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

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Abstract

The interaction of CO with an attapulgite-supported Cu(II)Cl\textsubscript{2} catalyst has been examined in a micro-reactor arrangement. CO exposure to the dried, as-received catalyst at elevated temperatures leads to the formation of CO\textsubscript{2} as the only identifiable product. However, phosgene production can be induced by a catalyst pre-treatment where the supported Cu(II)Cl\textsubscript{2} sample is exposed to a diluted stream of chlorine. Subsequent CO exposure at $\sim$370°C then leads to phosgene production. In order to investigate the origins of this atypical set of reaction characteristics, a series of x-ray absorption experiments were performed that were supplemented by DFT calculations. XANES measurements establish that at the elevated temperatures connected with phosgene formation, the catalyst is comprised of Cu\textsuperscript{+} and a small amount of Cu\textsuperscript{2+}. Moreover, the data show that unique to the chlorine pre-treated sample, CO exposure at elevated temperature results in a short-lived oxidation of the copper. On the basis of calculated CO adsorption energies, DFT calculations indicate that a mixed Cu\textsuperscript{+}/Cu\textsuperscript{2+} catalyst is required to support CO chemisorption.

Introduction

There is a rapidly increasing demand for polyurethanes as light weight, robust and transparent components in manufacturing. These polymers are prepared from isocyanates with methylene diphenyl diisocyanate being a representative material. Methylene diphenyl
diisocyanate is itself prepared by the phosgenation of 4,4’-methylenedianiline, for which the total global production capacity in 2010 was estimated to be 5 million tonnes. Consequently, there is a high global demand for phosgene. Typically, phosgene production is undertaken alongside isocyanate production facilities as part of an integrated chemical complex. Chlorine, as a component of phosgene, is a major feedstock in the process but no chlorine is incorporated into the isocyanate product; it all ends up as HCl which represents a significant burden to the manufacturer and the environment. Cavani has previously considered routes by which the chlorine cycle in certain chemical industry operations could be made more efficient by the means of the direct use of HCl as a co-reactant in oxychlorination reactions. More specifically, Zhang and co-workers have described how the oxychlorination of carbon monoxide may be exploited to produce phosgene. In order to effect sufficient separation of reagents/products, Zhang et al. propose a three stage process in which the first stage involves the chlorination of CO to produce phosgene over a supported copper(II) chloride catalyst whilst simultaneously reducing the catalyst to copper(I) chloride (Cu(I)Cl).

Despite the potential of an oxychlorination process cycle capable of producing phosgene whilst consuming the HCl by-product of isocyanate manufacturing, there is a paucity of data on the surface chemistry of this process. This communication will examine aspects of the surface chemistry exclusively associated with the first stage of the oxychlorination cycle outlined by Zhang et al, namely the interaction between CO and a supported Cu(II)Cl₂ catalyst. In an attempt to concentrate on durable materials, an industrial grade attapulgite supported Cu(II)Cl₂ catalyst is examined. This catalyst has previously been investigated for the manufacture of trichloroethene and tetrachloroethene (Attapulgite is the mineralogical name for palygorskite a porous material formed from interspersed sheets of silica and sheets of octahedrally co-ordinated cations drawn from Mg²⁺, Al³⁺ and Fe³⁺.)

Related materials such as Cu(II)Cl₂/γ-Al₂O₃, which finds applications in the synthesis of the vinyl chloride monomer via the oxychlorination of ethene, have been studied with a range of techniques including UV/Vis, XANES and EXAFS. These studies have identified at least two distinct Cu species, at low loadings (< 2%) Cu is found to be accommodated in surface sites on the alumina support with no Cl⁻ in the first co-ordination sphere. These species show EPR signals with axial symmetry. The Cl⁻ released from the CuCl₂ appears as surface Al-Cl species. At higher loadings a second Cu species appears with Cu-Cl bonds present.
This secondary species is found to be soluble in ethanol and the material loaded in this way leads to a more complex EPR spectrum. EXAFS measurements on the high loading samples show that Cu\(^{2+}\) is reduced in the presence of the ethene reagent.\(^{13}\) It was also suggested that KCl can act to stabilise Cu(II)Cl\(_2\), making the reduction processes more challenging and switching the rate determining step for dichloroethane production from Cu(I)Cl oxidation to Cu(II)Cl\(_2\) reduction by ethene.\(^{14}\)

Respecting the theme of this Faraday Discussion meeting, this paper will concentrate on how a specific catalyst pre-treatment is able to facilitate favourable CO turnovers, in this case for the synthesis of phosgene. After a preliminary consideration of phosgene production in the presence of an as-received Cu(II)Cl\(_2\) catalyst and a Cu(II)Cl\(_2\) catalyst that has been pre-treated with dichlorine, the paper adopts a two-strand approach to address the detailed structural and oxidation state changes that occur as CO interacts with the supported Cu(II)Cl\(_2\) material. Firstly, a series of synchrotron x-ray absorption (XAS) experiments will be described that provide information on oxidation states and structure. Secondly, and on the basis of the XAS measurements, a series of DFT calculations are presented that explore possible structural motifs and energetics of the interaction between CO and Cu(II)Cl\(_2\). A follow-up paper will describe the reaction chemistry involved in this complex, but technically relevant, reaction system more comprehensively.\(^{15}\) The relevance of the catalyst pre-treatment stage to phosgene production is described in the Results and Discussion section.

Previous work using DFT to study the surface chemistry of related structures has employed the DFT+U approach to account for the strongly correlated nature of electrons at cationic Cu centres. For example, Lebernegg et al.\(^{16}\) have considered magnetic coupling between Cu\(^{2+}\) centres in copper halides, CuX\(_2\) structures (X=F, Cl, Br), which all form edge sharing linear chains of square planar complexes as described for Cu(II)Cl\(_2\) in the Experimental section below. In the calculations presented here we also use a DFT+U approach and include the effect of the U parameter on the calculated properties of interest for catalysis.

**Experimental**

**Chemicals and materials**

CuCl\(_2\) (Sigma-Aldrich, 97%), CuCl\(_2\)-H\(_2\)O (Sigma-Aldrich, 99.99%), CuO (Acros Organics, 97%) and Cu\(_4\)(OH)\(_6\)Cl\(_2\) (Supelco, <= 100%) were used as received. The catalyst supplied by Ineos Chlor Ltd. contains 10% CuCl\(_2\) and 8% KCl supported on an attapulgite clay and is
described elsewhere. Before use the material was dried under a continuous stream of N\textsubscript{2} (BOC, 99.998%) at a flowrate of 50 mL min\textsuperscript{-1} and a temperature of 110\degree C for 12 h. Chlorine pre-treated catalyst samples were prepared by exposing the dried catalyst to a Cl\textsubscript{2}/N\textsubscript{2} co-feed (6 mL min\textsuperscript{-1} Cl\textsubscript{2}, 50 mL min\textsuperscript{-1} N\textsubscript{2}) for 10 min at 370\degree C. This chlorine exposure was repeated a further three times before reverting the carrier gas back to pure N\textsubscript{2}. The sample was maintained at 370\degree C for 30 minutes, when the heating was turned off and the sample allow to cool to ambient temperature in the presence of flowing nitrogen. For the XAS measurements, the dried and chlorine pre-treated copper chloride catalyst samples were isolated in a nitrogen atmosphere for transportation to the synchrotron.

Reaction testing was performed using a micro-reactor facility located at the University of Glasgow. A detailed description of that apparatus will appear in a subsequent publication. Briefly, a combination of in-line UV-visible spectroscopy and infrared spectroscopy was used to monitor the gas phase exiting the reactor.

**Catalyst testing**

Reactions were carried out using a flow reactor charged with varying amounts of catalyst (~0.500 g). A by-pass reactor positioned alongside the principal reactor within the furnace was loaded with a comparable mass of ground quartz. All experiments were carried out with an overall flow rate of 159 SCCM (standard cubic centimetre per minute, cm\textsuperscript{3} min\textsuperscript{-1}) in order to keep the contact time the same for all experiments. All gas flows were controlled by mass flow controllers (Hastings GFC-202, 0 – 100 SCCM). In order to avoid corrosion, an N\textsubscript{2} purge system was connected to the mass flow controllers to ensure the lines were purged when not in use.

Reagent gases were mixed in a mixing vessel with Ballotini balls to ensure dispersion of the gases, followed by an in-line filter to retain catalyst particles in the reactor. The reaction temperature was monitored using a thermocouple (HANNA HI 93532) with a probe in the sleeve of the reactor loaded with the catalyst. Post-reactor, an N\textsubscript{2}-drive line feeds into the flow before a second in-line filter; this arrangement ensures that all reagents remain in the gaseous phase. A three-way valve allows the reactor exit flow to be directed either to the IR and UV-Vis spectrophotometers or directly through a chemical scrubber to the vent. The scrubber was filled with an aqueous solution of NaOH that ensured the chlorinated products were neutralised before exiting via the vent.

**XAFS**
Copper K-edge XAFS studies of the catalyst materials and a series of reference standards were carried out on the B18 beamline at the Diamond Light Source, Didcot, UK. Measurements were performed using a quick extended (QE) XAFS set-up with a fast-scanning silicon (111) double-crystal monochromator. The time resolution of the spectra reported herein was 49 seconds per spectrum ($k_{\text{max}} = 14$), and on average three scans were acquired to improve the signal-to-noise ratio of the data. All ex situ samples were diluted with cellulose to optimize the effective-edge step of the XAFS data and measured in transmission mode using ion-chamber detectors. Reference samples were CuO, CuCl$_2$, CuCl$_2$·H$_2$O, and Cu$_4$(OH)$_6$Cl$_2$. A reference spectrum of anhydrous CuCl$_2$ was prepared in situ by heating CuCl$_2$ (Sigma Aldrich 99.995%, with boron nitride) in a 3 mm O.D. quartz capillary under flowing helium. After reaching 100°C the XANES spectra resembled that reported earlier by Ferrandon et al.$^{17}$ All transmission XAFS spectra were acquired concurrently with the copper reference foil placed between $I_t$ and $I_{\text{ref}}$ XAS data processing, and EXAFS analysis were performed using IFEFFIT$^{18}$ with the Horae package$^{19}$ (Athena and Artemis).

In situ XAFS measurements were performed in transmission mode using a fixed-bed quartz microreactor (O.D. 5.6 mm, length 200 mm, Hilgenberg), with a gas flow set up similar to that described by Matla et al.$^{20}$ Due to the high loading of Cu in the catalyst the samples were mixed with boron nitride to achieve an optimal absorption in the XAFS spectra. The temperature was controlled with a Eurotherm controller with a type K thermocouple positioned in the centre of the heater block. The reactor was heated to 370 °C at a ramp rate of 10 °C min$^{-1}$ under a flow of He (50 mL min$^{-1}$, 99.99% BIP, BOC). The reactor was then held at this temperature for 30 min under a flow of CO in He (50 mL min$^{-1}$, 10% CO in He). Finally, the reactor was cooled down to room temperature under He.

**Density functional theory**

All calculations were carried out using the VASP package$^{21}$ with the PBE functional.$^{22}$ Core states for all atoms were represented using the projector augmented wave (PAW) method.$^{23}$ The PAW potentials for Cu and Cl left 11 and 7 electrons in the valence states for the respective neutral atoms, while all other atoms have their expected number of valence electrons.

The crystal structure of Cu(II)Cl$_2$ is shown in Figure S1. The material has a layered structure with Cu$^{2+}$ cations in rows of edge sharing square planar structures aligned with the $b$-axis of
the unit cell. Neighbouring Cu$^{2+}$ ions are bridged by two co-ordinated Cl$^{-}$ anions. The rows are arranged to give each Cu$^{2+}$ ion an additional two axial Cl$^{-}$ ligands in neighbouring chains. This leads to an experimental crystal structure for anhydrous Cu(II)Cl$_2$ in which each Cu$^{2+}$ cation has 4 short Cu-Cl (2.35 Å) and 2 long Cu-Cl distances (2.9 Å), so that the Cu$^{2+}$(d$^9$) centres can be thought of as having a strongly Jahn-Teller distorted environment. Beside this weak axial co-ordination between Cu$^{2+}$ and Cl$^{-}$, inter-row and inter-layer spacing is dependent on dispersion interactions and so all calculations included a parameterised representation of the dispersion interaction using the Grimme D2 approach. We use reciprocal space (k-point) sampling following the Monkhorst-Pack scheme. Convergence of the bulk energy for Cu(II)Cl$_2$ with respect to planewave cutoff and k-point sampling was tested (Figure S2) resulting in a planewave cutoff of 500 eV and k-point sampling of 5×5×5 for the bulk unit cell. For density of states (DOS) calculations the density of the k-point sampling was increased to 7×7×7. The k-point sampling was adjusted for the larger unit cells used to represent surfaces to 3×3×1 with only 1 k-point used in the direction perpendicular to the surfaces of slab models. A check of the calculated surface defect energy using 5×5×1 k-point sampling showed a variation of only 0.003 eV. A dipole correction perpendicular to the surface plane was used for all slab calculations.

In addition, as discussed in the Introduction section, the strong correlation effects for electrons located at the Cu sites require the application of the DFT+U approach. From analysis of the calculated electronic structure Lebernegg et al. suggested that Cu(II)Cl$_2$ can be described with a Hubbard model with $U_{\text{eff}} = 4.0$. However, they also point out that differences in local basis set and planewave approaches require higher $U$ values when calculations are carried out with VASP. More extensive computational literature is available for Cu$^{2+}$ and Cu$^{+}$ in oxide materials, due to the promising combination of transparency and electrical conductivity for Cu$^{+}$ containing oxides. Scanlon et al. have considered p-type defects in Cu$_2$O with the PBE functional and found that a U value of 5.2 best reproduced the valence band features expected from x-ray photoelectron spectroscopy. However, they also concluded that the DFT+U approach cannot reproduce the detailed electronic structure of polaronic defects in this material. Mishra et al. have applied DFT+U calculations to study the surface structure and adsorption of CO$_2$ to both CuO and Cu$_2$O. They employed a range of U values and identified U=7 as giving the best match to the experimental band gap and ion magnetic moments for CuO. While the electronic structure of Cu$_2$O was found to be more challenging, U=7 was found to give a good account of the geometric structure of the material.
In this work we have also looked at the effect of the U parameter on the calculated energetics through a comparison of results for values of U = 4 and U = 7, this allows us to show the sensitivity of the calculated material properties to the choice of this parameter.

The d⁹ configuration of the Cu²⁺ centres leads to magnetic interactions between Cu centres which have previously been studied in some detail.¹⁶ We have tested the magnet ordering in the bulk unit cell. This unit cell contains two Cu²⁺ ions within each row and two rows of CuCl₂ (Figure S1). We find that having parallel spins at adjacent Cu centres within a CuCl₂ row is favoured by 0.01 eV atom⁻¹ but the coupling between rows is much weaker with practically no difference between Cu atoms on adjacent rows having a ferromagnetic or antiferromagnetic alignment. The spin arrangement used in our calculations is illustrated in figure S3.

For surface calculations we use a four layer slab model with the lowest layer of CuCl₂ chains frozen at bulk positions to represent the constraint of the surface matching to a more extended crystal bulk.

The surface energy is calculated with the fixed lower layer taken into account using:²⁹

\[
E_{\text{surf}}^{\text{opt}} = \frac{E_{\text{slab}} - nE_{\text{bulk}}}{S} - E_{\text{surf}}^{\text{term}}
\]

(1)

where \(E_{\text{slab}}\) is the energy of the slab calculated with a fixed region at the bottom of the slab and a geometry optimised region for the upper surface. The slab has a surface area, \(S\), and contains \(n\) stoichiometric units of the bulk cell composition for which the calculated energy is \(E_{\text{bulk}}\). \(E_{\text{surf}}^{\text{term}}\) is the calculated surface energy for the slab without geometry optimisation, in this case the two sides of the slab are equivalent and so \(E_{\text{surf}}^{\text{term}}\) can be obtained using:

\[
E_{\text{surf}}^{\text{term}} = \frac{E_{\text{slab}}^{\text{fixed}} - nE_{\text{bulk}}}{2S}
\]

(2)

where \(E_{\text{slab}}^{\text{fixed}}\) is the calculated energy for the slab without relaxation of the ionic positions.

The adsorption energy, \(E_{\text{ads}}\), of CO to the Cu sites of various slab models of the surface were calculated using:

\[
E_{\text{ads}} = E_{\text{CO+slab}} - E_{\text{slab}} - E_{\text{CO}}
\]

(3)
where $E_{CO+slab}$ is energy for the geometry optimised structure with the CO molecule at its adsorption site, $E_{slab}$ is the geometry optimised energy of the slab alone and CO is the energy of an optimised structure of CO in the gas phase using the same periodic boundary conditions as for the slab model. In all slab calculations the lowest lying CuCl$_2$ chains were frozen at their bulk co-ordinates as described for surface energy calculations.

**Results and Discussion**

![FT-IR spectra](image)

Figure 1. In-line FT-IR spectra of outlet gas mixture of CO reacting with the catalyst at 370 °C showing the effect of pre-treating the catalyst with Cl$_2$(g). (a) as-received catalyst; (b) chlorine pre-treated catalyst.

The FT-IR spectra of the products resulting from CO reacting with the as-received catalyst (Figure 1a) indicated that, as well as the signal of unreacted C≡O observed at 2140 cm$^{-1}$, there is a large peak at 2343 cm$^{-1}$ due to the asymmetric C=O stretching mode of CO$_2$. The bending mode of O=C=O at 660 cm$^{-1}$ can also be seen in the spectra. Importantly, no phosgene formation was observed for the as-received catalyst reacting with CO. A variety of sample conditioning steps were explored but no combination of heating pre-treatments was able to induce phosgene production on CO exposure from this industrial grade Cu(II)Cl$_2$ oxychlorination catalyst. In contrast, a chemical pre-treatment using short exposures of diluted chlorine (see Experimental section), was able to induce phosgene synthesis. Figure
Figure 2 Ex situ XANES spectra - Left: Cu$^{2+}$ reference compounds, Right: Cu$^0$ and Cu$^+$ reference compounds, spectra are vertically offset for clarity.

To investigate the differences between the as received and Cl$_2$ pre-treated material in more detail we turned to XANES measurements. The Cu$^+$ or Cu$^{2+}$ oxidation states show a number of characteristic features in the XANES region of the Cu K-edge XAFS spectra and a series of reference materials were examined to support the analysis, Figure 2 (left frame). All the
Cu$^{2+}$ reference compounds show a weak pre-edge feature at 8977 eV, due to the 1s→3d transition. This is forbidden for Cu$^+$ species. Apart from the pre-edge feature, Kau et al. observed no other significant peaks below 8985 eV for any Cu$^{2+}$ species. However, for Cu$^+$ species, a sharp feature below the dashed line in Figure 2 would be expected, around 8983 eV due to the 1s→4p transition, this is evident in the spectra for the Cu$_2$O materials shown in Figure 2 (right frame).

![XANES Spectra](image)

**Figure 3 XANES Spectra** - Fresh catalyst as received, chlorine pre-treated and the anhydrous CuCl$_2$ (prepared in situ)

The XANES spectra, shown in Figure 3, of the as-received and Cl$_2$ pre-treated catalysts are both consistent with Cu$^{2+}$ species, exhibiting the characteristic features at 8986 eV and 8977 eV and without the strong feature at 8983 eV associated with Cu$^+$. The chlorine pre-treated sample resembles that of anhydrous CuCl$_2$, which may imply that the Cl$_2$ pre-treatment has, to some extent, driven off adsorbed water or hydroxyl groups from the Cu(II)Cl$_2$ catalyst.
Figure 4. *In situ* XANES spectra - Temperature ramp of chlorine pre-treated catalyst showing loss of anhydrous-like Cu$^{2+}$ to Cu$^{+}$ species.

On heating the chlorine pre-treated sample from RT to 200 °C the sample initially resembles anhydrous CuCl$_2$, but by 300°C, the 1s→3d feature at 8977 eV and the feature at 8986 eV consistent with Cu$^{2+}$ species loses intensity (figure 4). By 360°C the edge has shifted to lower energy and a pronounced pre-edge feature at 8983 eV is observed consistent with the presence of a Cu$^{+}$ species. The small feature at 8978 eV is still present, (more easily observed in the 1st derivative spectrum, Figure S4). We therefore conclude that by the end of the temperature ramp at 367 °C, which corresponds to the temperature at which phosgene production is obtained (Figure 1b), the sample consists of a mixture of Cu$^{+}$ and a small amount of Cu$^{2+}$. This reduction to Cu$^{+}$ is also observed for the fresh catalyst.

Figure 5 shows that, after the heating ramp and exposure of the Cl$_2$ pre-treated sample to CO (1 min), the characteristic Cu$^{+}$ feature at 8983 eV significantly diminishes in intensity, the adsorption edge shifts to higher energy, and the first feature after the edge (at 8992 eV) increases. In addition, the small pre-edge feature of Cu$^{2+}$ at 8977 eV increases, more easily observed in the insert to Figure 5a. This pre-edge feature, unique to Cu$^{2+}$ species, becomes visible on introduction of CO and then disappears almost completely after 10 min exposure. Although CO is well known as a reducing agent, these changes point unambiguously, to an oxidation of Cu$^{+}$ to Cu$^{2+}$ during the first minute of CO exposure. Interestingly, this re-oxidation is not observed for the fresh catalyst (Figure 5b).
Figure 5. In situ XANES spectra - (a) From the end of the temperature ramp (367°C, under helium) then on exposure to CO. The insert shows the pre-edge region around 8977 eV in more detail. (b) The time dependence of the pre-edge feature at 8983 eV, characteristic of Cu$^+$ species during the ramp and on exposure to CO, (blue dots: fresh catalyst, black squares: Cl$_2$ pre-treated catalyst). Negative time points represent the temperature ramp; time t = 0 indicates the time that the catalyst was exposed to CO (temperature = 367°C).

From 10 min to 30 min of CO exposure, the spectra resemble Cu$^+$ species, with an increasing intensity of the feature at 8983 eV.

The observations on Cu oxidation state from this series of experiments is summarised in Scheme 1: for the Cl$_2$ pre-treated catalyst, at the end of the ramp we have a mixture of Cu$^+$ and Cu$^{2+}$ then, on introduction of CO, re-oxidation occurs giving Cu$^{2+}$, which is quickly reduced to Cu$^+$ after 10 min exposure. The oxidation of Cu$^+$ to Cu$^{2+}$ on introduction of CO to the gas feed is difficult to justify. We speculate that excess chlorine adsorbed within the pore network of the Cl$_2$ pre-treated material is released when CO is first introduced, and it is this Cl$_2$ that oxidises Cu. Interestingly, this re-oxidation step is not observed for the fresh catalyst, which only produces CO$_2$, whereas the pre-treated catalyst produces both CO$_2$ and COCl$_2$ (Figure 1). Further work is required to better understand the origins of the oxidation process revealed in Figure 5(b).
Scheme 1. A representation of the copper oxidation states accessible to the chlorine pretreated catalyst on (i) thermal ramping to 350° in a flowing stream of He, (ii) initial exposure to a flowing mixture of He + CO at 367°C and (iii) extended exposure to a flowing mixture of He + CO at 367°C.

EXAFS

Analysis of the extended X-ray absorption fine structure (EXAFS) region was performed on the spectrum after 1 min CO exposure Figure 6, Table 1. This corresponds to the conditions under which a maximum in the rate of phosgene production is observed. The magnitude component of the \( k^2 \) weighted Fourier Transform of the data of the spectra recorded at 1 min CO exposure, Figure 6, hint that a low Z-number scatterer is present. This is similar to the work of Lamberti et al.\(^ {32} \) who propose a mixture of copper aluminate and active CuCl\(_2\) in their CuCl\(_2\)/Al\(_2\)O\(_3\) catalyst. Our data fits well to Cu-O and Cu-Cl contributions at 1.84 ± 0.02 and 2.21 ± 0.01 Å, respectively, Figure 6 and Table 1. From the XANES spectrum after 1 min CO (Figure 5a), we expect the Cu to exist in a distorted octahedral environment, however, the refined coordination numbers from the EXAFS analysis are lower than expected. There are two possibilities to explain this. Firstly, if a mixture of Cu species is present, the coordination number obtained from the fit would only be proportional to the contributions of each species.\(^ {32} \) Secondly, destructive interference of the scattering paths from the axial and equatorial neighbours 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.\(^ {33} \) As EXAFS is an averaging technique, we cannot rule out that, in our case, we may also have a mixture of Cu\(^{2+}\) species present at this point in the reaction coordinate.
Table 1. 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.

<table>
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<th>Samples</th>
<th>Abs - Sc</th>
<th>N</th>
<th>$R$ / Å</th>
<th>$2\sigma^2$ / Å$^2$</th>
<th>$E_0$ / eV</th>
<th>$R_{\text{factor}}$</th>
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<td>2.21±0.01</td>
<td>0.007</td>
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</tr>
<tr>
<td>1 min CO</td>
<td>Cu-O</td>
<td>0.50±0.08</td>
<td>1.84±0.02</td>
<td>0.003</td>
<td>-2±1</td>
<td>0.005</td>
</tr>
<tr>
<td>(CuCl$_2$.2H$_2$O)</td>
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<td></td>
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</table>

Figure 6. EXAFS spectra - Magnitude component of the $k^2$ weighted Fourier Transform of the data and fit for the 1 min CO exposure spectrum, and the imaginary component of the paths used in the fit.

To complement these XAS measurements we have carried out electronic structure calculations on the copper chloride lattice in order to better understand the energetics and structural implications of Cl removal from the Cu(II)Cl$_2$ lattice during heat treatment or reduction by reaction with CO. The next section covers this work and demonstrates the structural motifs that are induced on the chlorine pre-treated support that can, intermittently, support phosgene production.
DFT Results

DFT calculations began with the optimisation of the bulk unit cell lattice parameters by relaxing the atom positions for a series of cell expansion/contraction values. The resulting plot of calculated energy vs cell volume was fitted using the Murnaghan equation of state\textsuperscript{34} (Figure S6). The resulting bulk structure geometry gives in plane the expected CuCl\textsubscript{2} row structures with in plane Cu-Cl distances of 2.285 Å and inter-layer axial Cu..Cl = 3.001 Å at the PBE+U(=7) with D2 level of theory.

The calculated density of states with each of the two U values is shown in Figure S7. In both cases the band gap is defined by the top of the valence band consisting of majority spin Cu\textsuperscript{2+} d-states and empty d-states of the minority spin. In the case of U=4 the calculated band gap is small (0.3 eV) while for U=7 a clear gap exists of around 0.9 eV. The choice of U parameter is made so that we can demonstrate the influence of U on the calculated energies comparing the lowest value for which a band gap is present to the most commonly used value for oxidised Cu in the literature.

Table 2. Calculated defect formation energies for removal of a Cl atom following equation (4). The Cu\textsubscript{X}Cl\textsubscript{Y} given in the structure definition column refers to the stoichiometric slab used for the defect calculation. Cu\textsubscript{16}Cl\textsubscript{32} is shown in figure 7a and Cu\textsubscript{32}Cl\textsubscript{64} is created by doubling the cell in the direction of the CuCl\textsubscript{2} chains.

<table>
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<th>Structure / simulation slab</th>
<th>$E_{def}$ (U=4) / eV</th>
<th>$E_{def}$ (U=7) / eV</th>
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<tr>
<td>surface defect / Cu\textsubscript{16}Cl\textsubscript{32}</td>
<td>1.23</td>
<td>1.32</td>
</tr>
<tr>
<td>2\textsuperscript{nd} layer defect / Cu\textsubscript{16}Cl\textsubscript{32}</td>
<td>1.32</td>
<td>1.41</td>
</tr>
<tr>
<td>surface defect / Cu\textsubscript{32}Cl\textsubscript{64}</td>
<td>1.19</td>
<td>1.25</td>
</tr>
<tr>
<td>2\textsuperscript{nd} layer defect / Cu\textsubscript{32}Cl\textsubscript{64}</td>
<td>1.28</td>
<td>1.38</td>
</tr>
</tbody>
</table>

In our XANES data we have seen changes in oxidation state for Cu when the Cl\textsubscript{2} pre-treated samples are subjected to a heating ramp or when CO is introduced into the system. Reduction of Cu will take place as Cl is removed from the lattice and so we have calculated the defect energies, $E_{def}$, for the creation of an anion vacancy in the surface. The DFT calculations also give information on the structural changes that are caused by the removal of Cl. The defect energy is calculated as the energy change for the simple reaction:

$$\text{Cu}_m\text{Cl}_{2m} = \text{Cu}_m\text{Cl}_{2m-1} + \frac{1}{2} \text{Cl}_2$$ (4)
where \( m \) is the number of Cu cations present in the simulation slab. Table 2 gives the calculated energies for this process with the Hubbard U parameter set at 4 and at 7 and figure 7 shows the structures of the stoichiometric surface and defect structures calculated with \( U=7 \) using the \( \text{Cu}_{16}\text{Cl}_{32} \) four layer slab model. The stoichiometric surface consists of the same CuCl\(_2\) chains that were noted in the bulk (figure S1). For the surface there are some small distortions of the positions of the surface Cu centres which move out of the Cl plane within the CuCl\(_2\) chains toward the centre of the slab. This reduces the axial Cu\(^{2+}\)..Cl\(^-\) distance from the optimised bulk value of 3.001 Å to 2.845 Å, consistent with the loss of the second axial Cl\(^-\) ligand that these surface Cu cations experience on creation of the surface. A smaller contraction for the second layer Cu…Cl (third layer) distance is also observed, with an axial separation in this case of 2.963 Å, while the Cu atom distance to Cl\(^-\) in the fourth (fixed) layer are 3.075 Å, very similar to the bulk value. The surface Cu..Cl axial distance is also closer to the value measured by EXAFS (2.86 Å, Table S1, Figure S5) than that for the DFT+U optimised bulk. This could suggest that the CuCl\(_2\) supported on attapulgite clay is present with a high ratio of (010) surface to bulk. For the surface layer there is also some loss of symmetry within the chains with two Cu-Cl bonds slightly longer than found in the bulk (2.296 Å \( \text{cf.} \) 2.285 Å) and two bonds shorter than the bulk (2.270 Å). The creation of the (010) surface only involves the removal of axial Cu..Cl interactions in the strongly Jahn-Teller distorted geometry of the bulk. The calculated surface energy based on equation (1) is correspondingly low with practically the same value obtained for \( U=4 \) or \( U=7 \) (0.121 J m\(^{-2}\) (\( U=4 \)) and 0.129 J m\(^{-2}\) (\( U=7 \))).

From the stoichiometric surface, a defect was created by removal of a single Cl\(^-\) ion, to leave a vacancy, V, in the surface. The electron associated with this defect would be expected to reduce a single Cu\(^{2+}\)(d\(^9\)) cation to Cu\(^+\)(d\(^{10}\)) and so the initial spin state arrangement used for defect calculations was adjusted to have one Cu site neighbouring the defect assigned zero spin. As the CuCl\(_4\) units are edge sharing, this results in two surface Cu ions being bridged by a single Cl\(^-\) anion. The relaxed structure (Figure 6b) shows that the remaining Cl\(^-\) ion in the Cu-Cl-Cu-V- square has moved out of the plane of the CuCl\(_2\) chain with one Cu cation moving closer to a second layer Cl\(^-\) (Cu..Cl(2\(^{\text{nd}}\) layer) = 2.372 Å) giving it a pseudo-tetrahedral (4-fold) geometry and one Cu cation moving further from the second layer and adopting a pseudo-trigonal planer (3-fold) geometry (Cu..Cl(2\(^{\text{nd}}\) layer) = 3.017 Å). Analysis of the final spin state shows that the 4-fold Cu has practically 0 spin while the 3-fold Cu has associated spin density. This suggests that the 4-fold Cu is formally a Cu\(^+\)(d\(^{10}\)) cation while
the 3-fold remains a Cu$^{2+}$($d^{9}$) cation. Within the defective chain, Cu-Cl distances are also affected, with shorter Cu-Cl to the single bridging Cl$^{-}$ ion than seen in the stoichiometric surface (Cu(4-fold)-Cl=2.214 Å and Cu(3-fold)-Cl=2.151 Å).

The calculated energy to form the surface defect in the Cu$_{16}$Cl$_{32}$ slab is 1.32 eV (U=7, Table 2) increasing to 1.41 eV if a defect is created in the second layer of the same slab model (Figure 6c). There is very little structural re-arrangement following relaxation of the second layer defect structure compared to that discussed above for the surface defect. Hence, the higher energy to create a sub-surface defect may result from the more constrained environment of the sub-surface Cl$^{-}$ sites.

Doubling the cell in the CuCl$_{2}$ chain direction to give a Cu$_{32}$Cl$_{64}$ slab gives a calculated surface defect energy 5 % lower than calculated for the smaller cell while the second layer defect has a calculated energy around 2 % lower. In the chain direction the Cu$_{16}$Cl$_{32}$ cell has only two Cu sites while in the doubled cell there are four so that it should be expected, given the observed surface geometry changes, that there are defect-defect interactions present in the smaller slab. Indeed, for the surface defect model, using the larger cell, the movement of the Cl$^{-}$ anion in the -Cu-Cl-Cu-V- square is significantly smaller than seen for the Cu$_{16}$Cl$_{32}$ slab so that there is practically no difference in the geometries of the two Cu cations that this anion bridges (Figure S8). This comparison of the Cu$_{16}$Cl$_{32}$ and Cu$_{32}$Cl$_{64}$ slab models also suggests that at low anion defect concentrations the disruption of the lattice will be relatively minor while at high concentrations, where the Cu$^{+}$ content contributes significantly to the XANES, we should also expect significant geometric changes around the Cu sites, particularly near to the surface of the Cu(II)Cl$_{2}$ crystallites.

Table 2 also gives data for defect creation using the U=4 Hubbard parameter which consistently gives lower calculated defect energies by between 0.06 and 0.10 eV depending on the position of the defect and the cell size employed. Even so the differences observed between different defect locations or slab sizes follow the same trend for either choice of U, suggesting that the properties of interest here are relatively insensitive to this parameter.
Table 3. Calculated CO adsorption energies, $E_{ads}$, following equation (3). The Cu$_Y$Cl$_X$ given in the structure definition column refers to the slab composition. Cu$_{16}$Cl$_{32}$ is shown in figure 7a and Cu$_{32}$Cl$_{64}$ is created by doubling the cell in the direction of the CuCl$_2$ chains. Each defect containing slab has a single Cl atom removed from the position indicated.

<table>
<thead>
<tr>
<th>Structure / simulation slab</th>
<th>$E_{ads}$ (U=4) / kJ mol$^{-1}$</th>
<th>$E_{ads}$ (U=7) / kJ mol$^{-1}$</th>
<th>Cu..CO$^a$ / Å</th>
<th>CuC-O$^a$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric (010) / Cu$<em>{16}$Cl$</em>{32}$</td>
<td>-7</td>
<td>-13</td>
<td>2.561</td>
<td>1.141</td>
</tr>
<tr>
<td>surf. def., Cu(4-fold)$^b$ site / Cu$<em>{16}$Cl$</em>{31}$</td>
<td>-55</td>
<td>-55</td>
<td>1.838</td>
<td>1.147</td>
</tr>
<tr>
<td>Cu$<em>{16}$Cl$</em>{31}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surf. def. Cu(3-fold)$^b$ site/ Cu$<em>{16}$Cl$</em>{31}$</td>
<td>-55</td>
<td>-55</td>
<td>1.840</td>
<td>1.147</td>
</tr>
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<td>2$^{nd}$ layer defect/ Cu$<em>{16}$Cl$</em>{31}$</td>
<td>-13</td>
<td>-16</td>
<td>2.432</td>
<td>1.141</td>
</tr>
<tr>
<td>Stoichiometric (010) / Cu$<em>{32}$Cl$</em>{64}$</td>
<td>-11</td>
<td>-12</td>
<td>2.614</td>
<td>1.141</td>
</tr>
<tr>
<td>surf. def./ Cu$<em>{32}$Cl$</em>{63}$</td>
<td>-39</td>
<td>-32</td>
<td>1.851</td>
<td>1.146</td>
</tr>
<tr>
<td>2$^{nd}$ layer defect/ Cu$<em>{32}$Cl$</em>{63}$</td>
<td>-13</td>
<td>-15</td>
<td>2.417</td>
<td>1.140</td>
</tr>
</tbody>
</table>

Note: $^a$) Geometry taken from the U=7 optimised structures. $^b$) Initial co-ordination of adsorption site in reference slab calculation.

Table 3 gives the calculated energies and some geometric data for the adsorption of CO to the CuCl$_2$(010) surface structures using the slab models for stoichiometric and defective surfaces and figure 8 shows the corresponding optimised geometries for the Cu$_{16}$Cl$_{32}$ slab based models. CO adsorbs weakly to the stoichiometric surface with a calculated adsorption energy of only -13 kJ mol$^{-1}$ (U=7) and a relatively long Cu..CO interaction distance (2.561 Å), although this is still shorter than the Cu..Cl distance for the inter-layer interactions in the bulk material. The C=O bond length is also close to that for the free gas phase CO reference state (1.143 Å). On introduction of a surface defect the calculated CO adsorption energy becomes considerably more favourable (-55 kJ mol$^{-1}$). As discussed above the surface defect in the Cu$_{16}$Cl$_{31}$ slab model is neighboured by one 4-fold and one 3-fold co-ordinated Cu centre and so we expected different behaviour for adsorption to each site. To test this two calculations were carried out and the results are compared in Table 3. The adsorption energies are actually the same irrespective of the choice of Cu site. Absorption of CO raises the Cu site out of the surface plane producing a 4-co-ordinate Cu centre in a pseudo-tetrahedral geometry in each case (figure 8b and 8c). The Cu-CO distance is considerably shorter and the CuC-O bond length longer than seen for the stoichiometric surface, consistent with the stronger interaction with the surface. Calculation of the spin density for either structure shows practically no spin density on the Cu centre to which CO co-ordinates suggesting that the electronic state is re-organised during optimisation to place the Cu$^{+}$(d$^{10}$) centre in the position bonding to CO (figure S9) so that the surface responds to the adsorbate and re-arranges to the same structure.
irrespective of the initial geometry of the defect site. Although we see significant surface re-
arrangement of the surface with the surface defect present the CO adsorption has a lower 
energy than seen for other surfaces. For example, calculations using a similar approach for 
CO on Fe(111) give adsorption energies of 119 kJ mol$^{-1}$ and a C=O bond length of 1.164 Å 
for CO at a Fe top site using a similar level of theory.$^{35}$

The strong adsorption of CO to a defect is only apparent for the Cl$^-$ vacancy at the surface. 
The calculated adsorption energy for CO in the presence of a 2$^{nd}$ layer defect, -16 kJ mol$^{-1}$ 
(U=7), is close to that for the stoichiometric surface and table 3, figure 8a and 8d also show 
that the calculated geometries of the adsorbed molecule are very similar.

Similar trends are seen for the larger slab model (Cu$_{32}$Cl$_{64}$) with CO adsorption to the Cu ions 
close to a surface defect notably more favourable than the stoichiometric surface or 
adsorption with a 2$^{nd}$ layer defect present. Even so, the calculated energy for CO at the 
surface defect is lower than that found with the smaller simulation slab, suggesting that a high 
density of defects will favour CO uptake by the catalyst.

It can also be noted from Table 3 that the choice of the U parameter has little influence on the 
ordering of the calculated adsorption energies for the surface sites. The absolute values of the 
adsorption energy are affected with the weaker interactions being more favourable by up to 5 
kJ mol$^{-1}$ when U=7 is used compared to U=4.
Figure 7. a) Slab model of stoichiometric CuCl₂(010) surface. b) Structure with Cl⁻ vacancy in surface layer of slab and c) structure with Cl⁻ vacancy in second layer of slab. Note that the position of the anion vacancy is indicated by a grey square in b) and c). All structures optimised with PBE+U using U=7 and Grimme D2 dispersion included. Atoms coloured Cu: pink, Cl: green.
Figure 8. Calculated CO adsorption geometries on a) Slab model of stoichiometric CuCl$_2$(010) surface. b) Structure with Cl$^-$ vacancy in surface layer of slab CO at Cu(3-fold) site, c) Cl$^-$ vacancy in the surface layer with CO at Cu(4-fold) site and d) structure with Cl$^-$ vacancy in second layer of slab. Note that the position of the anion vacancy is indicated by a grey square in b) - d) origin for cells in b) and c) has been shifted to place CO at the centre of the cell. All structures optimised with PBE+U using U=7 and Grimme D2 dispersion included. Atoms coloured Cu: pink, Cl: green, C: grey, O: red.
Conclusions

This study has examined the interaction of CO with an industrial grade Cu(II)Cl₂ oxychlorination catalyst. CO exposure to the dried, as-received catalyst at elevated temperatures leads to the formation of CO₂ as the only identifiable product, establishing a role for a CO oxidation pathway. Phosgene production could be induced by a catalyst pre-treatment where the supported Cu(II)Cl₂ is exposed to a diluted stream of chlorine. Subsequent CO exposure at ~ 370°C then leads to phosgene production. From x-ray absorption data supported by DFT calculations the following conclusions can be drawn.

- XANES shows a pre-chlorination step modifies the as-received Cu(II)Cl₂ catalyst so that it more closely resembles anhydrous Cu(II)Cl₂.
- On heating the as-received and chlorine pre-treated catalysts in an inert atmosphere up to 367°C, a temperature where phosgene formation is observed, XANES shows the samples to be comprised of a mixture of Cu⁺ and a small amount of Cu²⁺.
- XANES shows elevated temperature CO exposure to the untreated catalyst leads to no noticeable change in copper oxidation state. However, for the pre-treated catalyst an oxidation of Cu⁺ → Cu²⁺ is observed in the first minute of CO exposure. On continued exposure of CO, the XANES spectrum shows reduction and a return to the Cu⁺ species. It is tentatively proposed that the short-lived oxidation process occurs as a consequence of CO induced release of Cl₂ from the catalyst pore network.
- In conjunction with EXAFS measurements, DFT calculations have modelled the surface structure of copper chloride particles, respecting the Jahn-Teller distorted geometry of the bulk, and including a role for Cl⁻ defect sites that will be created as the Cu oxidation state changes and phosgene is produced.
- Calculated CO adsorption energies show that CO binds more strongly in the presence of a surface defect with CO adsorbing at the associated Cu⁺ site. This suggests that a mixed Cu⁺/Cu²⁺ catalyst is required to support CO chemisorption and subsequent chlorination in order to produce phosgene molecules.

Acknowledgements

The UK Catalysis Hub is kindly thanked for resources and support provided via our membership of the UK Catalysis Hub Consortium and funded by EPSRC (grants EP/I038748/1, EP/I019693/1, EP/K014706/1, EP/K014668/1, EP/K014854/1, EP/K014714/1 and EP/M013219/1). Via our membership of the UK’s HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202), this work made use of the facilities of ARCHER. Computing resource was also provided by Advanced Research Computing at
Cardiff (ARCCA) and the HPC-Wales supercomputer facilities. We acknowledge Diamond Light Source for beamtime through award SP10306, and thank the beamline scientists Dr Diego Gianolio and Dr Giannantonio Cibin. Ineos Chlor is thanked for the provision of the Cu(II)Cl$_2$ catalyst.

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