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Phosgene formation via carbon monoxide and dichlorine reaction over an activated carbon catalyst: Towards a reaction model

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Abstract

The reaction of carbon monoxide and dichlorine over an activated carbon (Donau Supersorbon K40) to produce phosgene is examined. Individual reagent and product breakthrough measurements over the clean catalyst establish the magnitude of adsorption coefficients (K) to follow the trend: $K_{\text{Cl}_2} > K_{\text{COCl}_2} \gg K_{\text{CO}}$. Chlorine adsorption measurements indicate a distribution of active sites that conforms to a two-site model, with the sites classified according to their enthalpy of adsorption. At 323 K, Type-I and Type-II sites exhibit respective adsorption capacities of 2.8 ± 0.3 and 1.5 ± 0.4 mmol $\text{Cl}_2 \text{ g}^{-1}_{\text{cat}}$. Post-reaction temperature-programmed desorption measurements alongside elemental analysis (SEM-EDAX) confirm the presence of retained chlorine moieties at the catalyst surface. These observations are rationalised within a postulated reaction scheme that accounts for sustained phosgene synthesis over the selected activated carbon.

Keywords

Phosgene synthesis; activated carbon; breakthrough measurements; temperature-programmed desorption; reaction scheme.

1. Introduction

Phosgene is an important intermediate used in the industrial manufacture of polyurethanes, polycarbonates, pharmaceuticals and agrochemicals [1]. It is typically manufactured industrially via the gas phase reaction between carbon monoxide and chlorine over an activated carbon catalyst [2].

The reaction is strongly exothermic ($\Delta H = -107.6 \text{ kJ mol}^{-1}$) [3].

Despite wide industrial application, there are surprisingly few reports of phosgene synthesis catalysis in the literature. Two recent publications from this group have examined the topic of phosgene synthesis catalysis over a commercial grade activated carbon (Donau Supersorbon K40). The first article described an apparatus and associated experimental protocols for investigating phosgene synthesis catalysts and included characterisation details of the selected carbon [4]. The second article concentrated on kinetic aspects of phosgene formation over Donau Supersorbon K40 and reported on matters such as activation energy, reaction profile as a function of time-on-stream (T-o-S) and mass balance relationships. The latter measurements showed a small degree of carbon retention and a greater degree of chlorine retention by the catalyst that compromised the atom economy of the phosgene synthesis process. Moreover, a rate law was determined, as represented by Equation 2 [5]:

$$r = \frac{d[\text{COCl}_2]}{dt} = k[\text{CO}]^1[\text{Cl}_2]^{0.5}[\text{COCl}_2]^0 \quad (2),$$

where k represents a rate coefficient. Thus, under the conditions studied, the rate of phosgene production was first order in carbon monoxide, half order in dichlorine and zero order in phosgene. Equation 2 is consistent with the phosgene synthesis rate law reported by Weller in 1956 [6], which represented a revised analysis of experimental outcomes reported earlier by Potter and Baron [7].

The current article uses this refined kinetic perspective [5] as a springboard to investigate further mechanistic issues for this commercially relevant reaction. Mechanistic insight may be gleaned from primarily kinetic studies that have been performed over the last ~70 years, which are summarized below.

In 1951 pioneering work from Potter and Baron investigated the reaction kinetics between 298 and 353 K over activated carbon (Columbia SXW) and used a Langmuir–Hinshelwood expression to describe the phosgene formation kinetics. The magnitude of the adsorption coefficients was reported as being $K_{\text{Cl}_2}, K_{\text{COCl}_2} > K_{\text{CO}}$ and it was deduced that Cl_2 and COCl_2 were physically adsorbed, whilst CO was thought to be chemisorbed [7]. In 1956 Weller re-analyzed Potter and Barons' data using a model based on power dependencies of the rate with respect to reagent concentrations and proposed a

relatively simple rate law that was first order in CO and half order with respect to dichlorine [6]. Over the period 1976-1978 Shapatina and co-workers produced several papers examining the kinetics of the catalytic synthesis of phosgene over activated carbon [8-10]. In 1976 inspection of phosgene synthesis over an activated carbon (Bayer AKT-4) operating in the temperature range 343-403 K led to the proposal of a two-stage reaction on an inhomogeneous surface: the first stage involved molecular adsorption of CO, whilst the second stage involved the surface reaction between CO and associatively adsorbed dichlorine [8]. A 1977 article examined phosgene synthesis over a sample of AR-3 activated carbon [9]. Subsequently, a 1978 article refined the associated kinetic model for the situation of low chlorine coverage over Bayer AKT-4; a condition that connects with industrial operation of the phosgene synthesis process [10]. Adding further breadth and diversification as to how Equation 1 could be operating on a mechanistic level, Satterfield in his comprehensive treatise on industrial heterogeneous catalysis speculated whether phosgene synthesis over charcoal operates via a process involving physical adsorption rather than chemisorption, that brings molecules close together into a quasi-liquid layer on the surface. No justification for this assertion is presented [11]. In 2012 Mitchell and co-workers examined a range of seven activated carbons (Chemviron Solcarb 208C DM4, Chemviron Solcarb 208C DR-P 4, Donau Supersorbon K40, DuPont IPC, Norit RB4C, Norit RX3 extra and Picatal G201 4) for their suitability as phosgene synthesis catalysts [3]. Within that body of work, they used a modified version of Potter and Baron's Langmuir-Hinshelwood expression that involved associative adsorption for CO and dichlorine but with an inhibiting role for dichlorine. No mechanistic details are reported [3]. In 2016 Gupta *et al.* examined phosgene synthesis over C₆₀ fullerene as a model catalyst, which was compared to a sample of high surface area graphite (Timcal) [12]. Following a combination of experiments backed up by DFT calculations, the authors proposed that a surface bound dichlorine species was the key intermediate during phosgene synthesis that reacted rapidly with physisorbed CO in a two-step Eley-Rideal type mechanism [12]. A subsequent publication from this group investigating N-modified carbon nanotube materials reported reaction orders with respect to CO and dichlorine of unity and, moreover, proposed that a concerted reaction between an acyl chloride cation ($\delta^+\text{COCl}$) and a weakly bound $\text{Cl}^{\delta-}$ species was the final step leading to COCl_2 production [13].

The above summary of phosgene synthesis catalysis indicates that there is little consensus for the form of the reaction mechanism associated with the phosgene formation process over carbon catalysts. Indeed, the most recent work of Gupta and colleagues proposes an Eley-Rideal type reaction to be active [12,13], whilst Langmuir-Hinshelwood expressions are favoured in the earlier studies [3,7,8]. Further contrasts exist. For example, several studies propose that the CO is chemisorbed

[3,7,8], whilst Gupta and co-workers assert CO to be present as a physisorbed entity [12,13]. Interestingly, there is a consensus that chlorine is associatively adsorbed [7,8,12,13], *i.e.* present as dichlorine at the catalyst surface. We acknowledge that some of these disparities as to how CO and dichlorine combine over activated carbon may reflect differences on the form of the carbon under investigation. Nonetheless, there is a driver to exploit the recently acquired kinetic awareness of a catalyst used in certain large-scale phosgene synthesis unit operations (Donau Supersorbon K40) [3-5] in order to understand better how this material can sustain phosgene synthesis as indicated by Equation 1. The driver extends to providing comment on the suitability of either Langmuir-Hinshelwood or Eley-Rideal kinetic expressions applied to this reaction system.

The paper, which exclusively examines a single industrial grade activated carbon (Donau Supersorbon K40) is laid out as follows. Firstly, reagent and product breakthrough measurements are presented for the fresh catalyst that provide information on adsorption strengths of the various molecular species. Significant differences are observed, with the dichlorine measurements indicating two distinct surface chlorine populations. Post-reaction temperature-programmed desorption profiles then provide insight on mass retention by the catalyst that is consistent with elemental analysis measurements. Finally, a reaction scheme is proposed to account for the observations.

2. Experimental

2.1 *Phosgene synthesis apparatus*

All reactions were performed in the vapour phase at ambient pressure on a catalyst test facility housed within the University of Glasgow's Chemical Process Fundamentals Laboratory that is described elsewhere [4]. Briefly, the apparatus used a combination of on-line FTIR spectroscopy and UV/vis spectrophotometry to speciate and quantify reactants and products for a variety of reaction conditions. The reactor (catalyst) and by-pass (quartz) were located within a programmable oven (Shimadzu GC14A) that had a maximum operating temperature of 673 K. Additionally, this work made use of in-line mass spectrometry (MS) that utilized a turbo-molecular pumped (Pfeiffer) quadrupole mass spectrometer (MKS Spectra Microvision Plus RGA) to sample the reactor eluting gas stream via a non-return valve, a fine control valve and a differentially pumped capillary inlet. A switchable valve enabled the mass spectrometer to be isolated when not in use. For the majority of reaction test experiments nitrogen (BOC, 99.998%) was used as a carrier gas and diluent [4]. However, for the temperature-programmed desorption measurements (sections 2.5 and 3.2), the nitrogen was replaced by helium (BOC A Grade, 99.996%) in order to avoid detection problems with CO.

2.2 Catalyst testing

Donau Supersorbon K40 activated carbon was used exclusively in this work. Characterisation details of this material are presented elsewhere [4], that include x-ray diffraction, Raman spectroscopy, nitrogen physisorption and scanning electron microscopy/energy dispersive analysis of X-rays. The reactor was typically charged with approximately 0.125 g of catalyst of size fraction 250-500 μm (Endcotts sieves). For activation, the sample was dried overnight at 383 K in flowing nitrogen (BOC, 99.998 %) at a flow rate of 20 $\text{cm}^3 \text{min}^{-1}$. Adopting a procedure encountered in certain industrial phosgene synthesis facilities [3,8], the feed-stream of CO and Cl_2 utilised a slight excess of CO. Standard flow conditions were as follows: CO (BOC, CP grade) 5 $\text{cm}^3 \text{min}^{-1}$, Cl_2 (Sigma $\geq 99.5\%$) 4 $\text{cm}^3 \text{min}^{-1}$, N_2 (carrier gas) 50 $\text{cm}^3 \text{min}^{-1}$, and N_2 (diluent post-reactor) 100 $\text{cm}^3 \text{min}^{-1}$; thus, reactor incident total flow rate = 59 $\text{cm}^3 \text{min}^{-1}$, reactor exit total flow rate 159 $\text{cm}^3 \text{min}^{-1}$. The facility was equipped with a phosgene supply (BOC, 10% v/v COCl_2/He). The by-pass reactor was located within the oven and contained ground quartz (250-500 μm) of comparable volume to the reactor containing catalyst. The reactor-by-pass facility was used to establish stabilized gas flows, as measured by FTIR/UV-vis/MS, prior to switching the gas flow over to the catalyst. For comparable reaction conditions explored in this communication, mass transport experiments established the phosgene synthesis reaction over the catalyst to be operating in the absence of both inter-phase and intra-phase mass transfer and that the reaction was operating under chemical (or kinetic) control [4].

2.3 Breakthrough measurements (non-competitive adsorption)

Reagent/product breakthrough measurements were undertaken in order to determine the extent of non-competitive single molecule adsorption (CO , Cl_2 , COCl_2) over a sample of fresh, activated catalyst. Initial gas flow was established using the by-pass reactor (containing quartz), then the gas flow was rapidly switched to pass over the catalyst held at a fixed temperature (323 K). The degree of gas adsorption was then determined by monitoring the IR (CO , COCl_2) or UV-Vis (Cl_2) spectra as a function of time as the adsorbent flow rate returned to baseline levels. As the switching process momentarily interrupted the flow into the spectrometer gas cells, blank runs were also recorded where the gas flow was simply switched over quartz. These measurements established a 'dead time' during this switching period of ~ 3 min. Subtraction of the quartz profile from that of the catalyst profile enabled the quantity of retained adsorbate to be determined. As the breakthrough measurements were performed only on fresh catalyst, it is acknowledged that adsorption over an aged catalyst may convey different characteristics.

2.4 Post-reaction temperature-programmed desorption

The catalyst was exposed to a standard set of reaction conditions for a 2 h period at 298 K: catalyst charge = 0.125 g, CO flow rate = $5 \text{ cm}^3 \text{ min}^{-1}$, Cl_2 flow rate = $4 \text{ cm}^3 \text{ min}^{-1}$, helium carrier gas (pre-reactor) = $50 \text{ cm}^3 \text{ min}^{-1}$, helium diluent flow (post-reactor) = $100 \text{ cm}^3 \text{ min}^{-1}$. As noted above (section 2.1), for these measurements only, helium was substituted for nitrogen. At 120 min the CO and Cl_2 gas flows were stopped and the reactor continuously purged with helium for 120 min. Maintaining the helium purge, the catalyst was heated via a linear ramp rate of 5 K min^{-1} up to 673 K whilst the exit stream was sampled by the mass spectrometer that analysed for CO, Cl_2 and COCl_2 . Thus, these experiments provided information on material retained on the catalyst surface after sustained phosgene production.

2.5. *Post-reaction catalyst characterization*

The catalyst was exposed to a standard set of reaction conditions for a 4 h period at 323 K: catalyst charge = 0.125 g, CO flow rate = $5 \text{ cm}^3 \text{ min}^{-1}$, Cl_2 flow rate = $4 \text{ cm}^3 \text{ min}^{-1}$, nitrogen carrier gas (pre-reactor) = $50 \text{ cm}^3 \text{ min}^{-1}$, nitrogen diluent flow (post-reactor) = $100 \text{ cm}^3 \text{ min}^{-1}$. Reaction was terminated by shutting off the flow of reagents (CO and Cl_2) leaving only nitrogen flowing. The reactor was then purged in a continuous stream of nitrogen for 16 h at 323 K. The resulting catalyst sample was extracted from the reactor and transferred to a glass sample vial. The sample was subsequently analysed by scanning electron microscopy (SEM) (Philips XL30 ESEM, operating at an acceleration voltage of 25 kV) that is additionally equipped with an energy dispersive analysis of X-rays (EDX) facility (Philips FEI XL30 ESEM).

3. Results

3.1 *Breakthrough measurements*

3.1.1 *Carbon monoxide*

The profile for the breakthrough measurements as CO was passed over a fresh, activated catalyst charge that is maintained at 323 K, is presented in Figure 1. The flow conditions were as follows: CO $5 \text{ cm}^3 \text{ min}^{-1}$, N_2 (carrier gas) $54 \text{ cm}^3 \text{ min}^{-1}$ and N_2 (diluent post-reactor) $100 \text{ cm}^3 \text{ min}^{-1}$; total flow into the gas cells = $159 \text{ cm}^3 \text{ min}^{-1}$. The CO flow rate was monitored by FTIR spectroscopy [4]. Figure 1(a) (black squares) represents a 'blank' run, where a stabilised flow of CO is switched across to the bypass reactor that contains ground quartz. The switching process momentarily interrupts the reagent flow to the spectrometer that registers a decrease in signal. As this 'dip' in reagent intensity is unconnected with adsorption events, it needs to be accounted for in the subsequent runs where the reagent is passed over the fresh catalyst. Figure 1(a) shows the CO flow rate for the blank run requires approximately 2-3 min to return to baseline levels. Figure 1(b) (red circles) shows the profile observed

when the CO flow is passed over the catalyst, with the profile almost exactly matching that of the blank run, indicating minimal CO adsorption. A minor drop in intensity for the catalyst/CO run relative to the quartz/CO run is evident for $t > 3$ min that cumulatively corresponds to 8×10^{-3} mmol CO g⁻¹_{cat.}. This low level of CO retention is almost within experimental error and indicates minimal CO adsorption for non-competitive adsorption over the process catalyst at this temperature. This outcome contrasts with previous comparable studies that report CO to be chemisorbed over activated carbon [3,7,8].

Figure 1. Time response of switching the flow of CO over the catalyst at 323 K (CO 5 cm³ min⁻¹, N₂ (carrier gas) 54 cm³ min⁻¹, N₂ (diluent post-reactor) 100 cm³ min⁻¹): CO flow switched over (a) ground quartz and (b) a fresh catalyst charge. The error bar at $t = 1$ min represents the standard deviation of 3 repeat measurements.

3.1.2 Dichlorine

The profile for the breakthrough measurements as Cl₂ was passed over a fresh, activated catalyst charge that is maintained at 323 K is presented in Figure 2. The flow conditions were as follows: Cl₂ 4 cm³ min⁻¹, N₂ (carrier gas) 55 cm³ min⁻¹ and N₂ (diluent post-reactor) 100 cm³ min⁻¹; total flow into the gas cells = 159 cm³ min⁻¹. The Cl₂ flow rate was monitored by UV-visible spectrophotometry [4]. Figure 2(a) (black squares) represent a 'blank' run, where a stabilised flow of Cl₂ is switched to the by-pass reactor that contains ground quartz. Figure 2(b) (red circles) shows the profile observed when the dichlorine flow is passed over the catalyst. In marked contrast to that observed for CO (Section 3.1.1), a substantial degree of dichlorine retention is evident that significantly exceeds the decrease in reagent flow rate seen for the blank run (Figure 2(a)). Indeed, for a period of approximately 12 min, no dichlorine is detectable in the exit stream. Over the period 12-20 min the quantity of reagent

detected slowly increases, whilst the period 20-40 min defines the eventual return towards baseline levels. Figure 2(b) shows complete saturation of the catalyst to be complete by ~40 min. In this way, Figure 2(b) defines the dichlorine adsorption profile over the activated carbon at 323 K. Subtraction of the integrated intensity of the blank run (Figure 2(a)) from the integrated intensity of the catalyst/ Cl_2 measurement (Figure 2(b)) leads to a total dichlorine adsorption capacity of $4.3 \pm 0.4 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$. The major contributor to the error in this measurement is the determination of the time when the adsorbent returns to baseline levels. This parameter, on the basis of repeat runs is estimated to be $\pm 10\%$ of the total adsorption value, makes a more substantial contribution to the final uptake value than the imprecision of the individual point measurements, as indicated by the error bars in Figure 2, which represent variance in the single point measurements and not the overall methodological error.

Figure 2. Time response of switching the flow of Cl_2 over the catalyst at 323 K (Cl_2 $4 \text{ cm}^3 \text{ min}^{-1}$, N_2 (carrier gas) $55 \text{ cm}^3 \text{ min}^{-1}$, N_2 (diluent post-reactor) $100 \text{ cm}^3 \text{ min}^{-1}$): Cl_2 flow switched over (a) ground quartz and (b) a fresh catalyst charge. The error bars represent the standard deviation of 3 repeat measurements.

Given the clear distinction between the adsorption characteristics of carbon monoxide and chlorine, it was decided to explore further the matter of chlorine adsorption. So, after this initial dichlorine exposure and on continuous purging with nitrogen, the reactor was heated to 673 K and held at this temperature for 2 h. The reactor was then cooled to 323 K and the dichlorine dosing process repeated. The results are presented in Figure 3(c). (For comparison purposes, Figure 3(a) and (b) respectively present the blank and dosed runs shown in Figure 2.) Figure 3(c) (upside down triangles, dark cyan)

possesses the same shape as Figure 3(b) but with a reduced dichlorine uptake. Specifically, no dichlorine is detectable in the exit stream for exposure times up to 9 min, the dichlorine signal recovers over the period 9-11 min and returns to baseline levels in the period 11-20 min, *i.e.* dichlorine saturation is complete by ~ 20 min. On subtraction of the blank dosing experiment (Figure 3(a)), this second chlorine breakthrough run corresponds to a dichlorine take-up of $2.8 \pm 0.3 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$. The desorption/adsorption process was repeated for a second time, with the outcome presented in Figure 3(d) (triangles, blue). The profile is very similar to that for the second dichlorine dosing (Figure 3(c)). Table 1 presents the dichlorine adsorption capacities connected with the three sequential chlorine exposure runs presented in Figure 3.

Figure 3. Time response of switching the flow of Cl_2 over the catalyst at 323 K (Cl_2 $4 \text{ cm}^3 \text{ min}^{-1}$, N_2 (carrier gas) $55 \text{ cm}^3 \text{ min}^{-1}$, N_2 (diluent post-reactor) $100 \text{ cm}^3 \text{ min}^{-1}$): Cl_2 flow switched over (a) ground quartz; (b) a fresh catalyst charge; (c) after the initial dichlorine exposure, (b), the catalyst was held at 673 K for 2 h, cooled to 323 K and then re-dosed with dichlorine; (d) a subsequent further chlorine desorption/adsorption run. The nitrogen flow over the catalyst was maintained for the full sequence of 3 successive runs. The error bars represent the standard deviation of 3 repeat measurements.

Figure 3 indicates the presence of a distribution of adsorbed chlorine that exhibits a range of adsorption enthalpies. The observed profiles suggest that the distribution can be divided into two populations of surface chlorine that are classed as Type-I and Type-II. The following explanation is proposed. The initial chlorine adsorption over a fresh catalyst charge is significant: $4.3 \pm 0.4 \text{ mmol Cl}_2$

$\text{g}^{-1}_{\text{cat}}$ (Table 1). Heating the dosed catalyst to 673 K leads to desorption of a fraction of the total chemisorbed chlorine. This is the population occupying Type-I adsorption sites of the activated carbon; chlorine adsorbed in Type-II sites that possess a higher enthalpy of adsorption remains at the catalyst surface. Re-exposing the catalyst to further dichlorine (Run 2) leads to a reduced up-take ($2.8 \pm 0.3 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$) that represents re-population of the Type-I sites. As a repeat thermal desorption/adsorption cycle (Run 3) leads to an almost exact level of chlorine adsorption ($2.7 \pm 0.3 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$), the experimental procedure is reproducible, with the division between Type-I and Type-II sites linked to the desorption temperature selected. Supportive evidence for the validity of the two-site model for chemisorbed chlorine is considered in the Discussion section.

Run	Sample	Dichlorine adsorption capacity ($\text{mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$)
1	Sample 1: Fresh catalyst	4.3 ± 0.4
2	Sample 2: Dichlorine saturation, ΔT , 2 nd dichlorine exposure	2.8 ± 0.3
3	Sample 3: Dichlorine saturation, ΔT , 3 rd dichlorine exposure	2.7 ± 0.3

Table 1. Dichlorine adsorption values for repeat dosing at 323 K. Sample 1: dichlorine exposure to fresh catalyst; Sample 2: on completion of Run 1, catalyst heated to 673 K for 2 h then cooled to 323 K for a second exposure to dichlorine; Sample 3: on completion of Run 2, catalyst heated to 673 K for 2 h then cooled to 323 K for a third exposure to dichlorine. The errors represent the range for three replicate measurements.

A full desorption profile is required in order to define better the distribution of active sites but the maximum oven temperature of the apparatus was 673 K (Section 2.1), which was insufficient to desorb fully chlorine from the catalyst surface. Nonetheless, accepting the somewhat arbitrary nature of classifying Type-I and Type-II site populations, Table 1 indicates the partitioning between these sites. A dichlorine capacity of $4.3 \pm 0.4 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$ represents the total chlorine capacity of the catalyst, *i.e.* Type-I + Type-II sites. On adopting the mean chlorine adsorption value for runs 2 and 3 ($2.8 \pm 0.3 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$) as representing chlorine in Type-I sites, this means that the density of Type-II sites corresponds to $1.5 \pm 0.4 \text{ mmol Cl}_2 \text{ g}^{-1}_{\text{cat}}$. Bähr et al. have recently reported on the matter of Cl_2 adsorption and desorption over ordered mesoporous carbon materials as an indicator for catalytic phosgene formation, with the work including measurements over a commercial grade activated

carbon as a reference material [14]. The extent of Cl_2 adsorption exhibited a temperature dependence. For Cl_2 adsorption at 683 K, EDAX analysis showed residual chlorine content to be in the range 4-8 wt % [14].

3.1.3 Phosgene

The time response for the breakthrough measurement when phosgene is passed over a fresh charge of catalyst at 323 K is presented in Figure 4. Here the profile more resembles that of dichlorine (Figure 2) than CO (Figure 1). After the initial switching pulse, Figure 4(b) shows no phosgene breakthrough is observed for 16 min, signifying total phosgene up-take. Over the period 16-18 min phosgene intensity recovers, not returning to baseline levels until ~ 30 min. Subtraction of the blank run from the profile shown in Figure 4(b) leads to a total capacity of $3.3 \pm 0.3 \text{ mmol COCl}_2 \text{ g}^{-1}_{\text{cat}}$.

Figure 4. Time response of switching the flow of COCl_2 over the catalyst at 323 K (10% COCl_2 /He, $30 \text{ cm}^3 \text{ min}^{-1}$, N_2 (carrier gas) $29 \text{ cm}^3 \text{ min}^{-1}$, N_2 (diluent post-reactor) $100 \text{ cm}^3 \text{ min}^{-1}$): COCl_2 flow switched over (a) ground quartz; (b) a fresh catalyst charge. The error bars represent the standard deviation of 3 repeat measurements.

3.1.4 Breakthrough measurements - Summary

The three sets of breakthrough measurements reveal the relative magnitude of adsorption coefficients (K) for the reagents and product over this material:

$$K_{\text{Cl}_2} > K_{\text{COCl}_2} \gg K_{\text{CO}} \quad (3).$$

The outcome broadly agrees with that reported by Potter and Baron, although the earlier work reported comparable absorption coefficients for dichlorine and phosgene [7]. The fact that this work shows dichlorine to exhibit a relatively higher adsorption coefficient than phosgene is thought to reflect the greater precision of the current measurements.

The dichlorine and phosgene adsorption capacities of, respectively, 4.3 ± 0.3 and 3.3 ± 0.3 mmol g⁻¹_{cat} appear contradictory to the reported rate law (Equation 2), where the rate of phosgene formation is zero order with respect to phosgene concentration [5]. Specifically, Equation 3 suggests phosgene should make a contribution to the kinetics connected with Equation 1. However, the rate law was determined under conditions of competitive adsorption, whereas the breakthrough measurements report on single molecule adsorption under conditions of non-competitive adsorption. It is therefore concluded that the origins of the non-dependency on phosgene concentration in the rate law (Equation 2) is a result of modification of the carbon surface by the more strongly bound chlorine; this process cannot occur during simple phosgene breakthrough measurements over a fresh catalyst. Moreover, with reference to the industrial operation of phosgene synthesis, and as noted in reference [5], one queries whether the phosgene zero order dependence applies to higher conversions.

3.2 *Post-reaction temperature-programmed desorption*

Although the breakthrough measurements provide useful information on the single molecule adsorption characteristics over this catalyst, it was deemed informative to supplement those measurements with post-reaction temperature-programmed desorption (TPD) experiments. A mass spectrometer was used to sample molecular entities experiencing thermally induced desorption from the catalyst surface after a period of phosgene production. Thus, these experiments are intended to reveal the presence of any material retained on the catalyst surface as part of the phosgene formation process; information that can be correlated with previously reported mass balance measurements [5].

Figure 5. Mass spectrometer phosgene profile for reaction at 298 K for 120 min. Gas flow: CO $5 \text{ cm}^3 \text{ min}^{-1}$, Cl_2 $4 \text{ cm}^3 \text{ min}^{-1}$, helium carrier gas (pre-reactor) $50 \text{ cm}^3 \text{ min}^{-1}$, helium diluent flow (post-reactor) = $100 \text{ cm}^3 \text{ min}^{-1}$; total gas flow at the reactor exit = $159 \text{ cm}^3 \text{ min}^{-1}$. The black arrow signifies the switch of the gas flow from the quartz containing by-pass reactor to the reactor containing the catalyst.

Flow conditions suited to phosgene formation were established over the quartz containing by-pass reactor ($\text{CO } 5 \text{ cm}^3 \text{ min}^{-1}$, $\text{Cl}_2 4 \text{ cm}^3 \text{ min}^{-1}$, helium carrier gas (pre-reactor) $50 \text{ cm}^3 \text{ min}^{-1}$, helium diluent flow (post-reactor) = $100 \text{ cm}^3 \text{ min}^{-1}$) then the flow was switched over a fresh charge of catalyst (0.125 g) at a temperature of 298 K. Figure 5 shows the mass spectrometer profile for phosgene, with the arrow in the figure signifying the switching of the gas flow from the by-pass to the catalyst. This induces a sudden steep rise in signal that corresponds to rapid and sustained phosgene production. At 120 min the CO and Cl_2 gas flows were stopped, and the reactor continuously purged with helium for 60 min. Maintaining the helium purge, the catalyst was heated via a linear temperature ramp whilst the exit stream was continuously sampled by the mass spectrometer, which analysed for CO, Cl_2 and COCl_2 . The resulting TPD plots are presented in Figure 6.

Figure 6. Post reaction temperature-programmed desorption profiles for (a) CO, (b) COCl_2 and (c) Cl_2 . The catalyst was first exposed to reaction conditions for a 2 h period at 298 K (CO flow rate = $5 \text{ cm}^3 \text{ min}^{-1}$, Cl_2 flow rate = $4 \text{ cm}^3 \text{ min}^{-1}$, helium carrier gas = $50 \text{ cm}^3 \text{ min}^{-1}$, helium diluent flow = $100 \text{ cm}^3 \text{ min}^{-1}$). At 120 min the CO and Cl_2 gas flows were stopped, and the reactor continuously purged with helium for 120 min. Maintaining the helium purge, the catalyst was heated via a linear ramp rate of 5 K min^{-1} up to 673 K whilst the exit stream was sampled by the mass spectrometer.

The contrast in Figure 6 is dramatic. Post-reaction (Figure 5), no CO or phosgene were detected to desorb from the catalyst surface up to 670 K (Figures 6(a and b)). However, a single dichlorine peak is observed in Figure 6(c) with a peak maximum $\sim 420 \text{ K}$. No dichlorine is detected from 490 K. Thus, of

the suite of reagents and products, the only entity retained at the catalyst surface under modest desorption conditions (<670 K) is chlorine, which desorbs as Cl₂. Linking this observation to the trends observed for the dichlorine breakthrough measurements (Figure 3), the peak in Figure 6(c) is attributed to a residual population of Type-I chlorine atoms, as the more strongly adsorbed chlorine species is retained at the catalyst surface for temperatures > 673 K (section 3.1.2). The desorption process is thought to represent re-combinative desorption of chlorine atoms that have formed via dissociative adsorption of Cl₂. Moreover, a T_{max} of 420 K is 127 K above ambient temperature; this is interpreted as illustrating chemisorbed species. With reference to Section 2.1, thermal ramping beyond 673 K was not possible with the oven configuration employed. This restriction meant that the presence of any strongly bound surface entities (*e.g.* chlorine adsorbed in high energy sites) would not be detectable in this sequence of TPD measurements. In their study of Cl₂ adsorption on ordered mesoporous carbon materials, Bähr et al report on a Cl₂ desorption feature at 683 K after Cl₂ adsorption at 623 K [14].

3.3 Post -reaction catalyst characterization

In terms of chemical hazard management, it is a non-trivial matter to remove a catalyst that has been employed in the production of phosgene and to characterise the material using conventional laboratory based analytical techniques. Section 2.5 describes an *in situ* post-reaction purge arrangement that is intended to remove phosgene from the carbon catalyst. Following this procedure, a post-reaction sample was analysed by SEM/EDAX. Figure S1 presents a representative micrograph that shows the carbon surface to be relatively smooth, with no pitting due to corrosive events evident. Figure S2 presents the EDAX spectrum of the area highlighted in Figure S1. In a previous communication, EDAX analysis of the fresh catalyst showed carbon and oxygen to be the only elements present [4]. In contrast, Figure S2 reveals the additional presence of chlorine. Table 2 presents the elemental composition from a sequence of three replicate measurements recorded over different regions of the sample. It shows chlorine to be present at a level of 10.6 ± 3.4 wt %, with the error representing the standard deviation for the set of triplicate measurements. This corresponds to a variance of ± 32 % that reflects the variability of the chlorine content observed in the different scans that ranged from 7.1 – 13.9 wt %. This dispersion indicates an uneven distribution of halogen throughout the areas examined. One possibility for the uneven distribution of chlorine could be a partial hydrolysis of chlorine containing moieties on exposure of the post-reaction sample to air, resulting in HCl formation and subsequent evaporation/vaporisation that depletes the quantities measured in the EDAX measurement. Small quantities (<1 wt %) of Si, Al and S are additionally

observed in Figure S2; the origins of these signals, not observed for the unreacted catalyst [4], are unknown.

Element	Weight %
Carbon	83.6 ± 3.4
Oxygen	4.3 ± 0.4
Aluminium	0.7 ± 0.1
Silicon	0.5 ± 0.2
Sulfur	0.3 ± 0.1
Chlorine	10.6 ± 3.4

Table 2. SEM/EDAX derived elemental composition of a post-reaction catalyst sample. Values presented are the mean and standard deviation from three replicate measurements.

Recently reported mass balance profiles for this reaction system have shown an overall mass imbalance at steady-state of $0.37 \text{ mmol min}^{-1} \text{ g}_{(\text{cat})}^{-1}$ within a total molar flow rate of $3.14 \text{ mmol min}^{-1} \text{ g}_{(\text{cat})}^{-1}$ [5]. This corresponds to a mass imbalance of $\sim 12\%$ of the total molar flow rate, with $\sim 32\%$ and $\sim 68\%$ of the imbalance attributed to carbon and dichlorine mass imbalances respectively [5]. The EDAX-derived post-reaction mean chlorine retention value of $10.6 \text{ wt \%}$ corresponds to $1.49 \pm 0.5 \text{ mmol Cl}_2 \text{ g}_{(\text{cat})}^{-1}$, which can be compared to the estimated density for Type-II sites of $1.5 \pm 0.4 \text{ mmol Cl}_2 \text{ g}_{(\text{cat})}^{-1}$ as reported in Section 3.1.2. This coincidence is thought to be fortuitous and potentially misleading in terms of assumed precision. Whilst the comparison indeed indicates representative levels of Type-II sites, the uneven distribution of chlorine throughout the carbon matrix, as considered above, indicates some inhomogeneity as to how the distribution of active sites are spatially located. Nonetheless, the extent of chlorine retention in Table 2 is consistent with the mass balance profiles [5] and also within the boundaries of a previous report by Shapatina and co-workers whose post-reaction examination of an activated carbon catalyst applied to phosgene synthesis over the temperature range 343-403 K was found to contain 23 wt.% of chlorine [8].

4. Discussion

Tobias and Soffer examined the chemisorption of dichlorine over carbon and identified a number of surface reactions associated with the adsorption process [15,16]. For example, saturation of carbon bonds of olefinic character imply a dissociative adsorption process to be active [15]. González *et al.* and co-workers correlate chlorine activity over carbon with surface functionalities such as carboxyl and hydroxyl groups [17]. They consider that the reactivity of the carbon in the presence of chemisorbed

chlorine is not related to the surface area, as determined by BET analysis, but rather that it is due to the number and type of surface functional groups with which the chlorine can react. In this way, the surface reactivity of the carbon is dependent on the characteristics of the particular carbon and its sample history [17]. Moreno-Castilla and co-workers have investigated the nature of acid sites of chlorinated activated carbons and show that chlorination of the carbon increases its Lewis acidity but decreases the Brønsted acidity [18].

The breakthrough measurements (Section 3.1) for single molecule adsorption show dichlorine to exhibit the greater adsorption coefficient (Equation 3). Section 3.1.2 proposes the presence of two populations of adsorbed chlorine, designated Type-I and Type-II. The post-reaction TPD profiles of Section 3.2 show only a single dichlorine desorption feature up to the maximum attainable temperature of 673 K. The peak is assigned to chlorine retained uniquely in Type-I sites. With reference to the breakthrough measurements (Section 3.1.2), chlorine occupying Type II sites is inaccessible in the TPD measurements of Section 3.2 due to the maximum temperature limitation of the oven that houses the reactor (see Section 2.1). EDAX analysis of the catalyst post-reaction shows chlorine retention at 10.6 ± 3.4 wt % chlorine; this represents total retained chlorine, which will have contributions from Type-I and Type-II sites. As mentioned in Section 3.3, the extent of chlorine retention is in line with previous elemental analysis of post-reaction activated carbon phosgene synthesis catalysts [8]. It is then informative to consider the molecularity of the dichlorine adsorption process. Equation 2 defines the rate law for phosgene formation over this catalyst, with dichlorine exhibiting a half-order dependence. With reference to the Langmuir adsorption isotherm [19], this indicates dissociative adsorption of dichlorine.

Building on the assumption of dissociative adsorption of dichlorine, we next need to confront the issue of a two site model. The following scheme is proposed.

where K_1 is the adsorption coefficient associated with the dissociative chemisorption of dichlorine at the carbon surface to form adsorbed chlorine atoms. The chlorine then partitions between two sites, as signified by K_2 . In Equation 4 chlorine in Type-I sites is designated as $\text{Cl}'_{(\text{ad})}$, whilst chlorine occupying Type-II sites is designated as $\text{Cl}''_{(\text{ad})}$. Equation 4 assumes that the distribution of adsorbed chlorine between the two sites constitutes an equilibrium condition. Combining inferences from the breakthrough and desorption experiments (Sections 3.2 and 3.3), Type-I sites are catalytically active. On account of a relatively greater enthalpy of adsorption, chlorine atoms in Type II sites are thought to be too strongly bound to the carbon surface to be catalytically active under the stated conditions.

The partitioning of dichlorine between two adsorption sites (Equation 4) is consistent with two previously reported observations. First, temperature-ramping experiments performed in the presence of excess CO show phosgene production to continue to increase on increasing temperature beyond the point when all the incident gaseous dichlorine has been consumed [4]. Evidently, chlorine occupying Type-II sites diffuses to Type-I sites, where it then reacts with the incident CO. Phosgene production continues until the retained chlorine reservoir is exhausted [4]. Second, under isothermal reaction conditions, the extent of dichlorine consumption exceeds that of phosgene formation [5]. In this case, chlorine residing in Type-I supports phosgene production but chlorine adsorbed in Type-II sites is retained at the catalyst surface. As considered in Section 3.1.2, this definition of Type-I and Type-II sites is a means of describing a distribution of chemisorbed chlorine that corresponds to the stated reaction conditions. For example, different operating temperatures are expected to affect the equilibrium constant (K_2) and any diffusion barriers that may be associated with specific sites.

In a further consideration of chlorine interactions over activated carbon, it is informative to consider possible bonding options. To this end, it is beneficial to review aspects of the reaction testing methodology outlined in the preceding two papers on phosgene synthesis catalysis from this group [4,5]. First, the fresh catalyst is activated by heating to 383 K in flowing nitrogen for 12 h. As evidenced by in-line IR spectroscopy, this procedure dries the catalyst, removing absorbed and physisorbed water [4,5]. Thereafter, a variety of surface functional entities are expected to be present, such as hydroxyl and carboxyl groups, lactones, phenols, pyrenes, *etc.* [20]. Reaction testing is commenced by passing a mixture of $\text{CO}/\text{Cl}_2/\text{N}_2$ over the catalyst that is maintained at a temperature; the reaction system is then normally left for 20 min before the first spectroscopic measurements are recorded [4,5]. This time lag is necessary to allow the catalyst to stabilise and achieve equilibrium within the catalytic process. Specifically, within the first ~ 15 min for a fresh catalyst the in-line FTIR detects small quantities of $\text{HCl}_{(\text{g})}$, which are formed from a reaction of dichlorine with surface hydroxyl groups. The HCl evolution ceases within 15 min, indicating termination of the chlorination-dehydroxylation process. Thereafter, no HCl is observed, indicating no further role for hydroxyl groups in the reaction chemistry. Also absent from the IR spectra of the reacting system is the presence of $\text{H}_2\text{O}_{(\text{g})}$ [4,5]. In their review of carbon/chlorine interactions, González et al. list five reactions possible at a carbon surface [17]. Four of these reactions involve the release of either HCl or H_2O ; the absence of these molecules in the IR spectra of the working catalyst [4,5] thereby excludes the possibility that those reactions are active over this catalyst. The remaining reaction, an addition reaction of dichlorine over non-conjugated carbon double bonds is presented in Equation 5.

In this way, it is tentatively proposed that chlorine adsorption over the activated carbon occurs via dissociative adsorption of dichlorine, with the chlorine addition occurring at unsaturated ethenic sites. This deduction can be elaborated upon further with reference to the thermal desorption measurements (Section 3.2, Figure 6). Equation 6 is intended to indicate the initial dissociative adsorption process and the subsequent Cl_2 desorption event witnessed in Figure 6c; the latter being re-combinative desorption of chlorine atoms residing in Type-I sites.

The Δ symbol in Equation 6 signifies the applied temperature ramp employed in the TPD experiment.

With the goal of working towards defining a probable reaction framework for this reaction, one can now consider a role for the other reagent, *i.e.* carbon monoxide. Equation 2 shows phosgene formation to be first order with respect to the concentration of carbon monoxide [5], whilst Figure 1 shows CO does not adsorb on the activated carbon under the conditions studied. This is indicative of CO being involved via the gas phase and is suggestive of an Eley-Rideal type reaction mechanism [19], *i.e.* $\text{CO}_{(\text{g})}$ is operating in a collisional or ballistic regime.

Bringing these various strands together, any reaction scheme must accommodate the following experimentally determined parameters.

- The reaction is heterogeneous. Under the conditions studied, there is no homogeneous contribution to the forward chemistry [4];
- Dichlorine is assumed to chemisorb dissociatively, with the chlorine atoms residing in a distribution of sites that conforms to a two-site model (Type-I and Type-II); the sites being discernible via their enthalpy of adsorption: (Section 3.1.2);
- Type-I is catalytically active, Type-II is not (Section 4);
- CO is not adsorbed but interacts via the gas phase (Section 3.1.1);
- The only gaseous product observed is phosgene [4,5];
- On increasing temperature and in the presence of excess CO, phosgene formation is observed to increase in a region exhibiting full dichlorine conversion [4];
- In contrast to the stoichiometric equation for phosgene synthesis (Equation 1), under isothermal conditions, dichlorine consumption exceeds that observed for CO [5];

Against this background, the following reaction model (Scheme 1) is proposed, where k_{1-3} are rate coefficients.

Scheme 1. A reaction model to account for the reaction of $\text{CO}_{(\text{g})}$ and $\text{Cl}_{2(\text{g})}$ over activated carbon (Donau Supersorbon K40) at 323 K to produce phosgene.

Firstly, dichlorine chemisorbs dissociatively, with chlorine atoms partitioning between Type-I ($\text{Cl}_{(\text{ad})}'$) and Type-II ($\text{Cl}_{(\text{ad})}''$) sites. An incident gaseous CO molecule then collides with a chlorine atom adsorbed on the weaker bound Type-I site ($\text{Cl}_{(\text{ad})}'$) to form an acyl chloride entity ($\text{COCl}_{(\text{ad})}$) that is retained at the surface; k_1 accounts for this transformation. CO collision with chlorine present in Type-II sites, as represented by k_2 , does not lead to further reaction. A surface reaction between the acyl chloride entity and a further chlorine atom residing in a Type-I site then takes place (k_3) that results in the formation of phosgene, which is released in to the gaseous phase. Within Scheme 1, the initial dichlorine adsorption process (K_1) and the interchange of adsorbed chlorine atoms between Type-I and Type-II sites (K_2) are the only reversible stages. A comprehensive analysis of the chemical kinetics associated with the proposed surface chemistry is beyond the scope of the present work. Nonetheless, some points pertinent to Scheme 1 are worth noting. For the limited temperature range studied, Equation 7 is believed to be irreversible. It is possible that at higher temperatures (as encountered in the industrial operation) that this could be a reversible process. Equation 9 is also thought to be irreversible, not least because this assumption is consistent with phosgene exhibiting a zero-order dependence in the rate law (Equation 2).

Thus, we describe principle stages of the surface chemistry associated with phosgene synthesis catalysis as involving a combination of Eley-Rideal and Langmuir-Hinshelwood reaction pathways. Equation 7 corresponds to an Eley-Rideal surface chemical reaction, whereas Equation 9 is classed as a Langmuir-Hinshelwood stage. Within the stated conditions of how CO and Cl_2 are seen to combine over this activated carbon to produce phosgene, it is difficult to see how physisorbed dichlorine could fulfil such an integrated role.

The Introduction outlined mechanistic scenarios from six research groupings; noting no consensus as to how the reagents combine on the carbon surface. This work utilises strands of the various

mechanistic proposals reported, with Scheme 1 proposing a role for Eley-Rideal *and* Langmuir-Hinshelwood mechanistic steps. The evolving picture exhibits complexity and multi-site adsorption phenomena over the industrial grade catalyst. It is acknowledged that this study has exclusively examined a single activated carbon. Further work is required to assess the generality of the proposed mechanistic insight; specifically, is Scheme 1 equally applicable to other activated carbons?

5. Conclusions

Upon examining aspects of phosgene synthesis catalysis over Donau Supersorbon K40 activated carbon, single adsorption breakthrough measurements on fresh catalyst samples at 323 K, temperature-programmed desorption measurements on post-reaction catalyst samples, and post-reaction SEM/EDAX analysis have been undertaken. The following conclusions have been drawn.

- Individual reagent and product breakthrough measurements over the clean catalyst establish the magnitude of adsorption coefficients (K) to follow the trend: $K_{\text{Cl}_2} > K_{\text{COCl}_2} \gg K_{\text{CO}}$.
- Chlorine adsorption measurements indicate a distribution of active sites that is described within the concept a two-site model; Type-I and Type-II exhibit respective adsorption capacities of 2.8 ± 0.3 and 1.5 ± 0.4 mmol Cl_2 g⁻¹_{cat}.
- Post-reaction temperature-programmed desorption measurements and elemental analysis (EDAX) confirm the presence of retained chlorine moieties at the catalyst surface.
- A reaction scheme is proposed to account for a number experimental observables reported for the reaction system that involves a combination of Eley-Rideal and Langmuir-Hinshelwood mechanistic stages.

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Supporting Information

Figure S1: SEM image of the Donau Supersorbon K40 catalyst post-reaction; Figure S2: EDAX spectrum for post-reaction catalyst sample.

CRedit authorship contribution statement

Giovanni E. Rossi: Investigation, Validation, Writing - review & editing, Data curation, Visualization;
 John M. Winfield: Methodology, Investigation, Writing - review & editing; Nathalie Meyer: Formal analysis; Methodology; Project administration; Don H. Jones: Formal analysis; Methodology; Validation; Writing - review & editing; Robert H. Carr: Conceptualization, Investigation, Funding acquisition, Project administration; David Lennon: Conceptualization, Methodology, Investigation, Project administration, Supervision, Writing - original draft, Writing - review & editing.

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Supporting Information

Phosgene formation via carbon monoxide and dichlorine reaction over an activated carbon catalyst: Towards a reaction model

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Figure S1. SEM image of the Donau Supersorbon K40 catalyst post-reaction [catalyst charge = 0.125 g; CO flow rate = $5 \text{ cm}^3 \text{ min}^{-1}$, Cl_2 flow rate = $4 \text{ cm}^3 \text{ min}^{-1}$, nitrogen carrier gas (pre-reactor) = $50 \text{ cm}^3 \text{ min}^{-1}$, nitrogen diluent flow (post-reactor) = $100 \text{ cm}^3 \text{ min}^{-1}$; temperature = 323 K; duration = 4 h]. The purple box indicates the area of the micrograph used to generate the EDAX spectrum (Figure S2).

Figure S2. EDAX spectrum for post-reaction catalyst sample. The spectrum was recorded over the area highlighted in Figure S1.