ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Unravelling key factors in the chlorine promoted epoxidation of ethylene over a silver-copper oxide nanocatalyst

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PART I. Theoretical exploration of the influence of chlorine considering on-surface and subsurface sites of CuO(111), with a single AgO atomic cluster.



Figure ESI-1. Influence of chlorine position relative to an AgO cluster attached to up to 5 monolayers of CuO with (111) orientation: a) Front and side views of the AgO cluster and tentative chlorine locations (atoms color codes: red: oxygen; light brown: copper and gray: silver); Green filled-circles show the position of adsorbed atoms on the surface; b) Energy normalization respect to the most stable configuration. The energy for each position coordinate has been calculated and defined by **E**_{rnCn} where n accounts for the number of row (r) and column (c) corresponding to each position. This energy increment is calculated as difference among the energies each row and column, and the minimum energy (most stable position) for the chlorine adsorbed on surface. For the chlorine atoms adsorbed on the surface, the most stable position is r2c1.



Figure ESI-2. Influence of chlorine position relative to an AgO cluster attached to up to 5 monolayers of **CuO with (111) orientation**: Front and side views of the AgO cluster and tentative chlorine locations (atoms color codes: red: oxygen; light brown: copper and gray: silver); Red atoms with a green surrounding border line represent the oxygen atoms that can be replaced by chlorine in the first and second layers (see side view for a better understanding)



Figure ESI-3. Influence of chlorine position relative to an AgO cluster attached to up to 5 monolayers of CuO with (111) orientation: a) Energy normalization respect to the most stable configuration for each case (first- and second-layer substitution). The energy for each position coordinate has been calculated and defined by E_{rncn} where n accounts for the number of row (r) and column (c) corresponding to each position. This energy increment is calculated as difference among the energies each row and column, and the minimum energy (most stable position) for the chlorine substituting to oxygen atoms in first or second layer, depending on the situation under analysis. The most stable position for the structure where the oxygen in the first layer has been replaced by a chlorine is denoted by r1c1. In the case of substitutions carried out in the second layer, the most favourable position is r2c2; b) Energy normalization by the most stable configuration considering the structures where the chlorine is replacing the oxygen in the first and second layers.



Figure ESI-4. Left side: front view of AgCuO at different chlorine positions and right side: snapshots of these minimized positions. (Atoms color codes: red: oxygen; light brown: copper; gray: silver and green: chlorine).

Table ESI-1. Minimized energies for AgCuO and Cl-AgCuO systems, with different spin configurations. The parameter NUPDOWN is defined as the difference between the number of electrons in the up and down spin polarizations.

	NUPDOWN=0	-501.47321 eV
AgCuO	NUPDOWN=1	-501.80932 eV
	NUPDOWN=2	-500.94490 eV
	NUPDOWN=0	-504.15178 eV
Cl-AgCuO	NUPDOWN=1	-503.90506 eV
	NUPDOWN=2	-503.59352 eV
	NUPDOWN=3	-503.07787 eV

The table shows the minimum energy values obtained in the optimisations of the AgCuO and Cl-AgCuO structures. The values highlighted in bold correspond to the most stable spin states, and those are the spin states that have been employed in the rest of the calculations of the corresponding system.

PART II. Energy evaluation of OMC, EO and AA adsorbed on AgCuO

For all the calculations, we have only considered the most favorable positions of the adsorbed chlorine on the surface (snapshots for these positions are depicted on Figure 3 of the main text).



Figure ESI-5. Left axis: Variation of stability, comparing OMC as starting position and EO or AA respectively. Right axis: Ratio between the variations of stability OMC/EO and OMC/AA. From a thermodynamic point of view, the r4c3 position is the best one, since in this position chlorine provides a greater increase in energy for EO production ($E_{EO}-E_{OMC}$) and proportionally smaller change for AA (ratio $\Delta E(EO)/\Delta E(AA)$).

	c1	c2	с3
r1	-	-	-
r2	-505.1828	-504.7686	-
r3	-504.7641	-504.8835	-504.7071
r4	-504.6048	-504.9314	-504.7525

Table ESI-2. Energy values (eV) for catalyst with chlorine and adsorbed OMC.

 Table ESI-3.
 Energy values (eV) for catalyst with chlorine and adsorbed EO molecule.

	c1	c2	с3
r1	-	-	-
r2	-505.7181	-505.5116	-
r3	-505.0319	-504.9719	-505.0223
r4	-505.6278	-505.8638	-505.8807

 Table ESI-4.
 Energy values (eV) for catalyst with chlorine and adsorbed AA molecule.

	c1	c2	с3
r1	-	-	-
r2	-506.7807	-506.5291	-
r3	-506.2337	-506.1169	-506.3261
r4	-506.7945	-507.0131	-506.9782

PART III. Calculation of Adsorption Energies

For the adsorption energy calculations, we have only considered the most favourable positions of the adsorbed chlorine on the surface (snapshots for these positions are depicted on Figure 3 of the main text). Table ESI-5 shows the adsorption energies for AgCuO without chlorine. Tables ESI-6 and ESI-7 show the energies of the catalyst (AgCuO) with a chlorine atom adsorbed and with the product molecule also adsorbed, EO and AA respectively. Tables ESI-8 and ESI-9 show the adsorption energies for EO and AA, for the different positions studied. The difference between the adsorption energies with and without chlorine catalyst are reported on Tables ESI-10 and ESI-11. The parameter $\delta \Delta \Delta E^{ADS}$ is reported in Table ESI-12.

Table ESI-5. Summary of the starting values in adsorption energy calculations (eV).

E _{catalyst} [AgCuO (non Cl)]	-463.14
E _{molecule} (EO)	-38.08
E _{molecule} (AA)	-39.107
Ecatalyst+molec [AgCuO+EO (non Cl)]	-502.094
Ecatalyst+molec [AgCuO+AA (non Cl)]	-502.854
Eads[AgCuO+EO (non Cl)]	-0.867
Eads[AgCuO+AA (non Cl)]	-0.602

Table ESI-6. Energy values (eV) for catalyst with chlorine and EO molecule adsorbed (Ecatalyst+molecule).

	c1	c2	c3
r1	-	-	-
r2	-505.71812	-505.51168	-
r3	-505.03195	-504.97191	-505.02233
r4	-505.62784	-505.86389	-505.88075

Table ESI-7. Energy values (eV) for catalyst with chlorine and AA molecule adsorbed (E_{catalyst+molecule}).

	c1	c2	c3
r1	-	-	-
r2	-506.78075	-506.529	-
r3	-506.23377	-506.11693	-506.32619
r4	-506.7945	-507.01315	-506.9782

	c1	c2	с3
r1	-	-	-
r2	-1.0052	-1.3536	-
r3	-0.5636	-0.4252	-0.5681
r4	-0.7029	-1.0672	-0.6882

Table ESI-8. Adsorption energies (eV) for catalyst with chlorine and EO molecule adsorbed (ΔE^{ADS}).

Table ESI-9. Adsorption energies (eV) for catalyst with chlorine and AA molecule adsorbed (ΔE^{ADS}).

	c1	c2	с3
r1	-	-	-
r2	-1.0425	-1.3456	-
r3	-0.7401	-0.5449	-0.8467
r4	-0.8443	-1.1912	-0.8081

Table ESI-10. Adsorption energy variations (eV) induced by the presence of the chlorine atom, with EO adsorbed ($\delta \Delta E^{ADS}$)

	c1	c2	с3
r1	-	-	-
r2	-0.1375	-0.4859	-
r3	0.3041	0.4424	0.2995
r4	0.1647	-0.1995	0.1794

Table ESI-11. Adsorption energy variations (eV) induced by the presence of the chlorine atom, with AA adsorbed ($\delta \Delta E^{ADS}$)

	c1	c2	c3
r1	-	-	-
r2	-0.4401	-0.7432	-
r3	-0.1377	0.0574	-0.2443
r4	-0.2418	-0.5887	-0.2057

Table ESI-12. Comparation of EO and AA adsorption energy variations (eV) induced by the presence of the chlorine atom, with $(\delta \Delta \Delta E^{ADS})$.

	c1	c2	c3
r1	-	-	-
r2	0.3025	0.2572	-
r3	0.4417	0.3849	0.5438
r4	0.4066	0.3892	0.3851