

Supplementary Information for:

Structural behaviour of copper chloride catalysts during the chlorination of CO to phosgene.

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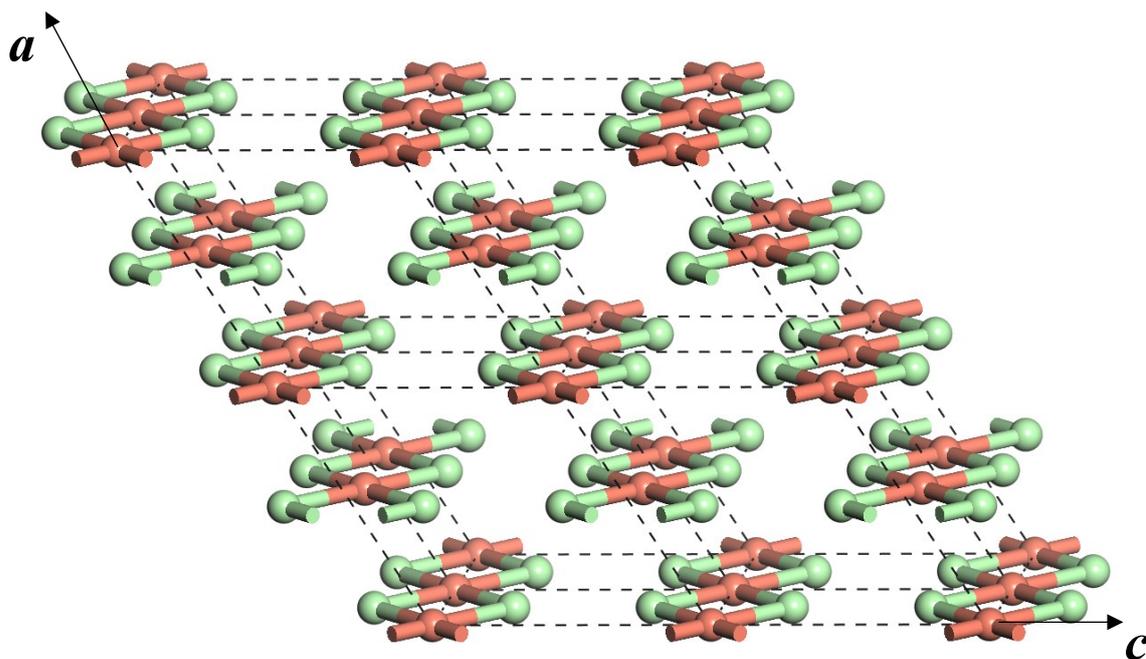


Figure S1. The crystal structure of CuCl_2 . A $2 \times 2 \times 2$ section of the structure is shown with black dotted lines denoting unit cell boundaries. Cell dimensions are $a = 6.85 \text{ \AA}$, $b = 3.30 \text{ \AA}$, $c = 6.70 \text{ \AA}$, $\beta = 121^\circ$ (expt.), $a = 6.878 \text{ \AA}$, $b = 3.313 \text{ \AA}$, $c = 6.727 \text{ \AA}$, $\beta = 121^\circ$ (PBE+U(=7) with D2): Atoms coloured Cu: pink, Cl: green.

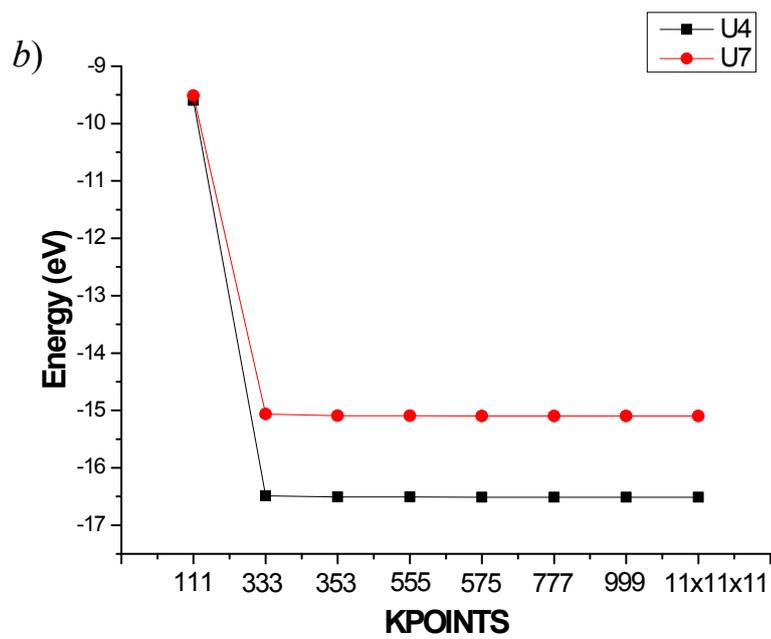
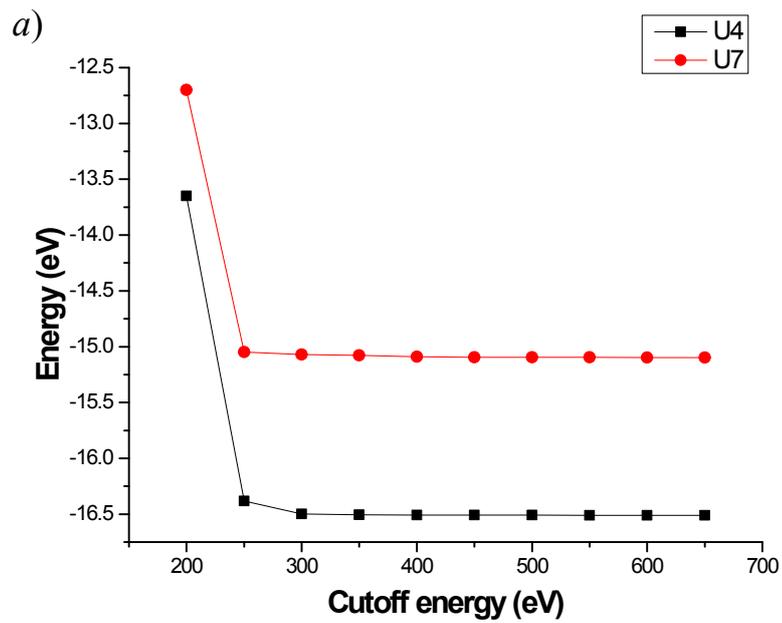


Figure S2. Calculated unit cell energy of CuCl_2 unitcell against a) cutoff energies and b) k -point sampling grid, for Hubbard $U=4$ (black) and $U=7$ (red) in each case.

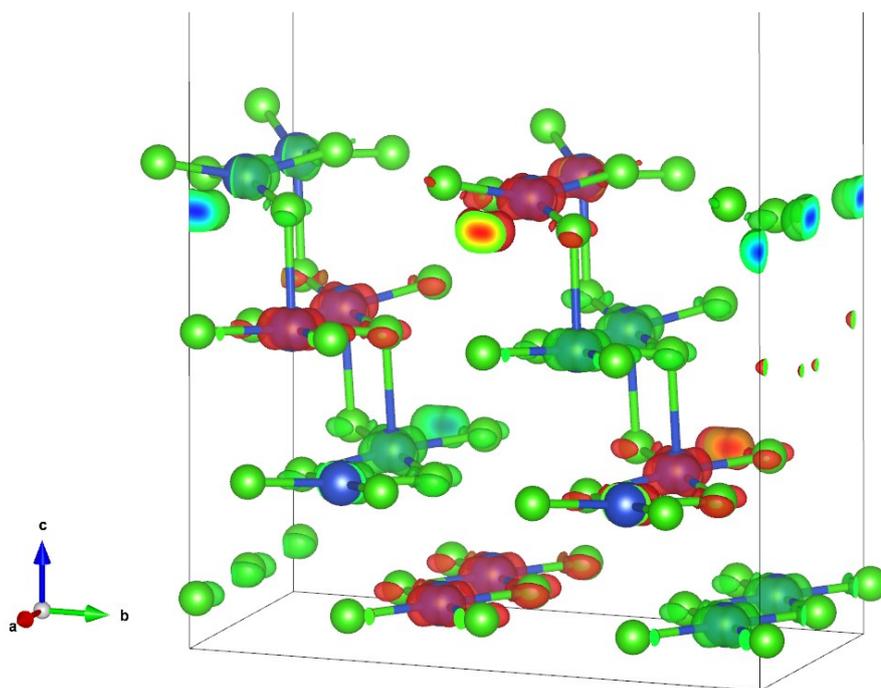


Figure S3. Spin density plot at $0.015 \text{ e } \text{\AA}^{-1}$ level for the (010) surface model of CuCl_2 calculated using PBE+U(=7) with D2. Up and down spin density are shown as red and green respectively. Atoms coloured Cu: Blue, Cl: green. Note that for surfaces the slab model is constructed from a cell redefined to have $a' = b$, $b = c$ and $c = 2a + c$ with respect to the standard setting shown in Figure S1.

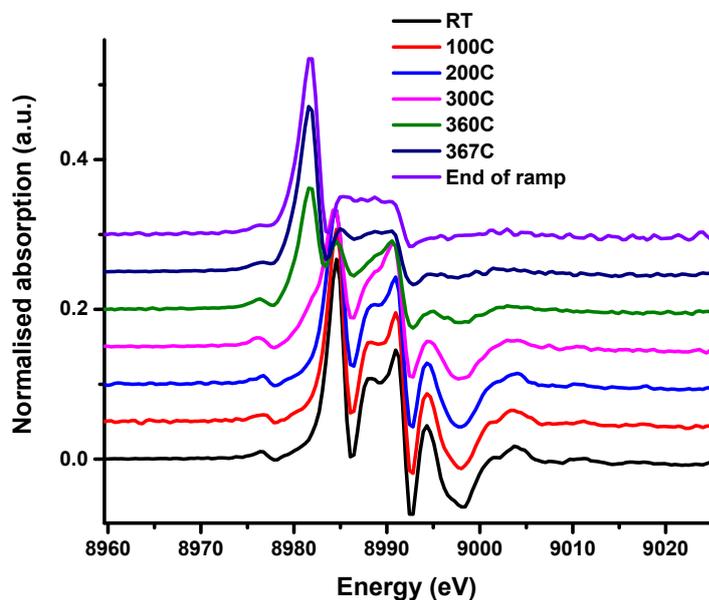


Figure S4. Normalised derivative of the spectra recorded during the temperature of the pre-treated sample.

Analysis of the extended X-ray absorption fine structure (EXAFS) region was performed on the chlorine pre-treated sample. The resulting fit and parameters are shown in Figure S6 and Table S1. Our data fits well to two Cu-Cl contributions at 2.282 ± 0.005 and 2.86 ± 0.03 Å, respectively. From the XANES spectrum we expect this to be anhydrous CuCl_2 , where the Cu would have a distorted octahedral environment with 4 Cl's at 2.3 Å and 2 Cl's at 2.95 Å.¹ However, our refined coordination numbers from the EXAFS analysis are lower than expected, 3.5 and 0.5. This could be due to destructive interference of the scattering paths from the axial and equatorial neighbours which has previously been observed for distorted octahedral Cu species, resulting in only the equatorial contributions being observed, leading to difficulties in refining the coordination numbers.²

Samples	Abs - Sc	N	R / Å	$2\sigma^2 / \text{Å}^2$	E_0 / eV	R_{factor}
RT pretreated	Cu-Cl (CuCl ₂)	3.5±0.1	2.282±0.005	0.007	3.1±0.6	0.003
	Cu-Cl (CuCl ₂)	0.4±0.2	2.86±0.03	0.007		

Table S1. EXAFS fitting parameters, $S_0^2=0.9$, as determined by the use of a Cu foil standard. Fit range $3.3 < k < 10.1$, $1 < R < 3$; number of independent points=8.4

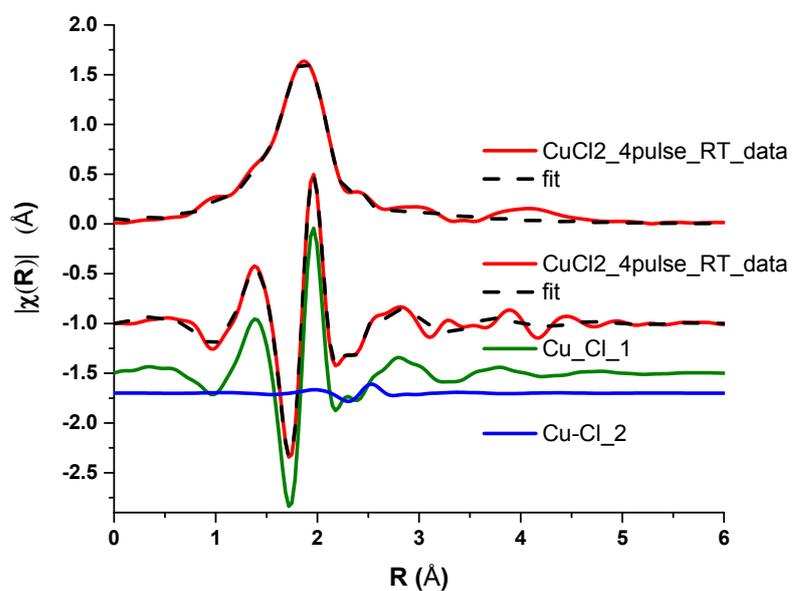


Figure S5. Magnitude component of the k^2 weighted Fourier Transform of the data and fit for the RT spectrum of the Cl₂ pre-treated sample, and the imaginary component of the paths used in the fit.

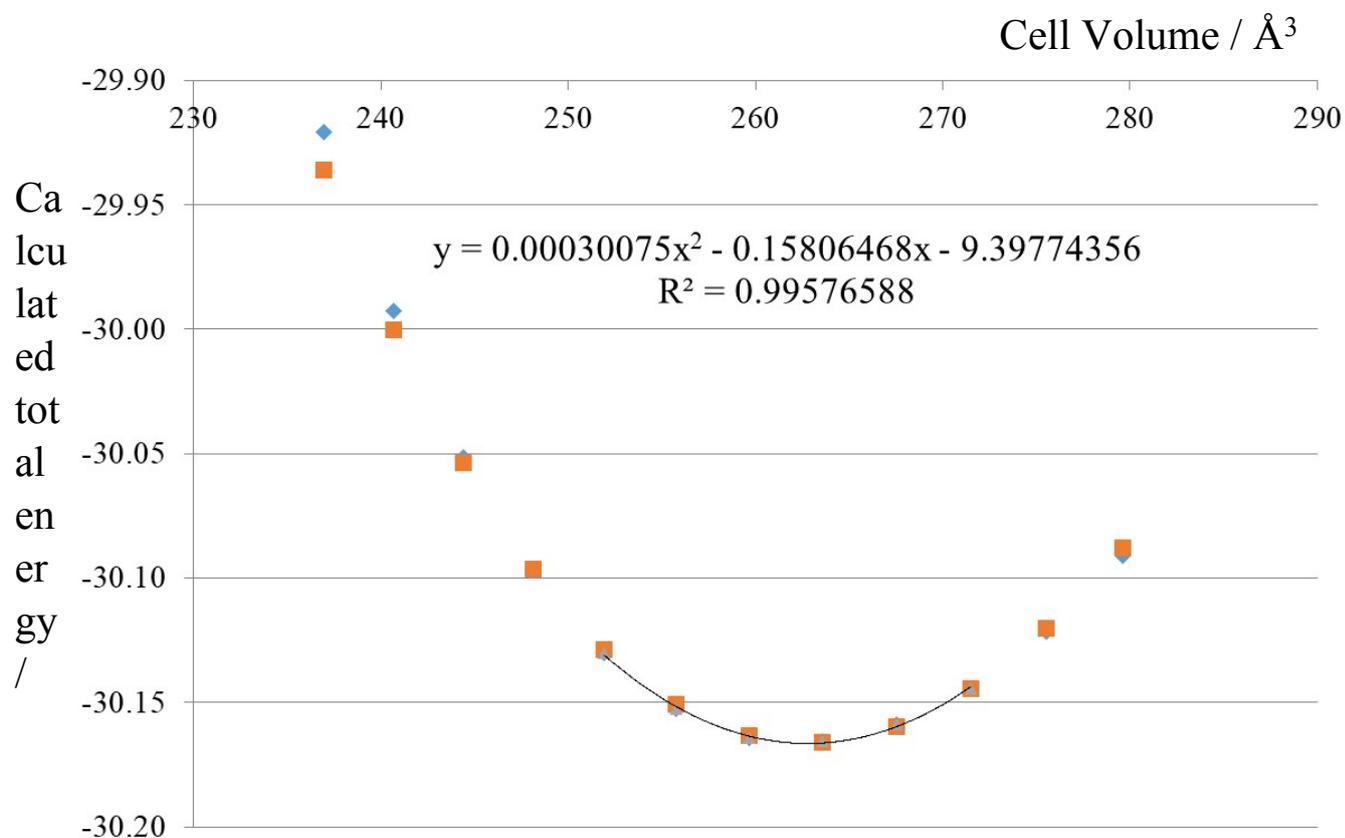


Figure S6. Variation of calculated total energy as a function of cell volume, calculated points are shown as blue diamonds, fit according to the Murnaghan equation as orange squares, the line shows a quadratic fit to the points closest to the minimum that was used for the initial parameter set of the least squares refinement of the Murnaghan parameters.

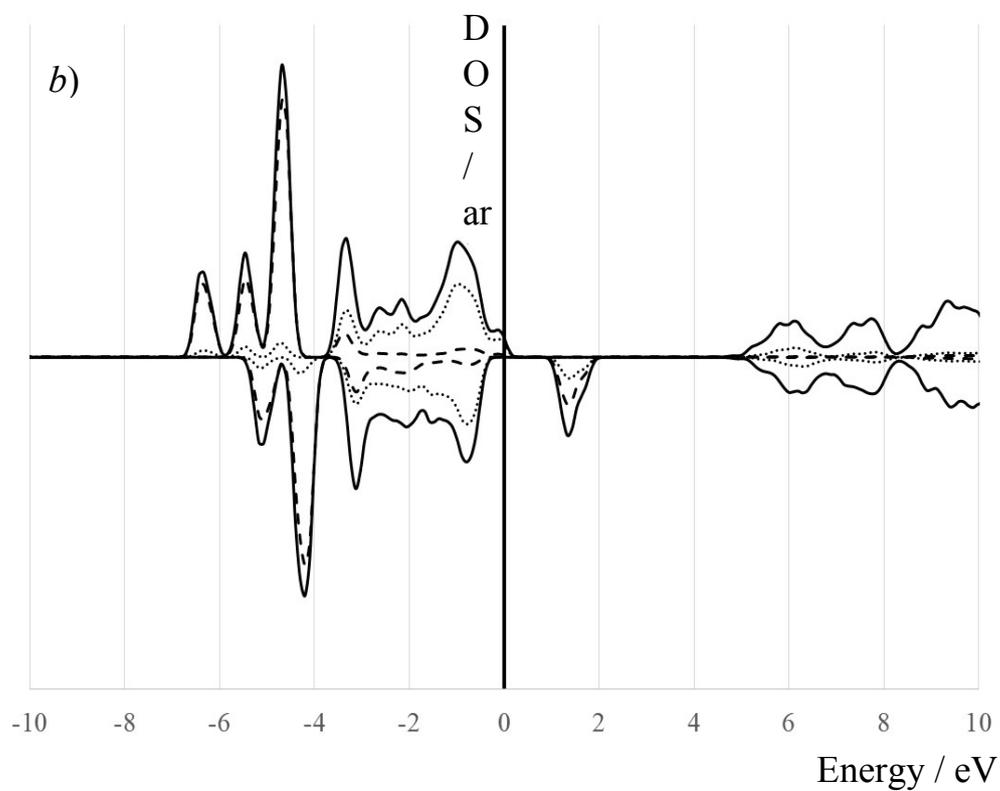
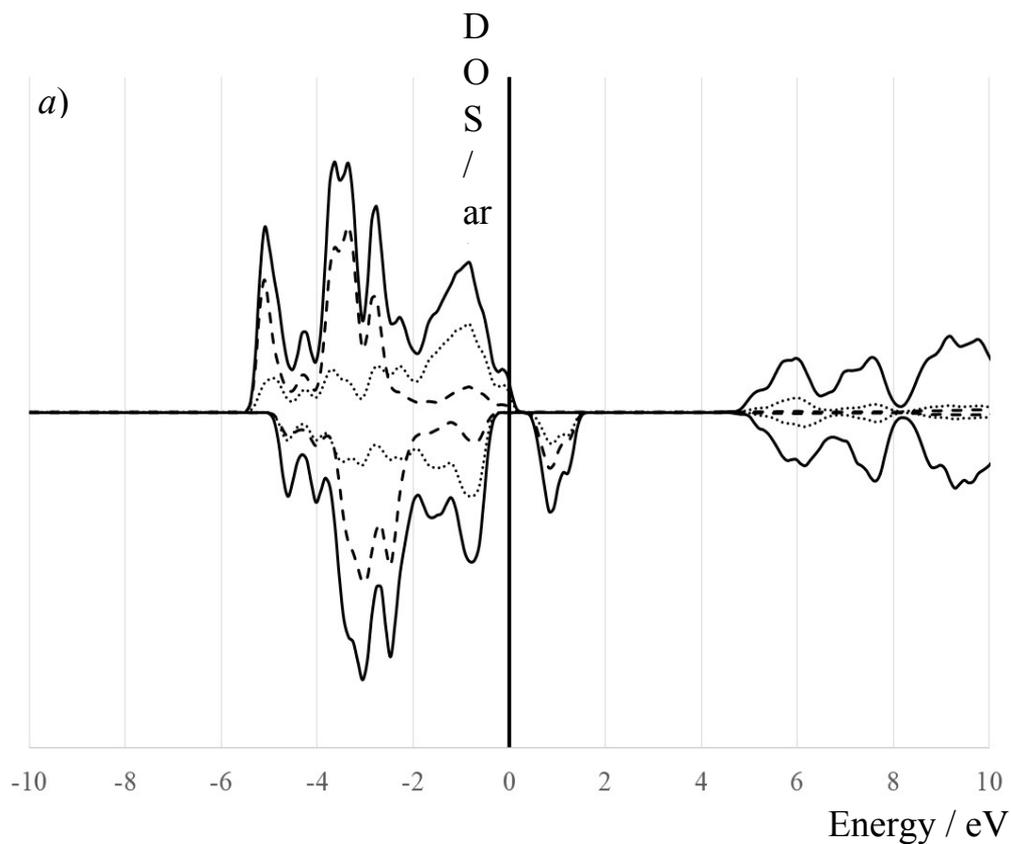


Figure S7. Density of states for CuCl_2 (solid lines) with partial density of states for Cu-d orbitals (dashed lines) and Cl orbitals (dotted lines). *a)* $U=4$, and *b)* $U=7$. Calculations carried out using bulk cell of stoichiometry Cu_2Cl_4 with $7 \times 7 \times 7$ k-points and each calculate DOS point has been Gaussian smeared using a width of 0.1 eV.

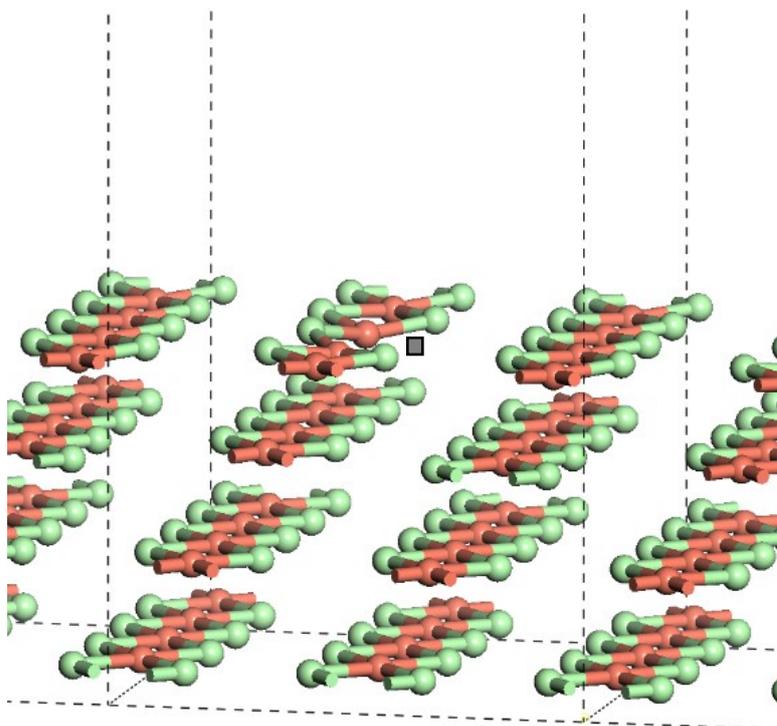


Figure S8. *a*) Slab model of $\text{CuCl}_2(010)$ surface using $\text{Cu}_{32}\text{Cl}_{64}$ slab with Cl^- vacancy in surface layer. Note that the position of the anion vacancy is indicated by a grey square. Structure optimised with PBE+U using $U=7$ and Grimme D2 dispersion included. Atoms coloured Cu: pink, Cl : green.

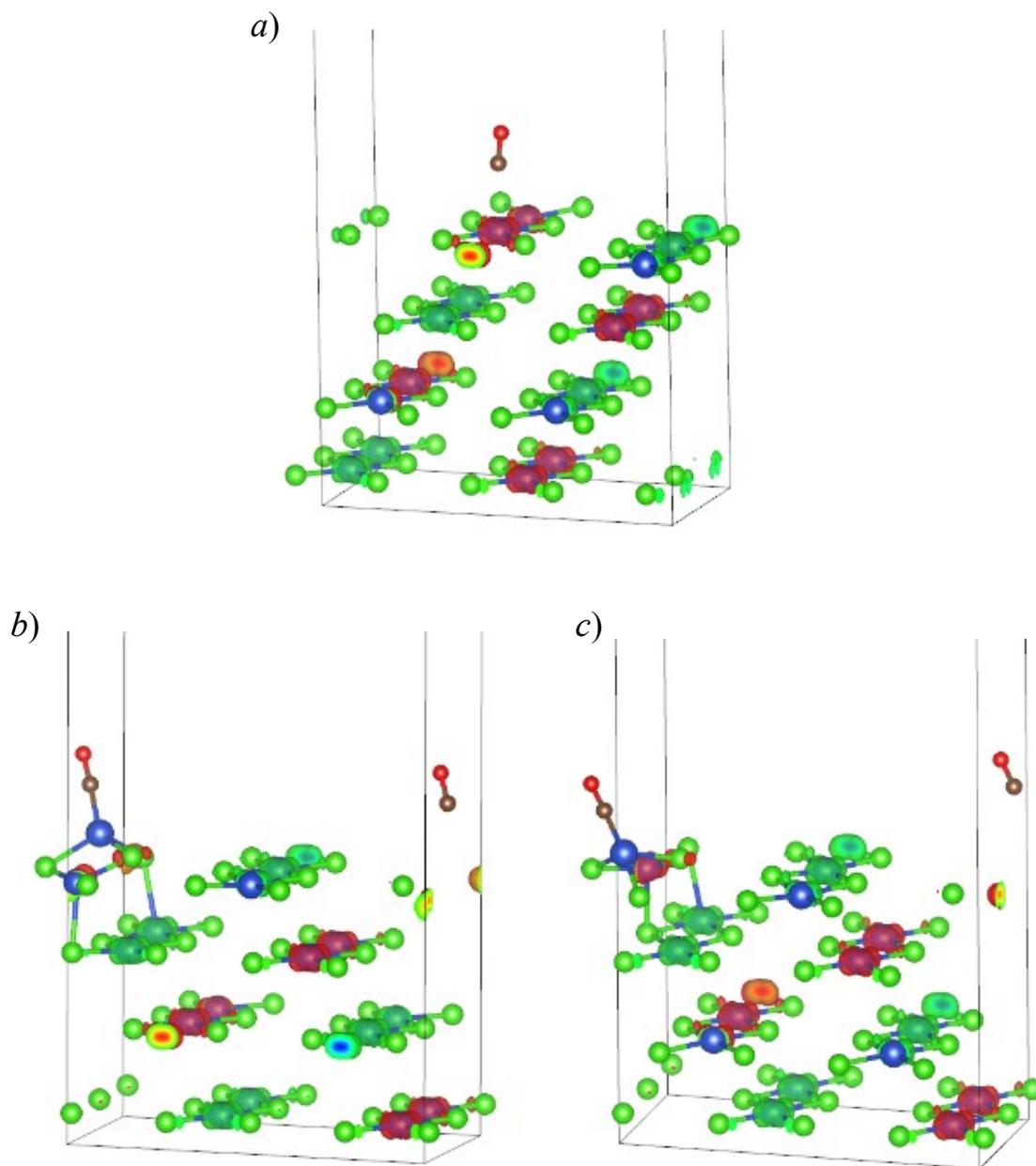


Figure S9. Spin density plot at $0.015 \text{ e } \text{\AA}^{-1}$ level for the (010) surface models of CuCl_2 with CO adsorbed calculated using PBE+U(=7) with D2. *a)* Stoichiometric surface, *b)* surface defect with CO originally placed at the 4 fold Cu site and *c)* surface defect with CO originally placed at the 3 fold Cu site. Up and down spin density are shown as red and green respectively. Atoms coloured Cu: Blue, Cl: green, C: grey, O: red.

References

1. A. F. Wells, *J. Chem. Soc.*, 1670, (1947).
2. K. Kervinen, P. C. A. Bruijninx, A. M. Beale, J. Gerbrand Mesu, G. van Koten, R. J. M. Klein Gebbink, B. M. Weckhuysen, *J. Am. Chem. Soc.* **128**, 3208, (2006).