Supporting Information for the Manuscript:
“On the Stability of Cu$_5$ Catalysts in Air Using Multi-Reference Perturbation Theory”

Alexandre Zanchet,$^{†, †}$ Patricia López-Caballero,$^{†}$ Alexander O. Mitrushchenkov,$^{¶}$ David Buceta,$^{§}$ Manuel Arturo López-Quintela,$^{§}$ Andreas W. Hauser,$^{*, ‖}$ and María Pilar de Lara-Castells$^{*, †}$

$^{†}$Instituto de Física Fundamental (AbinitSim Unit), CSIC, Serrano 123, 28006 Madrid, Spain
$^{‡}$Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Salamanca, 37008 Salamanca, Spain
$^{¶}$Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS 5 bd Descartes, 77454 Marne-la-Vallée, France
$^{§}$University of Santiago de Compostela, Laboratory of Nanotechnology and Magnetism, E-15782 Santiago de Compostela, Spain
$^{‖}$Graz University of Technology, Institute of Experimental Physics, Petersgasse 16, 8010 Graz, Austria.

E-mail: Andreas.W.Hauser@gmail.com; Pilar.deLara.Castells@csic.es
Phone: +34 5616800 (941026)
This Supporting Information is organized as follows:

- The first section presents an exploratory analysis of the crossing point between neutral and ionic potential energy curves for the complex formed by O$_2$ and quasi-one-dimensional copper nanowires Cu$_n$ ($n = 6, 10, 16, 24, 30$).

- The second section compares the energies of planar trapezoidal and trigonal bipyramidal Cu$_5$ structures using the MP2 method.

- The third section presents two pictures with fully optimized Cu$_5$–O$_2$ structures at MP2 level at the physisorption region of the potential energy surface, with the physisorption energies presented in the corresponding captions. Comments on the comparison between MP2 and wB97X-D3 levels are also included in the second section.

- The fourth section discusses the expression used to calculate the fraction of O$_2$ molecules with energies above a established threshold (e.g., the value of the physisorption well-depth).

- The fifth section shows the reaction energy path to O$_2$ splitting into two individual atoms bound to the copper cluster from the chemisorption minimum for both Cu$_5$ (planar)–O$_2$ and Cu$_5$ (trapezoidal)–O$_2$ structures.

- The sixth section presents a reaction pathway to the chemisorption minimum using a single-reference DFT-based method.

- The seventh section shows the frontier orbitals characterizing the O$_2$–Cu$_5$ interaction.
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S1 Exploring the Crossing Region for O₂ Interacting with Copper Nanowires Cuₙ (n=6, 10, 16, 24, 30)

Assuming atomic units for the energies and distances, the position of the crossing point Rₓ can be estimated by assuming a $-e^2/R$ asymptotic behavior (with $e$ denoting the charge of an electron) of the ionic potential energy curve and solving the following equation (Equation (1) of the main manuscript),

$$R_x = \frac{1}{\Delta E}$$

with $\Delta E = IE - EA$, where IE is the ionization energy of the Cuₙ nanowire fragment and EA is the electron affinity of the O₂ molecule. For the latter, the experimental value has been used (EA=0.4480 ± 0.0060 eV from Ref. 1), while the ionization energy of the Cuₙ nanowire has been estimated at wB97X-D3 level through the energy difference between neutral Cuₙ and cationic Cuₙ⁺ species. The def2-SVP basis set² was employed using the ORCA package³ and the geometry of the Cu₁₆ fragment was fully optimized. IE values for the planar trapezoidal Cu₅ cluster calculated with the wB97X-D3 and CCSD(T) approaches differed by less than 0.1 eV.

Table 1 presents the calculated IE and $\Delta E$ values along with the estimated crossing points Rₓ following Eq. 1 for Cuₙ nanowires with n=6, 10, 16, 24, and 30. Table 1 nicely shows

Table S1: Ionization energy (IE), energy gap between neutral and ionic states at infinite separation of O₂ and Cuₙ fragments ($\Delta E$), estimated crossing point between neutral and ionic states (Rₓ), and interaction energy of the O₂–Cuₙ complex at the estimated crossing point.

| System | IE, eV | $\Delta E$, eV | Rₓ, Å | $E_{Rₓ}$, eV |
|--------|--------|----------------|-------|--------------|
| Cu₂    | 7.31   | 6.86           | 2.1   | 0.56         |
| Cu₆    | 6.19   | 5.74           | 2.5   | 0.07         |
| Cu₁₀   | 5.64   | 5.24           | 2.8   | −0.05        |
| Cu₁₆   | 5.03   | 4.58           | 3.1   | −0.04        |
| Cu₂₄   | 4.69   | 4.25           | 3.4   | −0.04        |
| Cu₃₀   | 3.90   | 3.45           | 4.2   | −0.03        |
that, upon increasing the copper wire length, the estimated crossing point becomes located at the attractive region of the potential energy surface characterizing the physisorption \( \text{O}_2 - \text{Cu}_n \) interaction. This is in contrast with the cases of the \( \text{O}_2 - \text{Cu}_2 \) and \( \text{O}_2 - \text{Cu}_6 \) complexes as well as the \( \text{O}_2 - \text{Cu}_5 \) system (see Figure 2 of the main manuscript). Interestingly, the change occurs when the wire length is beyond one nanometer.

![Figure S1: Geometry of the Cu\textsubscript{30}-O\textsubscript{2} complex at the estimated crossing point between neutral and ionic potential energy curves.](image)

**S2 Optimizing the Geometry of the Bare Cu\textsubscript{5} Cluster**

![Figure S2: Optimized geometries of the bare Cu\textsubscript{5} cluster with planar trapezoidal (left-hand panel) and trigonal bypiramidal (right-hand panel) structures. The values of the distances between Cu atoms are given in Å.](image)

Optimized structures of the bare Cu\textsubscript{5} cluster were calculated at second-order Møller-Plesset perturbation theory (MP2) level using the aug-cc-pVTZ-PP basis set\textsuperscript{4,5} including a small-core (19-valence-electron) relativistic pseudopotential.\textsuperscript{6} For this purpose, the ORCA program package\textsuperscript{3} has been used (version 4.0.1.2). As can be seen in Figure S2, planar trapezoidal
(left-hand panel) and trigonal bypiramidal (right-hand) geometries were obtained. The calculations predicted the planar trapezoidal structure to be energetically favored by 0.01 eV only. This energy difference was further reduced when employing the def2-TVZPP basis set instead, with the Cu–Cu distances characterizing both planar and trapezoidal structures being about 0.04 Å longer. A reoptimization of the planar trapezoidal geometry using the def2-QVZPP basis set provided Cu–Cu distances differing by less than 0.01 Å from those obtained with the def2-TVZPP set.

S3 Physisorption-type $\text{O}_2$–$\text{Cu}_5$ Interaction with MP2

Figure S3: Optimized geometries of the $\text{O}_2$–$\text{Cu}_5$ system, with $\text{Cu}_5$ in a planar trapezoidal structure, considering the complex in a quartet spin-multiplicity state. The values of the distances are given in Å. The physisorption energies are $-0.03$ eV for the “symmetric parallel” configuration (left-hand panel), $-0.04$ eV for the “asymmetric” configuration (middle panel), and $-0.02$ eV for the “perpendicular” configuration (right-hand panel).

Full optimizations of $\text{O}_2$–$\text{Cu}_5$ geometries were carried out at MP2 level using the def2-TVZPP basis set and the ORCA program package. For the symmetric parallel $\text{O}_2$–$\text{Cu}_5$ configuration shown in the left-hand panel of Figure 1 of the main text, it was found that the optimization using the def2-QVZPP basis set instead is producing a similar $\text{Cu}_5$–$\text{O}_2$ distance (within 0.1 Å). Using the same basis set employed in MS-CASPT2 calculations (see main
Figure S4: Optimized geometries of the O$_2$–Cu$_5$ clusters, with the Cu$_5$ bearing a trigonal bypiramidal structures, considering the complex in a quartet spin-multiplicity state. The values of the distances are given in Å. The physisorption energies are $-$0.09 eV for the “symmetric parallel” configuration (left-hand panel) and $-$0.08 eV for the “perpendicular” configuration (right-hand panel).

It was found that the MP2 and MS-CASPT2 methods deliver similar well-depth values in the physisorption region.

Altogether, it can be observed from the results shown in Figures 2 and 3 that the potential energy surface in the physisorption region is extremely shallow, containing several local potential minima which are characterized by well-depth values below $-$0.05 and $-$0.1 eV for the planar and the bypiramidal Cu$_5$ structure, respectively. Notice also that molecular oxygen adsorption clearly favors the bypiramidal over the planar Cu$_5$ structure. As can be expected for a physisorption-type interaction, the O$_2$ and Cu$_5$ structures in the O$_2$–Cu$_5$ complex are not distorted as compared with those of the isolated fragments.

Interestingly, very similar adsorption energies were obtained using the dispersion-corrected DFT method wB97X-D3$^7$ and the def2-TVZPP basis set. For example, the adsorption energy for a “perpendicular” attachment of O$_2$ to the planar trapezoidal structure (see right-hand panel of Figure 2), adsorption energies of $-$0.02 eV were obtained both at MP2 and wB97X-D3 levels. Considering the trigonal bypiramidal structure and a “symmetric parallel” attachment of O$_2$ instead (see left-hand panel of Figure 2), adsorption energies increase to values of $-$0.09 and $-$0.08 eV at MP2 and wB97X-D3 levels, respectively. It was also observed that the wB97X-D3 method predicted optimized O$_2$–Cu$_5$ distances which are shorter than those estimated with the MP2 method, by about 0.2 Å in average.
S4 Fraction of O$_2$ Molecules with Energies Above a Given Threshold

S4.1 Monoatomic Ideal Gas

The density probability that one atom of ideal gas has a value of the energy $\epsilon$ is given by:

$$\rho(\epsilon) = \sqrt{\frac{4\epsilon}{k_B^3 T^3 \pi}} \times e^{-\epsilon/k_B T}$$

(S2)

This is in fact the Maxwell-Boltzmann distribution expressed in energy terms, with $T$ as the temperature and $k_B$ as the Boltzmann constant. By integrating from 0 to $\infty$, we obtain a value of 1. The average energy would be $\int_0^\infty d\epsilon \rho(\epsilon)\epsilon$, providing a value of $\frac{3k_B T}{2}$. This is in agreement with the equipartition theorem, establishing that the average energy has to be $\frac{k_B T}{2}$ for each degree of freedom (three in this case).

The probability that the atom has an energy in between 0 and $\epsilon_0$ is $P(\epsilon_0) = \int_0^{\epsilon_0} d\epsilon \rho(\epsilon)$. Then, the probability that the particle has an energy above $\epsilon_0$ is $1 - P(\epsilon_0)$. By performing the corresponding integration, we obtain:

$$1 - P(\epsilon_0) = 1 - \text{erf} \left( \sqrt{\frac{\epsilon_0}{k_B T}} \right) + \sqrt{\frac{4\epsilon_0}{k_B^3 T^3 \pi}} \times e^{-\epsilon_0/k_B T}$$

(S3)

with erf denoting the Gauss error function:

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

(S4)

In this work, we have used a value of the Boltzmann constant $k_B$ equal to $8.617332478 \times 10^{-5}$ eV.
S4.2 Ideal Gas of Diatomic Molecules

Within the rigid rotor approximation, the density probability that one diatomic molecule of an ideal gas without excited vibrational (nor electronic) degrees of freedom has a value of the energy \( \epsilon \) is:

\[
\rho(\epsilon) = \sqrt{\frac{\epsilon^3}{9k_B^5T^9\pi}} \times e^{-\epsilon/k_B T} \tag{S5}
\]

By integrating from 0 to \( \infty \), a value of 1 is obtained. The average energy would be \( \int_0^\infty d\epsilon \rho(\epsilon)\epsilon \), providing a value of \( \frac{5k_B T}{2} \). Again, this is in agreement with the equipartition theorem, which states that the average energy has to be \( \frac{k_B T}{2} \) for each degree of freedom (five in this case).

The probability that the diatomic molecule has an energy in between 0 and \( \epsilon_0 \) is \( P(\epsilon_0) = \int_0^{\epsilon_0} d\epsilon \rho(\epsilon) \). Then, the probability that the particle has an energy above \( \epsilon_0 \) is \( 1 - P(\epsilon_0) \). By performing the corresponding integration, we obtain:

\[
1 - P(\epsilon_0) = 1 - \text{erf} \left( \sqrt{\frac{\epsilon_0}{k_B T}} \right) + \sqrt{\frac{4\epsilon_0}{k_B^5 T^3 9\pi}} \times (3k_B T + 2\epsilon_0) \times e^{-\epsilon_0/k_B T} \tag{S6}
\]

The expression above has been used to calculate the fraction of \( \text{O}_2 \) molecules with energies above a given threshold \( \epsilon_0 \) (the value of the physisorption well-depth in this work).

S5 Reaction Energy Pathway from Chemisorption to \( \text{O}_2 \) Dissociation

As mentioned in the main manuscript, the chemisorption geometries shown in Figure 3 are just intermediate states which are followed by the actual splitting of the O–O bond (i.e., the dissociation of \( \text{O}_2 \) into two individual O atoms attached to the Cu\(_5\) cluster). Figures S5 and S6 show the extended energy pathways, calculated at the same level of theory as used in the main manuscript, describing the \( \text{O}_2 \) dissociation for the trapezoidal and the bipyramidal

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Figure S5: Approximation to the reaction energy pathway for O\textsubscript{2} splitting into two individual O atoms bound to the copper cluster from the chemisorption minimum of the O\textsubscript{2}–Cu\textsubscript{5} complex, with Cu\textsubscript{5} arranged in a planar trapezoidal structure. Interaction energies are shown as a function of the distance between the two O atoms from chemisorbed O\textsubscript{2} (denoted as r\textsubscript{O–O}). The internal coordinates of the Cu\textsubscript{5} cluster have been optimized while the O\textsubscript{2}–Cu\textsubscript{5} distance, as defined in Figure 1 of the main manuscript, has been either kept fixed (shown in red) or also optimized (shown in blue). In other words, the blue crosses mark energies of fully optimized minima and transition state structures.

As shown in Figure S5, a splitting of O\textsubscript{2} into two individual O atoms (bound to the copper cluster) should happen in the next step of oxidation from the precursor charge-transfer state when Cu\textsubscript{5} arranged in a planar trapezoidal structure (i.e., the chemisorption potential minimum in the ionic state presented in Figure 3 of the main manuscript). Thus, the O\textsubscript{2} splitting barrier is just 0.12 eV, much lower than the barrier due to state crossing, i.e. for the transition from physisorption to chemisorption (0.42 eV, see Table 1 from the main
manuscript). Hence, as discussed in the main manuscript, the hopping to the ionic state is clearly the rate-limiting step in the oxidation process.

Figure S6: Approximation to the reaction energy pathway for O₂ dissociation (into two individual O atoms bound to the copper cluster) from the chemisorption minimum of the O₂–Cu₅ complex, with Cu₅ arranged in a bipyramidal structure. Interaction energies are shown as a function of the distance between the two O atoms from chemisorbed O₂ (denoted as \( r_{\text{O-O}} \)). The internal coordinates of the Cu₅ cluster as well as the O₂–Cu₅ distance have been optimized while the O₂–Cu₅ distance, as defined in Figure 1 of the main manuscript), has been varied.

The same O−O splitting reaction is illustrated in Figure S6 for the bipyramidal Cu₅ structure. In this case, the energy penalty for dissociation is extremely high, which is a consequence of a strongly quenched charge transfer in the “chemisorbed” intermediate state in comparison to the planar structure. Even if the whole structure is fully relaxed, the energy increases by 0.8 eV when the O−O bond increases by just 0.2 Å. In fact, the charge transfer from Cu₅ to the anti-bonding \( \pi^* \) orbital of O₂ is very small at the chemisorption minimum
(0.2 $|e|$, see main manuscript) and, then, the destabilization of the O–O bond is not strong enough to allow a lowering of the barrier to O$_2$ dissociation to smaller values.

**S6 Frontier Orbitals Characterizing the O$_2$–Cu$_5$ Interaction**

An interesting feature of the binding mechanism between O$_2$ and Cu$_5$ is that the lowest-energy singly-occupied molecular orbital (referred to us SOMO) of the copper cluster is not involved. This is the case for both (planar and bipyramidal) isomers, with the binding mechanism involving the hybridization of $d$-shell double-occupied molecular orbitals (referred to as HOMOs) of the copper cluster with one of the anti-bonding $\pi^*$ orbitals of molecular oxygen. In Figure S7, a schematic molecular diagram illustrates how the HOMO-5 molecular orbitals of Cu$_5$ and one $\pi^*$ molecular orbital O$_2$ overlap at the chemisorption minimum. By sharing $\pi^*$ orbitals with the copper cluster, the oxygen molecule can drag electronic density toward itself, leading to a partial charge transfer, and a mixed ionic-covalent-type binding.

The case of the trapezoidal cluster is a little bit different. The shape of the cluster allows it to present several $d$-type molecular orbitals that can overlap favorably with the anti-bonding $\pi^*$ orbital of molecular oxygen. As can be seen in Figure S8, the $d$-orbitals, all located in the same plane, can adapt to maximize the overlap with the $\pi^*$ orbital of O$_2$. Since more orbitals are involved in the bonding, the stability of the O$_2$–Cu$_5$ complex is significantly higher as compared to that of the bipyramidal isomer. Particularly, more electronic density can be pumped by the oxygen molecule, providing a more complete charge-transfer from Cu$_5$ to O$_2$.  

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Figure S7: Molecular orbital diagram (top view) illustrating the binding mechanism to form the $\text{O}_2$–$\text{Cu}_5$ (bypiramidal) cluster. The hybridization of a double-occupied molecular orbital of $\text{Cu}_5$ (HOMO) and a single-occupied anti-bonding $\pi^*$ of $\text{O}_2$ gives rise to bonding and antibonding $\text{O}_2$–$\text{Cu}_5$ molecular orbitals. These orbitals have been calculated at Hartree-Fock level.
Figure S8: Main frontier orbitals illustrating the bonding of O$_2$ to the trapezoidal Cu$_5$ cluster.

Figure S9: Reaction pathway equivalent to that shown in Figure 3 (left-hand panel) of the main manuscript, but obtained at the PBE-D3(BJ) level of theory.
Figure S10: Approximation to the reaction energy pathway for O\textsubscript{2} splitting into two individual O atoms bound to the copper cluster from the chemisorption minimum of the O\textsubscript{2}–Cu\textsubscript{5} complex, with Cu\textsubscript{5} arranged in a planar trapezoidal structure, as calculated at the PBE-D3(BJ) level of theory. Interaction energies are shown as a function of the distance between the two O atoms from chemisorbed O\textsubscript{2} (denoted as $r_{O-O}$). The internal coordinates of the Cu\textsubscript{5} cluster as well as the O\textsubscript{2}–Cu\textsubscript{5} distance have been optimized.

Figure S11: Optimized Structure of the O\textsubscript{2}–Cu\textsubscript{5} cluster at one saddle-point found in the global potential energy surface using at PBE-D3(BJ) level. The energy of the saddle point is about 0.63 eV above that of the chemisorption minimum.
Figure S12: Calculated Gibbs energy profiles for dissociation of molecular O$_2$ into two adsorbed O atoms at 0 K (green), room temperature (blue), and 423 K (orange), as calculated with the PBE-D3(BJ) method (quartet spin state). The optimized structures of reactant (R), transition state (TR), and product (P) are also shown.
Figure S13: Figure illustrating the main frontier orbitals involved in the bonding of $O_2$ to the planar trapezoidal $Cu_5$ cluster, as calculated at PBE-D3(BJ) level.
S7 Reaction Energy Pathway using DFT

For comparison purposes, the same reaction energy pathway shown in Figure 3 (left-hand panel) of the main manuscript has been computed using a single-reference DFT-based method for the O$_2$–Cu$_5$ (planar trapezoidal) interaction in the quartet spin state. These calculations were performed with the ORCA$^3$ suite of programs (version 4.0.1.2), using an atom-centered def2-TZVPP$^2$ for both copper and oxygen atoms, and employing a dispersion-corrected DFT-D3 ansatz.$^8,^9$ Specifically, structural optimizations and the calculation of interaction energies were performed with the Perdew-Burke-Ernzerhof (PBE) density functional and the Becke-Johnson (BJ) damping$^8$ for the D3 dispersion correction. We will refer to this combination as the PBE-D3(BJ) scheme. This scheme has been chosen due to its excellent performance when describing the interaction of the Cu$_5$ cluster with the rutile TiO$_2$(110) surface.$^{10}$

As can be seen in Figure S9, the reaction path lacks of any barrier, predicting a spontaneous chemisorption of O$_2$ onto the Cu$_5$ (planar) cluster. Contrarily, the employment of multi-reference perturbation theory predicts a value of the energy barrier for the same reaction of 0.43 eV (see Table 1 of the main manuscript). The charge transfer from Cu$_5$ to antibonding orbitals O$_2$ is rather small at the chemisorption minimum (−0.2 |e|). Therefore, the activation of the oxygen molecule by a weakening of the O–O bond is very modest, with the O–O splitting into two O atoms bound to the copper cluster remaining the costly, rate-determining step for the oxidation. In fact, the energy barrier to O$_2$ dissociation on the planar Cu$_5$ structure becomes about 0.31 eV (see Figure S10). In contrast, the application of multi-reference perturbation theory (see Figure S5) yields a much lower energy barrier for O$_2$ dissociation (0.12 eV).

We have also searched saddle points in the O$_2$–Cu$_5$ potential energy landscape. Interestingly, a saddle point has been found when the O$_2$ molecule rotates around the C$_{2v}$ axis of the
planar structure by 90 degrees, as illustrated in Figure S11. This transition state structure lies 0.6 eV above the chemisorption minimum (see Figure S12) and 0.6 eV below the energy of the dissociation products. Similar structures for the reactant, the transition state, and the products upon dissociation have been reported in Refs. 11 and 12 at the DFT level. However, at a variance with the previous DFT study, we have included dispersion corrections and are considering a quartet spin state. Note further that no adsorption is predicted at 423 K.

Figure S13 illustrates how frontier HOMO and SOMO orbitals of the \( \text{Cu}_5 \) and \( \text{O}_2 \) reactive species combine to form SOMO and HOMO bonding \( \text{O}_2-\text{Cu}_5 \) orbitals. These orbitals have been calculated considering the optimized geometry at the chemisorption minimum. Note that the SOMO orbital of the copper cluster does not lead to a favorable interaction with the antibonding \( \pi^* \) orbitals of \( \text{O}_2 \). The opposite holds true with the HOMO orbitals of \( \text{Cu}_5 \). This picture agrees very well with that obtained from the analysis of the frontier Hartree-Fock orbitals in section S6.

Similarly, when analyzing the binding mechanism of \( \text{O}_2 \) to the bypiramidal \( \text{Cu}_5 \) cluster, we can notice (see Figure S14) the favored interaction between one HOMO orbital of the copper cluster and one \( \pi^* \) orbital of the \( \text{O}_2 \) molecule (see bottom panel of Figure S14) while the opposite holds true for the interaction with the SOMO orbital of \( \text{Cu}_5 \) (see top panel of Figure S14).
Figure S14: Figure illustrating the main frontier orbitals involved in the bonding of O$_2$ to the bypiramidal Cu$_5$ cluster, as calculated at PBE-D3(BJ) level.

| SOMO Cu$_5$ | SOMO O$_2$-Cu$_5$ | SOMO (Π*) O$_2$ |
|-------------|-------------------|-----------------|
| HOMO Cu$_5$ | HOMO O$_2$-Cu$_5$ | SOMO (Π*) O$_2$ |
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