper grids for microscopy. The observation was conducted using a TECNAI G² F20 HRTEM with a Bright Field detector and High Angle Annular Dark Field (HAADF) in STEM mode.

2.4 Catalytic Studies for Ethanol Dehydrogenation Reaction

The ethanol dehydrogenation reaction was studied in a fixed bed micro reactor of borosilicate. The ethanol was inside a water saturator at 30 or 55 °C to control the vapor pressure. The catalysts were first reduced in 20 mL/min of H₂ at 10 °C/min until 300 °C for 1 h. After, the materials were cooled in 20 mL/min of He until 200 °C. The reaction starts with He flow in the saturator. The catalyst mass and the He flow rate were chosen to each copper content to obtain ethanol conversions until 15%. The products were analyzed in a gas chromatography, Varian Star 3400 CX, with Chromosorb 102 column. Forward rate, r_f , was calculated from net rates, r_n , using equations 2 and 3. The TOF of acetaldehyde formation (TOF_{AcH}, s⁻¹) at 225 °C was calculated from the forward reaction rate per Cu⁰ atom on surface determined by reaction with N₂O, equation 4. The Apparent Activation Energy for AcH formation (E_{aap}) was obtained by Arrhenius plot with the reaction temperature range.

$$r_n \left(S\%_{AcH} + \frac{S\%_{AcOEt}}{2} \right) = r_f \left(1 - \frac{P_{AcH}P_{H_2}}{P_{EtOH}K_{eq}} \right) \quad (2)$$

$$r_n = \frac{F_{EtOH} \cdot X\%_{EtOH}}{\%Cu \cdot m_{cat}} \quad (3)$$

$$TOF_{AcH} = r_f \frac{MM_{Cu}}{Cu_{N_2O}^0 / 100} \quad (4)$$

Where P_{EtOH} ; P_{H_2} and P_{AcH} are the partial pressure of each component (atm); K_{eq} is the Equilibrium Constant for ethanol dehydrogenation reaction at 225 °C; F_{EtOH} is the ethanol molar flow ratio in the reactor entrance (mol/s); $X\%_{EtOH}$ is the ethanol conversion (%); $S\%_{AcH}$ and $S\%_{AcOEt}$ are the selectivities (%) to the products acetaldehyde and ethyl acetate, respectively; m_{cat} is the catalyst mass (g); $\%Cu$ is the Cu content (wt. %); MM_{Cu} is the Cu molar mass (63.55 g/mol) and $Cu^0_{N_2O}$ is the Cu dispersion determined by TPR-N₂O (%).

2.5 Theoretical calculations

Theoretical Study were performed considering the density functional theory (DFT) [36] with B3LYP hybrid functional (Becke's gradient-corrected exchange correlation with the Lee-Yang-Parr correlation functional with three parameters),[37] with medium atomic basis sets (TZVPP)[38] implemented in the TURBOMOLE software.[39] The numerical integration for DFT calculation was carried out considering the energy precision as 10^{-7} a.u. The geometry optimization procedure stops when a change in the total energy of 10^{-6} a.u. and a maximum norm of the gradient of 10^{-3} a.u. are obtained. The Cu₁₃ cluster was obtained elsewhere [40] and its geometry was reoptimized by the above method. The Cu₁₃ cluster was modified by the addition of oxygen atoms in its surface as Cu₁₃O_n, where n=1 to 4. The geometry of Cu₁₃O_n clusters was also optimized. After, an ethanol molecule was added over the Cu₁₃ and Cu₁₃O_n clusters and again optimized. The position of the ethanol molecule is comparable for all clusters. The transition state (TS) for hydrogen exchange between the ethoxy group and copper clusters was obtained starting from the intermediary geometry for ethoxy-H-copper clusters. The energy difference between the ground-state and TS and the imaginary frequency of the TS.

Periodic DFT calculations were carried out using the Vienna Ab initio Simulation package (VASP), version 1.4.4.[41-45] The cell energy was found to be converged to better than 0.01 eV per atom at a plane wave basis set cut-off of 400 eV. To ensure complete basis set convergence, a cut-off value of 450 eV was employed for all subsequent calculations.

The cell vectors for the bulk structure of Cu were first optimized using a Murnighan plot which resulted in an fcc cell dimension of 3.641 Å, *i.e.* 0.7 % greater than the experimental value of 3.616 Å from structures taken at 25°C [46]. Subsequently, optimized bulk slab models were created for the Cu(111) and Cu(100) surfaces, each consisting of 5 atomic layers with a vacuum gap of 15 Å. During the computation of adsorption energies of molecules on these surfaces, the lower layers were kept fixed while only the top layers were allowed to relax. This approach aimed to maintain the bulk lattice constraint within the simulation. To determine the number of atomic layers to fix the surface energy was calculated as a function of the number of fixed layers. The surface energy, E_{surf}^{term} , for the bulk terminated slab, can be calculated using the calculated energies of the slab, E_{slab} , and bulk unit cell E_{bulk} using Eq 5.

$$E_{surf}^{term} = \frac{E_{slab} - nE_{bulk}}{2S} \quad (5)$$

Where S is the surface area of the slab model. Here $2S$ appears in the denominator as the bulk terminated slab has both an upper and lower surface. However, when the slab undergoes optimization with fixed lower layers, the validity of Eq. 5 is compromised because the upper (relaxed) and lower (fixed) surfaces become dissimilar. In cases where the two surfaces act independently, a new equation, Eq. 6, is presented.

$$\frac{E_{surf}^{term} + E_{surf}^{opt}}{2} = \frac{E_{slab} - nE_{bulk}}{2S} \quad (6)$$

Where E_{surf}^{opt} , is the surface energy of the optimized surface. By rearranging this equation, we can derive the expression for the optimized surface energy, as shown in Eq. 7.

$$E_{surf}^{opt} = \frac{E_{slab} - nE_{bulk}}{s} - E_{surf}^{term} \quad (7)$$

The surface energy for no fixed layers is obtained from the right-hand side of expression 7 using the optimized slab energy, as in that case, both surfaces are equivalent and optimized. The surface energy is converged when three of the five layers of the slab are fixed at their bulk positions. Accordingly, this choice was made for all calculations involving adsorbates on slab models of surfaces.

The results were obtained using the QUANTUM ESPRESSO program [47]. Ultra-soft pseudopotentials described the electron-ion interaction with scalar relativistic correction generated by the RRKJUS method [48]. The DFT calculation was performed using the PBE functional [49] with D3 dispersion corrections [50]. The chosen energy cutoff was 30 Ry, and the threshold was set to 10^{-6} eV. The Cu and CuO surfaces are represented with (3×3) and (3×4) supercells of a slab with a thickness of three atomic layers, respectively. Approximately four layers of vacuum (15 Å thick) were used to separate the periodic images along the z-direction. The Brillouin zone is sampled with a uniform 3×3×1 k-points grid for Cu(100) and 2×2×1 for CuO(100) and CuO(111).[51]

In this study, a combination of computational approaches was employed to investigate the catalytic properties of copper nanoparticles. TURBOMOLE was used for cluster calculations with B3LYP, which is efficient for non-periodic systems, providing a balance between accuracy and computational cost. The localized functions in TURBOMOLE allowed for precise calculation of the activation energies for ethanol dehydrogenation steps, including the dissociation of ethanol (E_{app}^1) and the dehydrogenation of ethoxy (E_{app}^2).

For periodic solids, VASP with the PBE functional was selected due to its reliability in modeling bulk materials. Quantum Espresso, utilizing PBE-D3 for dispersion corrections, was

crucial for accurately describing van der Waals interactions in surface reactions. This multi-faceted approach allowed for cross-validation and yielded consistent results across different methods, thereby enhancing the reliability and comprehensiveness of the theoretical calculations.

3. Results and discussion

Silica was chosen as a support due to its low enthalpy for ethanol adsorption, thus rendering it a nearly inert support.[26] Cu nanoparticles supported on a laboratory-prepared SiO₂ (xCu/SiO₂) and CAB-O-SIL[®] (xCu/Cab) were synthesized using the ammonia evaporation method, employing different nominal Cu loadings ($x = 2.5, 5, 10$, and 20 wt.%).

The Cu loadings for the xCu/SiO₂ and xCu/Cab catalyst series are shown in Table S1. The unusual increase in specific surface area (SSA) observed with higher copper loadings can be attributed to several factors. Firstly, higher copper loadings result in better dispersion of copper nanoparticles on the support material, which can create additional micro- and mesopores, thus increasing the accessible surface area.[52] Moreover, the interaction between copper nanoparticles and the CAB-O-SIL[®] support may lead to the formation of new porous structures through sintering and restructuring facilitated by the presence of copper.[53] The ammonia-evaporation preparation method and specific thermal treatment conditions likely prevent the blockage of pores that typically occurs at higher metal loadings, ensuring that the pores remain open or even creating new pathways.[54] Besides, strong metal-support interactions at higher loadings could stabilize the support structure, preventing the collapse or blockage of pores and thereby maintaining or increasing the surface area.[55] These combined effects explain the observed increase in SSA despite the higher metal loadings.

Table 1 displays the specific reaction rates, Turnover Frequencies (TOFs), and apparent activation energies (E_{app}) for the dehydrogenation of ethanol. Arrhenius plots illustrating the

ethanol dehydrogenation reaction rates can be found in Figure S1. Overall, an increase in Cu loading resulted in an elevation of TOF and a reduction in E_{aap} . For instance, as the Cu loading escalated from 2.5 wt.% (2.5Cu/SiO₂) to 17.7 wt.% (20Cu/SiO₂), TOF rose from 31.9 to 113.0 s⁻¹, while E_{aap} decreased from 77 to 53 kJ mol⁻¹.

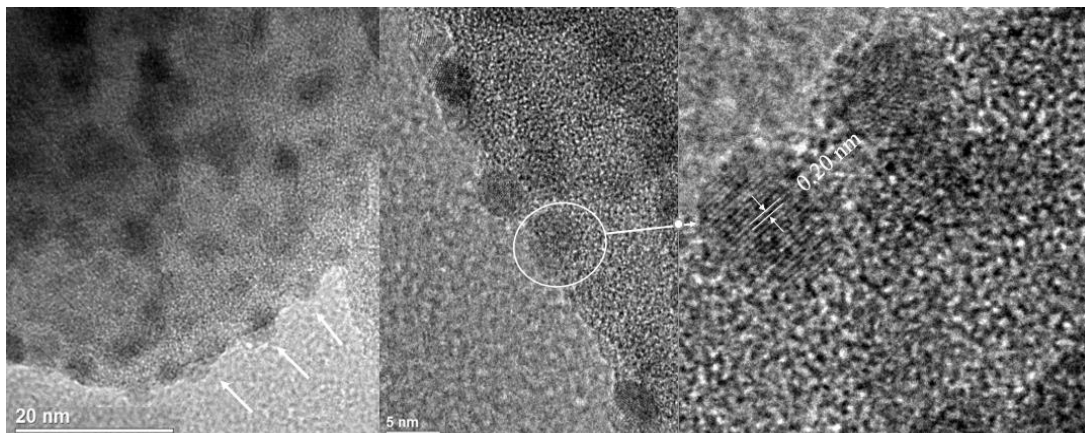
Table 1. Ethanol dehydrogenation rates (R_{AcH}), dehydrogenation Turnover Frequency (TOF_{AcH}), and apparent activation energies (E_{aap}) for different SiO₂-supported Cu catalysts.

Catalyst	R_{AcH} / 10 ⁻⁵ mol g ⁻¹ s ⁻¹	TOF_{AcH} / 10 ⁻³ s ⁻¹	E_{aap} / kJ mol ⁻¹
2.5Cu/SiO ₂	1.1 ± 0.1	31.9 ± 0.1	77 ± 0.2
5Cu/SiO ₂	2.5 ± 0.1	41.6 ± 0.1	73 ± 0.2
10Cu/SiO ₂	8.1 ± 0.1	96.0 ± 0.1	59 ± 0.4
20Cu/SiO ₂	20.2 ± 0.1	113.0 ± 0.1	53 ± 0.1
5Cu/Cab	2.6 ± 0.1	44.8 ± 0.1	55 ± 0.2
10Cu/Cab	9.8 ± 0.1	100.0 ± 0.1	49 ± 0.1
20Cu/Cab	22.7 ± 0.1	115.1 ± 0.1	46 ± 0.3

TEM images and particle size distributions can be found in Figure 1 and S2, with summarized results available in Table S2. Overall, the particles sizes increase along with the Cu loadings, consistent with the observed decrease in Cu dispersion degree (Table S2). The reduction degree, determined via TPR and XANES, yielded comparable results. The XANES results reveal an increase in the Cu⁺ fraction with decreasing Cu loading and Cu nanoparticle size. This

observation suggests an interaction between the Cu nanoparticle surface and oxygen, indicated by the presence of Cu^+ . [22, 56]

(a)



(b)

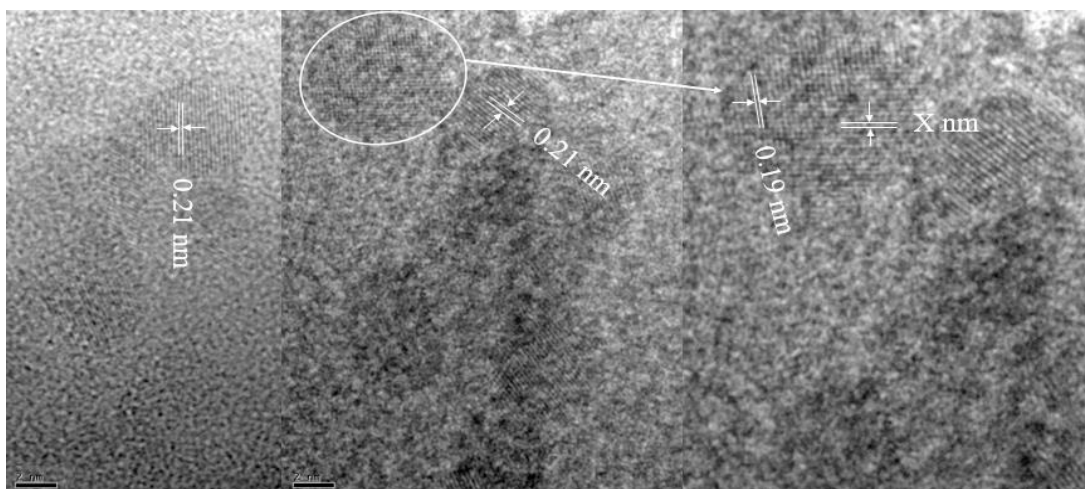


Figure 1. HAADF-STEM images of the reduced catalysts: (a) 20Cu/SiO₂ and (b) 10Cu/Cab catalysts.

The presence of Cu^+ species was also confirmed through FTIR of the samples adsorbing CO (FTIR-CO, Figure 2). This analysis differs from XANES as it specifically detects surface sites accessible to CO. The spectra exhibited bands at 2132, 2122, and 2111 cm^{-1} . Comparing the FTIR-CO spectra of 5Cu/SiO₂ reduced or oxidized with N₂O (Figure 2), indicated that the band at 2111

cm^{-1} corresponded to CO adsorbed on Cu^0 . Furthermore, the bands at 2132 cm^{-1} was associated with CO adsorbed on Cu^+ , and the band at 2122 cm^{-1} was attributed to contributions from both Cu^+ and Cu^0 . [8, 9, 26, 57] The ratio between the intensities of the bands at 2111 and 2032 cm^{-1} (Table S3) indicated a higher Cu^+ surface loading for xCu/SiO_2 compared to xCu/Cab with the same Cu loading (Table S3, Figure 3). Similarly, the ratio between the intensities of bands at 2111 and 2122 cm^{-1} suggests a higher Cu^+/Cu^0 ratio for xCu/SiO_2 materials compared to the xCu/Cab series. This finding is particularly intriguing given that XANES results suggested a similar reduction degree for xCu supported on silica or Cab.

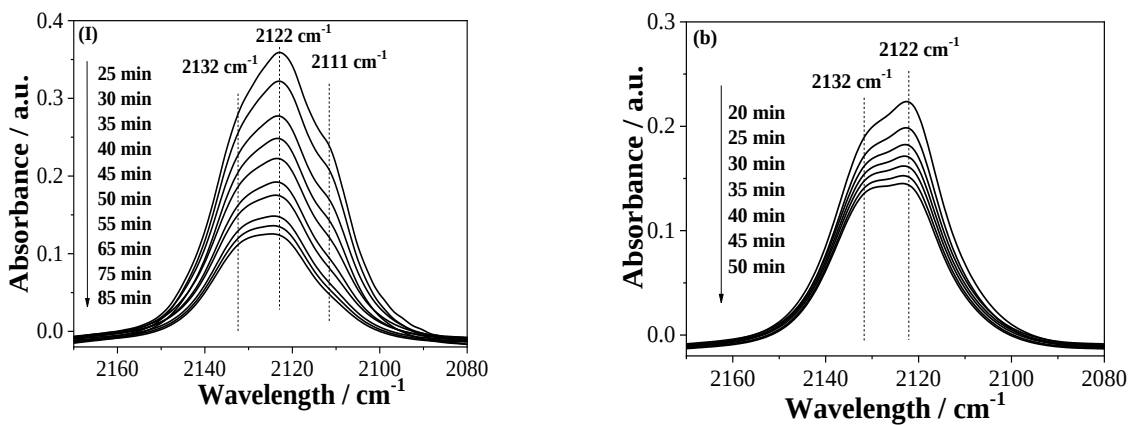


Figure 2. FTIR Spectra of adsorbed CO, collected during the CO desorption for the 5Cu/SiO₂ (a) reduced; (b) reduced and oxidized with N₂O at 25 °C.

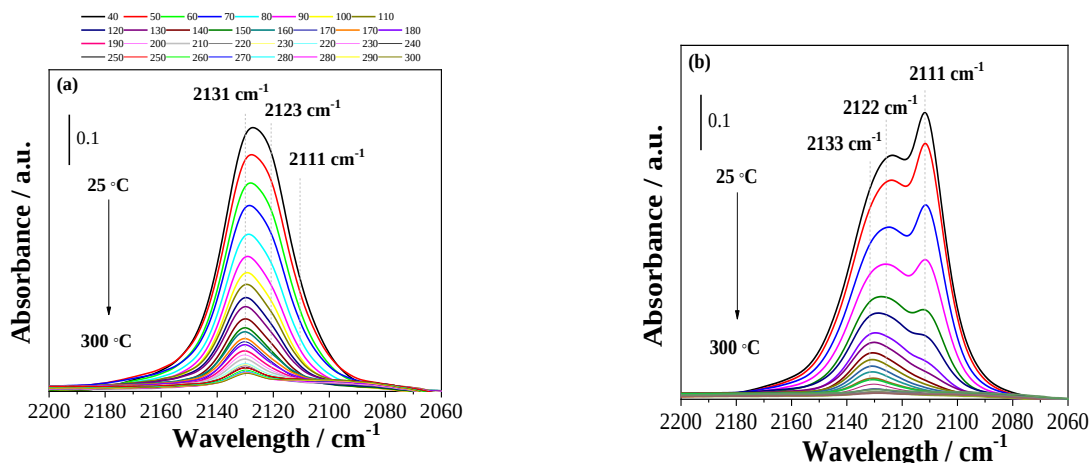


Figure 3. FTIR Spectra of (a) 2.5Cu/SiO₂ and (b) 20Cu/Cab adsorbing CO. Spectra collected during heating at 10 °C min⁻¹ in Temperature Programmed od CO desorption (TPD-CO).

To further understand the structural and electronic properties of the Cu nanoparticles, coordination numbers (N) and bond lengths (R) were calculated though the Cu K-edge EXAFS fitting (Table S4, Figure S3). As a general observation, the Cu-Cu first shell coordination number ($N_{\text{Cu-Cu}}$) increased with higher metal loading, although xCu/SiO₂ presented a lower $R_{\text{Cu-Cu}}$ than xCu/Cab at the same metal loading, indicating a higher electronic density for the former. Typically, the coordination number is often proportional to the metal particle size assuming a hemispherical morphology.[58] Consequently, 2.5Cu/SiO₂ and 20Cu/SiO₂ would theoretically present particles sizes of 0.8 and 2.9 nm, respectively. These calculated sizes are notably smaller than those observed by TEM (Table S2). Additionally, TEM data implies similar particle sizes for xCu/SiO₂ and xCu/Cab, despite their significantly different $N_{\text{Cu-Cu}}$ values. Therefore, the support can be affecting both morphological and electronic properties of the metal nanoparticle.

The choice of silica or CAB-O-SIL® as a support, which is an unstructured silica lacking a defined pore structure, has a significant impact on the structural and electronic properties of Cu nanoparticles. Initially, such unstructured silica would be expected to provide greater coverage of

the Cu particles, leading to a higher number of Cu-O-Si bonds on the surface. This should result in greater stability of the Cu particles. Silica, with its low enthalpy for ethanol adsorption, provides an almost inert support, allowing Cu nanoparticles to maintain their essential metallic properties. In contrast, Cab, with its greater interaction with the metal, can induce structural modifications in Cu particles. The different contractions observed in Cu-Cu bonds can be attributed to electronic density, which is determined by particle size and oxygen concentration on the surface. On the silica support, Cu-Cu bonds exhibit greater contraction due to lower coordination with the support, resulting in increased electron density on Cu surfaces. This is consistent with the EXAFS data, which indicate a lower coordination number for Cu on silica, suggesting a more pronounced quantum confinement effect. On the other hand, in Cab, the metal-support interaction seems to stabilize the Cu-Cu bonds, resulting in less significant contraction. These differences in the electronic and geometric structure of Cu particles, influenced by the choice of support, have direct consequences on catalytic activity. The higher electron density on silica supports can facilitate ethanol activation, promoting the formation of ethoxide species, while the interaction in CAB-O-SIL® can lead to greater structural stability but with lower surface reactivity. In addition to the discussed impacts on structural and electronic properties, CO desorption measurements indicate a high concentration of Cu⁺ on the surface. It is important to note that Cu-OSI on the surface of the support does not adsorb CO, suggesting a significant influence of surface curvature on the reaction dynamics. Therefore, the free energy of the reaction $2\text{Cu}^0 + \text{O} \rightleftharpoons 2\text{Cu}^+ + \text{O}^{2-}$ is critical in determining the oxygen concentration on the surface, highlighting the dependency on whether there is interaction with the support or not. This dependency underscores the role of surface curvature in modulating the free energy of these reactions.

The Cu-Cu bond distance exhibited a 4.9% contraction for the samples containing SiO₂ supports, corresponding to $N_{\text{Cu-Cu}}$ values of 4.4 and 8.2. In contrast, for the x-Cu/Cab samples, only 1.5% of contraction was observed, with $N_{\text{Cu-Cu}}$ values varying from 7.9 to 9.7. These findings suggest greater quantum confinement effects for the Cu particles in xCu/SiO₂, attributed to a lower number of coordination sites. Smaller Cu nanoparticles exhibit higher surface areas relative to their volume. Decreasing the particle size reduces the coordination number of atoms on the nanoparticle's surface, increasing reactivity. This is also interpreted thermodynamically, as variations in the curvature of the nanoparticle surface favor oxide formation. However, these small particles also have a higher tendency to undergo oxidation, leading to a higher concentration of Cu⁺ species. While Cu⁺ sites can enhance certain reactions by stabilizing reaction intermediates, excessive formation of Cu⁺ can decrease the overall catalytic activity. This effect is expected to enhance catalytic activity, especially for structure-sensitive reactions like ethanol dehydrogenation, by balancing particle size and oxygen coverage.

The activation of ethanol into ethoxide species (CH₃CH₂O*), often considered the rate-determining step for the ethanol dehydrogenation reaction on Cu surfaces by numerous authors,[59-62] is typically favored by an increase in electron density. For a clean Cu nanoparticle surface, a decrease in $N_{\text{Cu-Cu}}$ is followed by an increase in the electron density on the surface. However, contrary to expectations, the activity for ethanol dehydrogenation decreased as $N_{\text{Cu-Cu}}$ decreased (as depicted in Figure 4). Oxygen atoms tend to bind with low-coordination Cu atoms, altering the electron density and modifying the adsorption energies of reactants. A moderate level of oxygen coverage can enhance reactivity by creating a more favorable electronic environment for specific reaction pathways. However, excessive oxygen coverage can lead to the formation of

copper oxides, which may alter the electronic properties of the catalyst surface, reducing the availability of active sites and thereby inhibiting the catalytic process. Similarly, the reaction's apparent activation energy (E_{aap}) decreased in correspondence with $N_{\text{Cu-Cu}}$ (as shown in Figure 5a), suggesting that the observed effects of particle size and oxygen coverage need to be balanced for optimal catalytic performance.

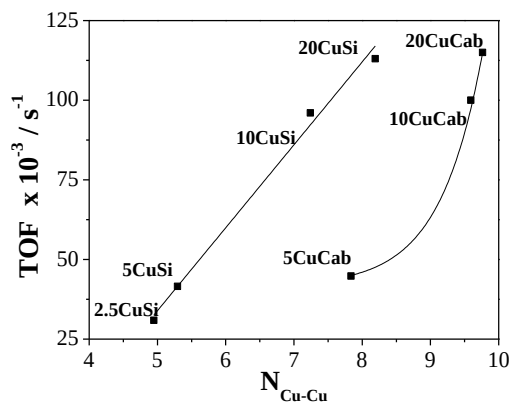


Figure 4. TOF ($10^{-3} \cdot \text{s}^{-1}$) versus $N_{\text{Cu-Cu}}$ for the $x\text{CuSi}$ and $x\text{CuCab}$ catalysts series.

Considering the linear correlation between the kinetic parameter E_{aap} and both the heat of chemisorption of undissociated ethanol (ΔH_{ads}) and the activation energy for the dissociation of ethanol (ΔE_i), leading to the formation of adsorbed ethoxide species or the dissociation of adsorbed ethoxide to adsorbed acetaldehyde, Figure 5a and 5b illustrate a strong dependence of these parameters on the nanoparticle size and the electron density of Cu nanoparticles. The plots clearly show how E_{aap} varies with $N_{\text{Cu-Cu}}$, which reflects changes in the coordination environment of Cu sites. Lower coordination numbers, when oxygen-free, typically result in higher local electron densities, leading to increased catalytic activity due to enhanced surface reactivity. This trend is evident from the decreasing E_{aap} with increasing $N_{\text{Cu-Cu}}$, highlighting the reduced barrier for the ethanol dehydrogenation process as the surface electron density increases. However, the

relationship between electron density and Cu nanoparticle size reveals complexities such as the impact of surface oxidation. Smaller nanoparticles, despite their lower coordination numbers, and theoretically higher electron densities, show a trend towards increased oxidation, which leads to the formation of Cu^+ species. This oxidation can decrease the effective electron density, particularly for catalytic reactions that are sensitive to the electronic state of the surface, as reflected in Figure 5b where E_{aap} is plotted against the binding energy (BE) of Cu $2p_{3/2}$. As the electron density effectively decreases due to oxidation, the Cu $2p_{3/2}$ binding energy increases, indicating a shift towards Cu^+ states with higher oxidation levels.

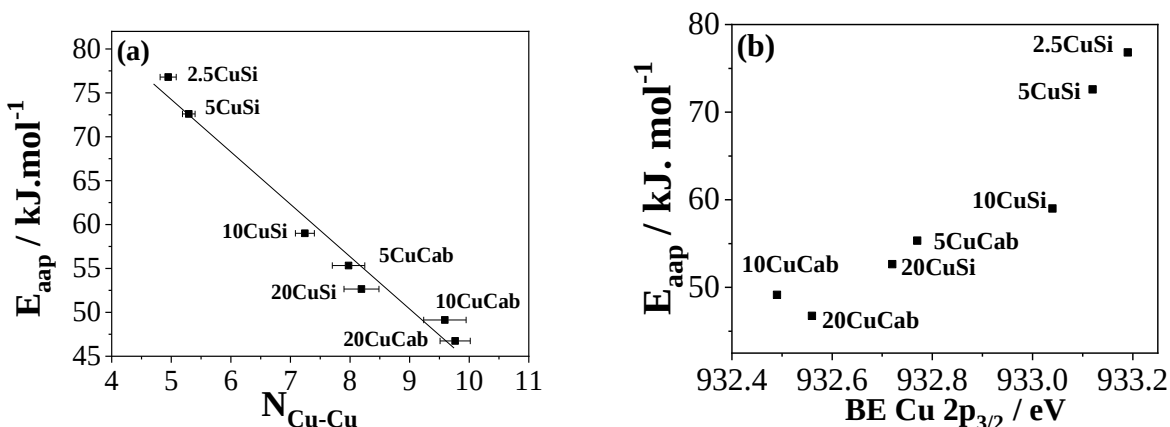


Figure 5. (a) E_{aap} (kJ mol⁻¹) versus $N_{\text{Cu-Cu}}$ and (b) E_{aap} (kJ mol⁻¹) versus BE Cu $2p_{3/2}$ (eV) for the Cu/SiO₂ and Cu/Cab catalysts.

Interestingly, the XPS data revealed an increase in the binding energy (BE) of Cu $2p_{3/2}$ as the $N_{\text{Cu-Cu}}$ decreased, as outlined in Table S5. For the Cu nanoparticles with oxygen-free surface, a negative shift of the BE values would be expected .[63] Considering that the final state of the system governs the ejected photoelectron, according to the drop model,³⁰ a positive shift of BE could be expressed in terms of decreasing $N_{\text{Cu-Cu}}$. [64] However, this study demonstrated an increase in BE Cu $2p_{3/2}$ for oxygen-containing Cu nanoparticles, accompanied by a rise in $\text{Cu}^+\text{-O}$ content as $N_{\text{Cu-Cu}}$ decreased. This shift suggested heightened electron density of surface Cu

concerning $N_{\text{Cu-Cu}}$, leading to an increase in E_{aap} with higher BE Cu 2p_{3/2} (Figure 5b). The modified Auger parameter (α_{Cu})[64] values for the xCu/SiO₂ and xCu/Cab series are approximately 1851.0 and 1848.1 eV, respectively, indicating Cu⁰ and Cu⁺ species (Table S5). The Cu LMN Auger spectra in Figure 6 align with CO-FTIR spectra, confirming a higher Cu⁺ loading in the xCu/SiO₂ compared to the xCu/Cab series.

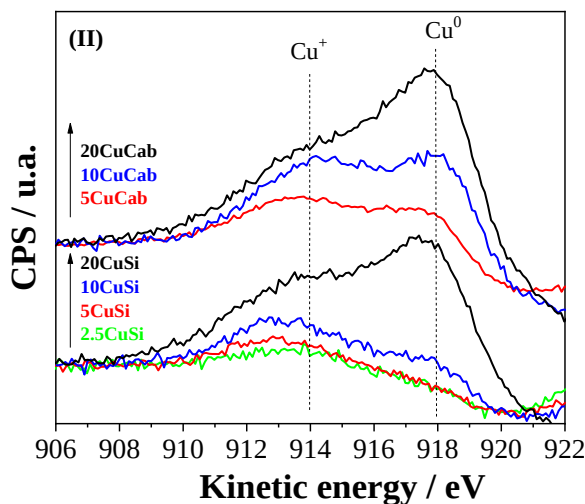


Figure 6. Auger spectra of reduced catalysts series: xCuSi and xCuCab

The evaluation of Cu-O scattering via EXAFS (Table S4) aimed to comprehend the impact of the aforementioned structural modifications on oxygen coverage and its stability. Reliable data on the Cu-O scattering were obtained solely for 5Cu/Cab and xCu/SiO₂ containing 2.5-10 wt. % of metal. This observation indicates that in cases such as 10Cu/Cab, 20Cu/Cab, and 20Cu/SiO₂, the oxygen content was insufficient to allow for accurate identification, which is expected for large Cu nanoparticles. Moreover, the $R_{\text{Cu-O}}$ value acquired was lower than that of the Cu₂O crystalline phase ($R_{\text{Cu-O}} = 1.855 \text{ \AA}$). The Cu-O bond distances ($R_{\text{Cu-O}}$) for 2.5Cu/SiO₂, 5Cu/SiO₂ and 10Cu/SiO₂ were 1.842, 1.847 and 1.853 $\text{\AA}$, respectively, indicating a contraction of $R_{\text{Cu-O}}$ with

decrease of $N_{\text{Cu-Cu}}$ (Table S4). Consequently, in catalysts exhibiting higher $N_{\text{Cu-Cu}}$ (and larger particle sizes), the oxygen tends to become more reactive or labile. Despite having significantly different $N_{\text{Cu-Cu}}$ levels, both 5Cu/Cab and 5Cu/SiO₂ exhibited similar $R_{\text{Cu-O}}$ values, suggesting a potential influence of the support on this phenomenon.

The plot depicting TOF of ethanol dehydrogenation as a function of $R_{\text{Cu-O}}$ (Figure 7) suggests that an increase in $R_{\text{Cu-O}}$ corresponds to a higher TOF for ethanol dehydrogenation. It is important to highlight this increase in $R_{\text{Cu-O}}$ results in greater electron density on the surface of the Cu nanoparticles (CuNP), consequently leading to a lower $R_{\text{Cu-Cu}}$ in CuNP when $N_{\text{Cu-Cu}}$ is higher (Table S4). Regarding the Cu nanoparticle surface, both CO-FTIR and XANES data indicated a decrease in the presence of Cu^+ and Cu^0 as $N_{\text{Cu-Cu}}$ and $R_{\text{Cu-O}}$ increase. Therefore, while the existence of Cu^+ species is essential, the most active samples are those with lower Cu^+/Cu^0 ratios. The enhancement in surface reactivity is not solely due to the predominance of metallic copper but also the changes in electron density resulting from electron transfer between Cu^0 and Cu^+ . This electron transfer alters the Cu-O bond distance, serving as a probe of electronic density on the surface. An increase in the Cu-O bond distance reflects a higher electronic density, thereby further enhancing catalytic activity.

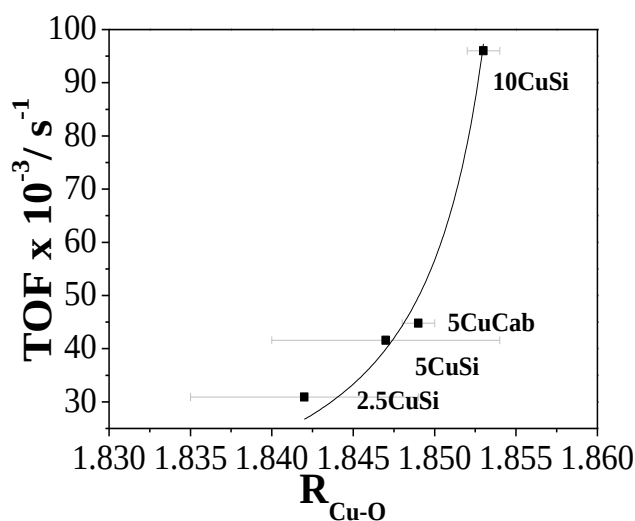


Figure 7. TOF ($10^{-3} \cdot \text{s}^{-1}$) versus $R_{\text{Cu-O}}$ ($\text{\AA}$) for the CuSi and CuCab catalysts.

The XAS, FTIR measurements, and catalytic activity indicated that Cu supported on silica comprises a core of Cu^0 decorated by a shell of Cu^0 , Cu^+ , and O^{2-} at different proportions. However, Cu^+ can interact with the oxygen within the support interface, while oxygen is expected to be present throughout the nanoparticle. While smaller Cu nanoparticles exhibited Cu atoms with lower coordination numbers, this often results in higher local electron density, facilitating specific catalytic processes. However, increased surface oxidation can lead to Cu^+ formation, which may reduce the effective electron density, cause greater contraction of $R_{\text{Cu-Cu}}$, and result in higher oxygen coverage on the surface.

The decrease of the particle size shifted the equilibrium of the reduction reaction ($\text{Cu}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Cu}^0 + \text{O}^{2-}$) favoring the oxide side to minimize surface free energy. This modification affected the superficial structure of the Cu nanoparticle. Therefore, the contraction of $R_{\text{Cu-Cu}}$ due to confinement effects, accompanied by decreasing $N_{\text{Cu-Cu}}$, did not exhibit a direct correlation with surface electronic properties. This finding is drawn from the analysis of superficial composition

(Cu/O) and structure of the Cu nanoparticle, contrary to initial expectations. Additionally, the increase in E_{aap} (Figure S4) corresponded with the decrease in $R_{\text{Cu-Cu}}$, suggesting a transformation of low-coordination Cu sites into less active Cu^+ species for dehydrogenation. The decrease of $N_{\text{Cu-Cu}}$ led to elevated Cu^+/Cu^0 ratios and $N_{\text{Cu-O}}$ (Table S2), resulting in shorter Cu-O bond lengths due to heightened oxygen coverage. Unlike the behavior observed within the core of the Cu nanoparticle, a decrease in $N_{\text{Cu-Cu}}$ indicated reduced electron density at the surface.

The difference of E_{aap} between the xCu/SiO₂ and xCu/Cab catalyst series was around 30 kJ mol⁻¹, significantly impacting the activity. Theoretical studies using the DFT method³¹ were used to explore the surface chemistry of the Cu nanoparticles containing oxygen and its effects on the activity in the ethanol dehydrogenation reaction. [36] Essential parameters affecting the experimentally obtained E_{aap} values include the heat of undissociated ethanol chemisorption (ΔH_{ads}), coverage degree, and enthalpies of intermediates and transition states.[39] The values of ΔH_{ads} and ΔE (transition states with dissociation of RCO-H to R-CO*) were calculated as a function of the number of oxygen ad-atoms ranging from 1 to 4 on the surface of Cu clusters (Cu₁₃), referred to as Cu₁₃O_x (where x denotes the number of O atoms).

Density Functional Theory (DFT) calculations, as detailed in Table 2 and Scheme 1, provide a comprehensive understanding of ethanol interaction with copper clusters. The adsorption energies (ΔE_{ads}) indicate a strong affinity of ethanol for Cu clusters, particularly when facilitated by bidentate coordination involving the hydroxyl and α -carbon of ethanol with an oxygen-modified Cu-Cu site (O-Cu-Cu*). However, the addition of a second oxygen atom weakens this interaction significantly, though further oxygenation beyond the second atom does not exacerbate this weakening effect. The most favorable reaction path is represented in green in Scheme 1.

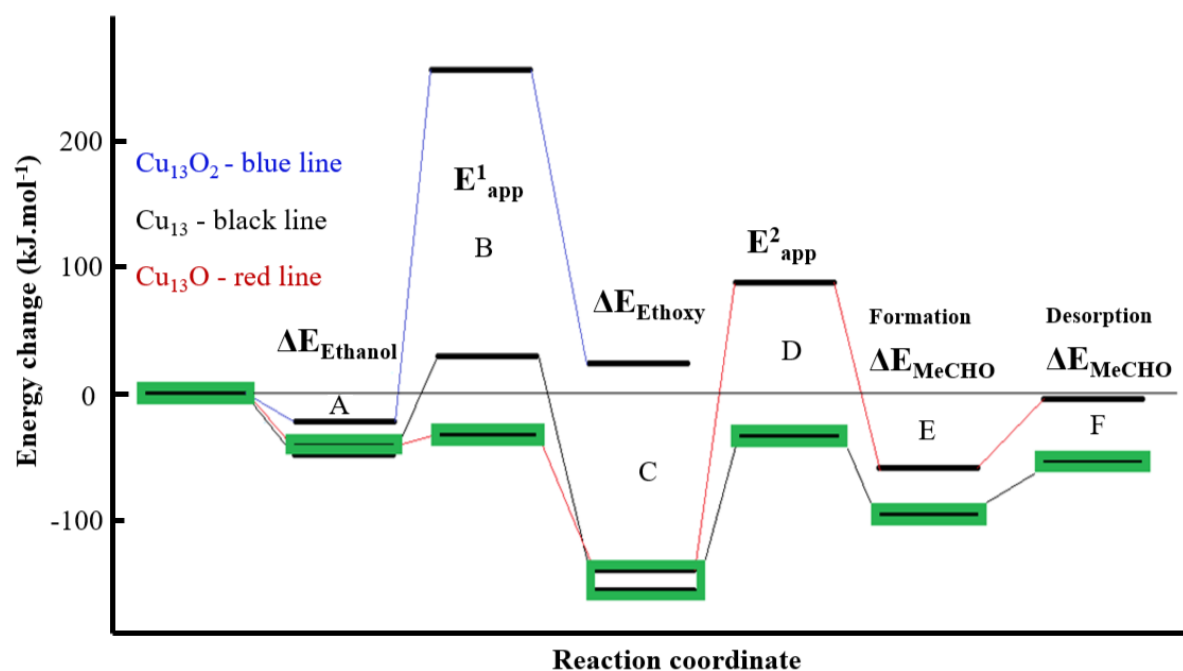
Table 2. Theoretical results for dehydrogenation of ethanol (Scheme 1): (A) Heat adsorption of molecular ethanol ($\Delta E_{\text{Ethanol}}$); (B) activation energy for dissociation of ethanol (E^1_{app}); (C) formation of adsorbed ethoxide species ΔE_{Ethoxy} ; (D) activation energy for dehydrogenation of ethoxy (E^2_{app}); (E) formation of acetaldehyde ($^{\text{formation}} \Delta E_{\text{MeCHO}}$); and (F) heat desorption of acetaldehyde ($^{\text{desorption}} \Delta E_{\text{MeCHO}}$). Energies given in kJ.mol^{-1} . Results for clusters with 13 atoms of Cu (Cu_{13}) and 1 until (2+k) atoms of O (Cu_{13}O_x , where x is the number of O atoms). For Cu(111) and Cu(100) surfaces containing 5 atomic layers.

	A	B	C	D	E	F
Systems	$\Delta E_{\text{Ethanol}}$	E^1_{app}	ΔE_{Ethoxy}	E^2_{app}	for- mation ΔE_{MeCHO}	desorp- tion ΔE_{MeCHO}
Cu₁₃	-52	30	-167	-36	-101	-26
Cu₁₃O*	-47	-37	-151	94	-65	-6
Cu₁₃O_{2+k}**	-27	272	23	---	---	---
Cu(111)	-4	---	-7	---	55	---
Cu(100)	-26/-46	---	-6/-101	---	65/-94	---
Cu(111)O_M L	-21	---	-48	---	---	---
Cu(100)O_M L	-59	---	-116	---	-52	---
Cu(111)O₁	-47/-50	---	-135/-135	---	-70/-58	---

Cu(100)O₁	-73	---	-200	---	-53	---
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*O-cluster forming a hydrogen bond with H atom of ethanol hydroxyl group; **only two O atoms of the cluster interact with ethanol with $k > 0$. Bold numbers represent results obtained using the VASP program, and italic numbers using the QUANTUM ESPRESSO program.

Scheme 1. Energy diagram for ethanol dehydrogenation to acetaldehyde by the Cu₁₃O_x catalyst corresponding to Table 2. The most favorable reaction path is indicated in green, involving the Cu₁₃O clusters in the first step and Cu₁₃ clusters in the second step.



For the Cu₁₃ cluster, ethanol adsorption is substantially exothermic at -52 kJ.mol⁻¹, in contrast to the less negative ΔE_{ads} of -27 kJ.mol⁻¹ for the Cu₁₃O₂ cluster. The trend in adsorption energies does not consistently increase with oxygen content. This is especially true for ethoxide (CH₃CH₂O*) and acetaldehyde (CH₃CHO), where the introduction of oxygen modifies the chemisorption bond, forming a Cu-O-H-O-CH₂CH₃ linkage. This bond alteration, together with the

electron density redistribution at the copper site, slightly affects the enthalpy of adsorption, suggesting a nuanced influence of oxygen presence on adsorption characteristics.

Periodic Density Functional Theory (DFT) calculations, as detailed in the Supplementary section, reveal distinctive adsorption behaviors of ethanol on copper nanoparticle facets. Adsorption on Cu(111) and Cu(100) surfaces yields ΔE_{ads} values of -4 and -26 (-46) $\text{kJ}\cdot\text{mol}^{-1}$, respectively, which are less favorable compared to the -52 $\text{kJ}\cdot\text{mol}^{-1}$ observed for the Cu_{13} cluster (Table 2). Complete oxidation of these surfaces, resulting in a monolayer of oxygen ($\text{Cu(111)O}_{\text{ML}}$ and $\text{Cu(100)O}_{\text{ML}}$), and also with 1 O atom (Cu(111)O_1 and Cu(100)O_1), enhances the adsorption energies due to stronger interaction mechanisms. On the Cu(111) facet, hydrogen bond formation between the adsorbed ethanol molecule and a surface oxygen atom contributes to this enhancement. In contrast, the Cu(100) surface undergoes significant rearrangement upon complete oxidation, with Cu atoms in the topmost layer adopting square planar geometries characteristic of Cu^{2+} ions. This rearrangement facilitates a dual interaction mechanism where ethanol is stabilized by both a hydrogen bond and additional coordination with Cu^+ , leading to an increased adsorption energy of -59 $\text{kJ}\cdot\text{mol}^{-1}$.

Similar trends are observed for the adsorption of reaction intermediates, such as ethoxide and acetaldehyde. On a partially oxidized Cu(111)O_1 surface with a single oxygen atom (1/9th monolayer), ethanol exhibits an adsorption energy of -47 (-50) $\text{kJ}\cdot\text{mol}^{-1}$, whereas ethoxide demonstrates a more substantial interaction with a ΔE_{ads} of -135 $\text{kJ}\cdot\text{mol}^{-1}$. These results suggest that lower oxygen coverages enhance molecular interactions with the metal surface, corroborating the cluster model observations where a balance of unoxidized and oxidized metal states is preferred for the energetically favorable conversion of ethanol to acetaldehyde. Notably, the surface

Cu(100)O₁ shows equivalent results. Hence, while partial oxidation appears to facilitate the reaction, complete surface oxidation to copper oxides seems to impede catalytic activity.

The influence of oxygen on the catalytic properties is further elucidated when considering the particle size of copper clusters. The interaction between ethanol and the copper-oxygen surface is modulated by Cu⁺, with smaller Cu nanoparticles exhibiting higher activity due to lower coordination environments. These nanoparticles typically feature a Cu⁰ core surrounded by Cu⁺ at the surface, with the extent of O coverage and the Cu⁺/Cu⁰ ratio diminishing as particle size increases. An increase in Cu⁺ enhances nanoparticle stability but concurrently reduces reactivity, especially as the particle size decreases. However, the presence of oxygen on the surface at a low Cu⁺/Cu⁰ ratio aid in ethanol adsorption through the formation of R- O- H— O-Cu bonds, suggesting that the availability of free oxygen on the surface subtly modulates both adsorption and dissociation processes. For larger Cu nanoparticles, structural features such as edges and corners could potentially promote oxygen reaction and subsequent formation of CuOCu sites for ethanol adsorption.

4. Conclusion

The correlations observed between E_{aap}, N_{Cu-Cu}, and BE Cu 2p_{3/2} suggest that the contraction of the R_{Cu-Cu} bond distance in line with the decrease in N_{Cu-Cu} is reflected in the electron density of Cu nanoparticles and their surfaces. However, the size of these nanoparticles and the density of oxygen on their surfaces are thermodynamically linked. As particle size decreases, the level of oxygen on the surface increases, which could be expected to modify catalytic activity. In Cu nanoparticles, oxygen is bound to cationic Cu⁺ species. DFT calculations indicate that lower activity is expected on oxygen-free Cu surfaces with high Cu coordination. However, while

decreasing Cu coordination does lead to increased oxygen coverage, facilitating ethanol adsorption and its dissociation through H transfer to OCu and OC₂H₅ to Cu, the overall catalytic activity decreases with reduced Cu particle size. This decline is due to the reduced TOF observed experimentally in smaller particles, despite the higher oxygen coverage. The experimental results suggest that the dehydrogenation of ethoxy to acetaldehyde is less favorable on smaller Cu nanoparticles, possibly due to changes in the surface electronic properties of active Cu sites. Thus, while the increase in Cu⁺ species might initially suggest enhanced catalytic activity, the observed decrease in TOF for smaller particles indicates that additional structural and electronic factors are influencing performance. This phenomenon illustrates a scenario where catalytic activity is not directly linked to the reduction in nanoparticle size, highlighting the complexity of the relationship between structure and function in Cu-based catalysts.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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