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Chlorination reactions relevant to the manufacture of trichloroethene and tetrachloroethene; Part 2: Effects of chlorine supply

Iain W. Sutherland[a], Neil G. Hamilton[a], Christopher C. Dudman[b], Peter Jones[b], David Lennon[a,*], John M. Winfield[a]

[a] School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK
[b] Ineos ChlorVinyls Ltd., Runcorn Site HQ, South Parade, PO Box 9, Runcorn, Cheshire WA7 4JE, UK

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ABSTRACT

The behaviour of 1,1,2,2-tetrachloroethane and trichloroethene in chlorination reactions where the supply of chlorine is varied, either by change in chlorocarbon: Cl_2 feed ratio or the quantity of supported copper(II) chloride catalyst or by the use of an anhydrous hydrogen chloride/dioxygen feed as the source of chlorine, i.e. oxychlorination conditions, is described. Depending on the exact conditions used, the products are trichloroethene, pentachloroethane or tetrachloroethene. The products and the conditions under which they are observed are both in harmony with a previously proposed reaction scheme in which there is interplay between heterogeneous and homogeneous reactions. It is possible to define sets of reaction conditions which lead to improvements in selectivity towards the formation of either $CHCl{=}CCl_2$ or $CCl_2{=}CCl_2$ without significant formation of oligomeric species.

1. Introduction

The term Industrial ecology [1], though controversial [2], encapsulates an approach which emphasizes the connectivity among different large scale chemical processes, for example in which the waste product of one process could act as the feedstock for another. The concept is well exemplified by anhydrous hydrogen chloride. This is a major waste product from the industrial synthesis of aryl isocyanates for polyurethane production; it is potentially also a feedstock for chlorohydrocarbon synthesis, via its oxidation to dichlorine, the Deacon reaction [2]. Waste HCl from polyurethane production can be used for the catalysed oxychlorination of ethene to give 1,2-dichloroethane and thence by dehydrochlorination, vinyl chloride [2,3]; this system has been examined in detail [4–7]. Active catalysts have been developed for the purpose [8–15]. However the fraction of waste HCl available that can be used for this outlet is limited increasingly by the mis-match between increasing, year-on-year tonnage of polyurethanes produced and the capacity of HCl to be used in the (mature) market for PVC [3]. For this reason there has been recent activity designed to improve the classical Deacon reaction [16–19,4,20–22] to oxidize HCl to Cl_2, using new catalysts [23–28] developed from work announced previously by Sumitomo [29]. Moreover, Over and Schomäcker have considered the stability of Deacon catalysts and identify promising catalyst materials for the Deacon process [30].

An attractive possibility to utilize unwanted HCl would be in syntheses of poly-chlorinated hydrocarbons under oxychlorination conditions. In Part 1 of this series of two papers, we reported the results of a study designed to establish a reaction scheme connecting 1,1,2,2-tetrachloroethane with hexachloroethane, trichloroethene and tetrachloroethene. That work included experiments performed under static and continuous flow conditions, with aspects of the study examining the influence of a commercial oxychlorination catalyst (Cu^{II}/KCl/attapulgite). Pathways for the chlorination and dehydrochlorination reactions involved were proposed [31], the reaction conditions being either homogeneous flow conditions in which dichlorine is the initiator for dehydrochlorination of $CHCl_2CHCl_2$, or heterogeneously in the presence of the conventional copper(II)-supported Deacon catalyst. Although the results were broadly consistent with earlier studies [32,33], conditions for selective formation of either $CHCl{=}CCl_2$ or $CCl_2{=}CCl_2$ have been defined more precisely, bearing in mind the need to avoid the formation of oligomeric side-products. Specifically, the proposed reaction scheme identified pentachloroethane as a reaction intermediate. A role for Lewis acid site promoted chemistry was also considered [31].

The reactions reported in the initial study, Part 1: reaction pathways [31], were investigated under conditions where the dichlorine

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* Corresponding author. Tel.: +44 141 330 4372; fax: +44 330 4888.
E-mail address: David.Lennon@glasgow.ac.uk (D. Lennon).

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in the feed was insufficient for chlorination to be complete (a chlorocarbon: Cl_2 ratio of 3:1 was used). The present work, Part 2, builds on the previous study and examines (i) the effects of operation under chlorine-rich conditions (a chlorocarbon: Cl_2 ratio of 1:3 is used) and (ii) the effect of alteration of the chlorine supply when operating under oxychlorination conditions.

2. Experimental

Details of the flow apparatus, on-line analyses and the protocols used for flow experiments have been described previously [31]. Feedstocks were those used for experiments carried out under chlorine-lean conditions [31] with the addition of anhydrous hydrogen chloride (Linde, 99.5%), and dioxygen (BOC, 5% O_2/N_2). Pressure was limited via a pair of mercury-filled lutes to ensure that the reactor pressure did not exceed 0.5 bar g. Reaction data are reported as feed conversions, product yields and selectivities, defined according to standard practice [34]. Carbon mass balances were determined in all chlorination/dehydrochlorination reactions; they are reported explicitly when they contain features of note The analytical procedure described previously [31] to obtain chlorine mass balances (relative error ± 10%) was used to measure yields of Cl_2 from the catalytic oxidation of HCl to Cl_2.

The catalyst under consideration here is the same commercial grade oxychlorination catalyst [35] as examined in Part 1 [31]. Briefly, the catalyst comprises copper(II) chloride supported on the clay mineral, attapulgite, that is doped with a promoter, KCl. Prior to use, it was calcined at 673 K in flowing N_2 for 4 h and is characterized by a BET surface area of 71.6 $m^2\,g^{-1}$ and a pore volume of 0.25 $cm^3\,g^{-1}$ [31].

The experiments reported in Part 1 [31] established the importance of certain reaction pathways accessible at elevated temperatures even in the absence of a catalyst. A mixing vessel, packed with quartz beads (diameter 2 mm), was fitted within the furnace immediately before the reactor. This arrangement ensured complete mixing and thermalization of the reactant gases. Similar measurements are undertaken here and, as before, the catalyst was replaced with ground quartz. These experiments, which ensure comparable contact times, are useful in defining non-catalytic pathways. Previously we have referred to non-catalyst assisted processes as being ‘homogeneous’ [31], however we acknowledge that the quartz does provide some form of ‘hold-up’ in the hot zone, which could possibly influence reaction probabilities. Thus, these type of reactions could more correctly be called ‘quasi-homogeneous’, however, for completeness and additionally recognising the caveat described above, we will continue to use the term ‘homogeneous’ in this context.

3. Results and discussion

The results from the previous study [31] establish the reaction pathways connecting 1,1,2,2-tetrachloroethane with tri- and tetrachloroethene under chlorine-lean conditions (3:1 chlorocarbon: Cl_2 mol ratio). One of the reaction parameters that potentially might control the selectivity of the system is the chlorine supply. Although radical chlorinations, for example chlorination of 1,1,2,2-tetrachloroethane to give pentachloroethane, appear to be disfavoured kinetically compared with dehydrochlorinations, for example 1,1,2,2-tetrachloroethane to trichloroethene, increasing the chlorine supply might reverse this situation. To test the role of the supply of chlorine on reaction selectivity and outcomes, the effect of increasing the relative chlorine concentration was examined. Specifically, the chlorocarbon feed ($CHCl_2CHCl_2$ or $CHCl{=}CCl_2$) to dichlorine mol ratio was changed from 3:1 (i.e. chlorine-lean), as used in our previous study [31], to 1:3, i.e. a chlorine-rich regime.

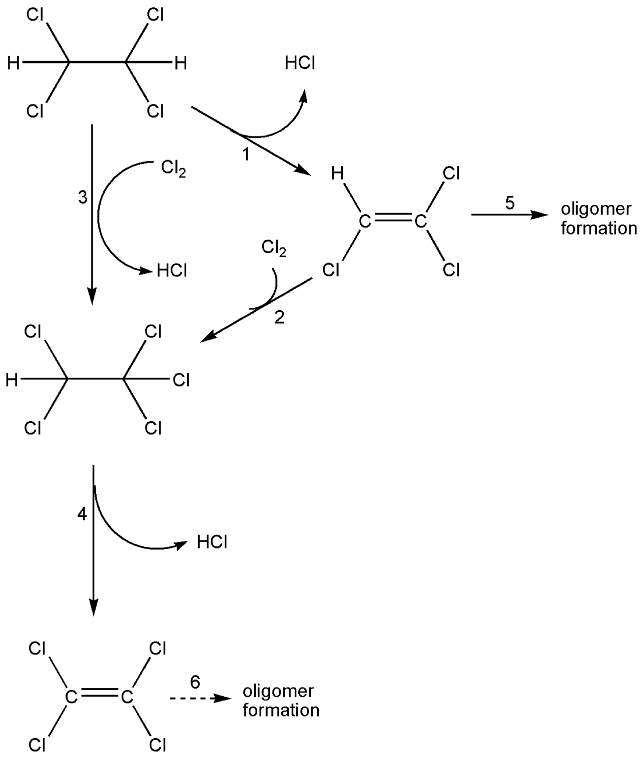

Fig. 1. The dehydrochlorination ((1) and (4)) and chlorination ((2) and (3)) processes that connect $CHCl_2CHCl_2$ with $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$. Possible oligomer formation ((5) and (6)). A pathway for reaction (5) is identified in Section 3.1.1. A pathway for reaction (6) is inferred in Section 3.1.2.

Nitrogen was used as a carrier gas for the chlorocarbon and a diluent for the feedstream to give a total volumetric flow rate of 25 ml min^{-1}. The chlorination and oxychlorination roles of the copper(II)/KCl/attapulgite catalyst were then examined over a range of conditions that have direct connectivity with an industrial process, as they potentially constitute external control parameters.

The changes in conditions have an implication for the reaction scheme that was reported earlier [31], notably an increased role for the chlorination route occurring via $CHCl{=}CCl_2$ (reactions (1) then (2) in Fig. 1) compared with the direct chlorination of $CHCl_2CHCl_2$ (reaction (3) in Fig. 1). They have also allowed clarification of conditions under which oligomerization, with its undesirable environmental and economic effects (reactions (5) and (6)), may occur.

3.1. Reactions under chlorine-rich conditions

3.1.1. 1,1,2,2-Tetrachloroethane with dichlorine (1:3 mol ratio) under homogeneous conditions, i.e. in the absence of Cu^{II} catalyst

The temperature relationships for mean conversions of $CHCl_2CHCl_2$ and mean carbon mass balances for 1,1,2,2-tetrachloroethane + $3Cl_2$, total volumetric flow 25 ml min^{-1}, are contained in Fig. 2(a) and (b), respectively.

The reaction profile is similar to that observed under chlorine lean conditions in that $CHCl{=}CCl_2$ is the only product observed, however, mean conversions of $CHCl_2CHCl_2$ at a given temperature, Fig. 2(a) are higher than those observed under a chlorine-lean regime [31]. The most significant difference is that the carbon mass balance shows a significant deficit (ca. 20%) at 623 K and above, Fig. 2(b). It is suggested that, when conversion of $CHCl_2CHCl_2$ becomes significant, the high concentration of carbon-centred radicals present, leads to the chlorine atom initiated formation of dimeric and oligomeric species, which being relatively involatile, results in the carbon mass imbalance observed. These results

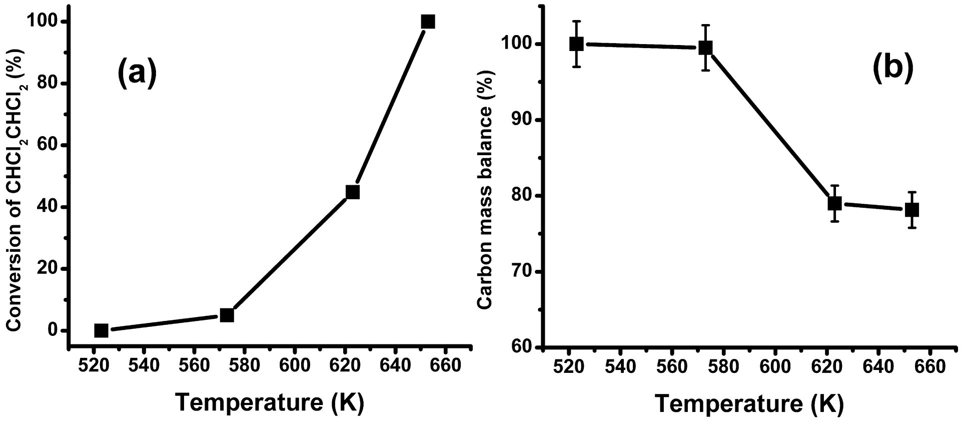

Fig. 2. Temperature relationships for (a) mean conversions of $CHCl_2CHCl_2$ and (b) mean carbon mass balance, both in the absence of catalyst or support, for 1:3 $CHCl_2CHCl_2:Cl_2$, total volumetric flow rate 25 $cm^3\ min^{-1}$, over the temperature range 523–653 K. Error bars are standard deviations on the mean values of four to nine measurements conducted at 10 min intervals.

indicate that, in order to avoid oligomer formation, the process should be operated at low conversions and/or low temperatures under chlorine-rich conditions. Mean yields of $CHCl{=}CCl_2$ are 28.8% at 623 K rising to 78.1% at 653 K. Corresponding mean yields under Cl-lean conditions are 25.9% and 57.3% [31].

3.1.2. *Trichloroethene with dichlorine (1:3 mol ratio) under homogeneous conditions, i.e. in the absence of Cu^{II} catalyst, and under heterogeneous conditions, in the presence of Cu^{II}/KCl/attapulgite catalyst (200 mg)*

In the absence of a catalyst and under Cl-lean conditions, no reaction between $CHCl{=}CCl_2$ and Cl_2 is observed up to 623 K [31]. Fig. 3 presents the corresponding $CHCl{=}CCl_2$ conversion plot for the homogenous chlorination of $CHCl{=}CCl_2$ in excess Cl_2 (1:3 ratio of reactants). Conversion commences above 523 K and a conversion of ca. 26% is observed at 653 K with $CHCl_2CCl_3$ and $CCl_2{=}CCl_2$ identified as products. This comparison between chlorine-lean [31] and chlorine-rich conditions (Fig. 3) indicates that direct chlorination of $CHCl{=}CCl_2$ (reaction (2)) is possible without a catalyst and providing excess Cl_2 is present.

Under chlorine-lean conditions and in the presence of the Cu^{II}/KCl/attapulgite catalyst, Part 1 reported $CCl_2{=}CCl_2$ to be the sole product from the reaction of $CHCl{=}CCl_2$ and Cl_2. This lead to the deduction that, providing a chlorination catalyst was present, chlorination of $CHCl{=}CCl_2$ was a significant route in the formation of chlorinated reaction products [31]. Data for the corresponding chlorination of trichloroethene occurring over 200 mg of catalyst in a chlorine-rich regime (trichloroethene + $3Cl_2$, total volumetric flow 25 ml min^{-1}, WHSV = 0.39 h^{-1}) are given in Fig. 4(a)–(d).

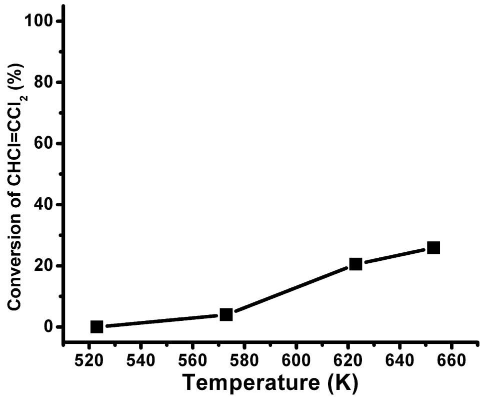

Fig. 3. The conversion of $CHCl{=}CCl_2$ as a function of temperature for the reaction of $CHCl{=}CCl_2$ and Cl_2 (1:3 mol ratio) in the absence of a catalyst, i.e. homogeneous conditions. Total volumetric flow rate 25 $cm^3\ min^{-1}$, over the temperature range 523–653 K. Error bars are standard deviations on the mean values of four to five measurements conducted at 10 min intervals.

As with the homogeneous case, the products are identified as $CHCl_2CCl_3$ and $CCl_2{=}CCl_2$ but the conversion of $CHCl{=}CCl_2$ is substantial already at 573 K, Fig. 4(a); at this temperature and above, deficiencies in C mass balances are significant (≥20%), Fig. 4(b). It is possible that the catalyst may have a positive effect in promoting the chlorination of $CHCl{=}CCl_2$, as a result the concentration of radical species in the reactor rises and oligomerization of $CHCl{=}CCl_2$, reaction (5) in Fig. 1, is increased. In addition, it is also possible that the heterogeneous reaction is taking place via organic species adsorbed on the catalyst surface. In the latter case, oligomers could additionally form in addition to the intended chlorination reaction. The selectivity to $CHCl_2CCl_3$ passes through a maximum at 563 K (Fig. 4(c)), which corresponds with an increased selectivity to $CCl_2{=}CCl_2$ with increasing temperature (Fig. 4(d)). This profile indicates $CHCl_2CCl_3$ to be an intermediate under these conditions, with reaction (2) preceding reaction (4) (Fig. 1).

Effects of excess Cl_2 (Cl-rich conditions) are manifest by, onset of reaction at a lower temperature (573 vs. 653 K in the Cl-lean case [31]) and the fact that both homogeneous and heterogeneous pathways operate.

3.1.3. *1,1,2,2-Tetrachloroethane with dichlorine (1:3 mol ratio) in the presence of Cu^{II}/KCl/attapulgite catalyst (200 mg)*

The mean feedstock conversions for the chlorination of 1,1,2,2-tetrachloroethane over 200 mg of catalyst in the presence of excess Cl_2 (1,1,2,2-tetrachloroethane + $3Cl_2$, total volumetric flow 25 ml min^{-1}, WHSV = 0.42 h^{-1}) is shown in Fig. 5. The extent of conversion is rather similar to its equivalents under chlorine-lean conditions [31].

Table 1
$CHCl_2CHCl_2 + 3Cl_2$: Mean values[a] of yields and selectivity with respect to the formation of $CHCl{=}CCl_2$, $CHCl_2CCl_3$ and $CCl_2{=}CCl_2$ obtained using 200 mg of catalyst at 653 K[b].

Product yield (%)			Selectivity (%) wrt		
$CHCl{=}CCl_2$	$CHCl_2CCl_3$	$CCl_2{=}CCl_2$	$CHCl{=}CCl_2$	$CHCl_2CCl_3$	$CCl_2{=}CCl_2$
45.1 (1.2)	11.2 (0.8)	8.1 (0.8)	64.4 (1.9)	16.0 (1.3)	11.5 (1.1)

[a] Determined from five measurements; standard deviations in parentheses.

[b] Cu^{II}/KCl/attapulgite catalyst; mol ratio $CHCl_2CHCl_2:Cl_2$ = 1:3; total volumetric flow 25 ml min^{-1}, WHSV = 0.42 h^{-1}.

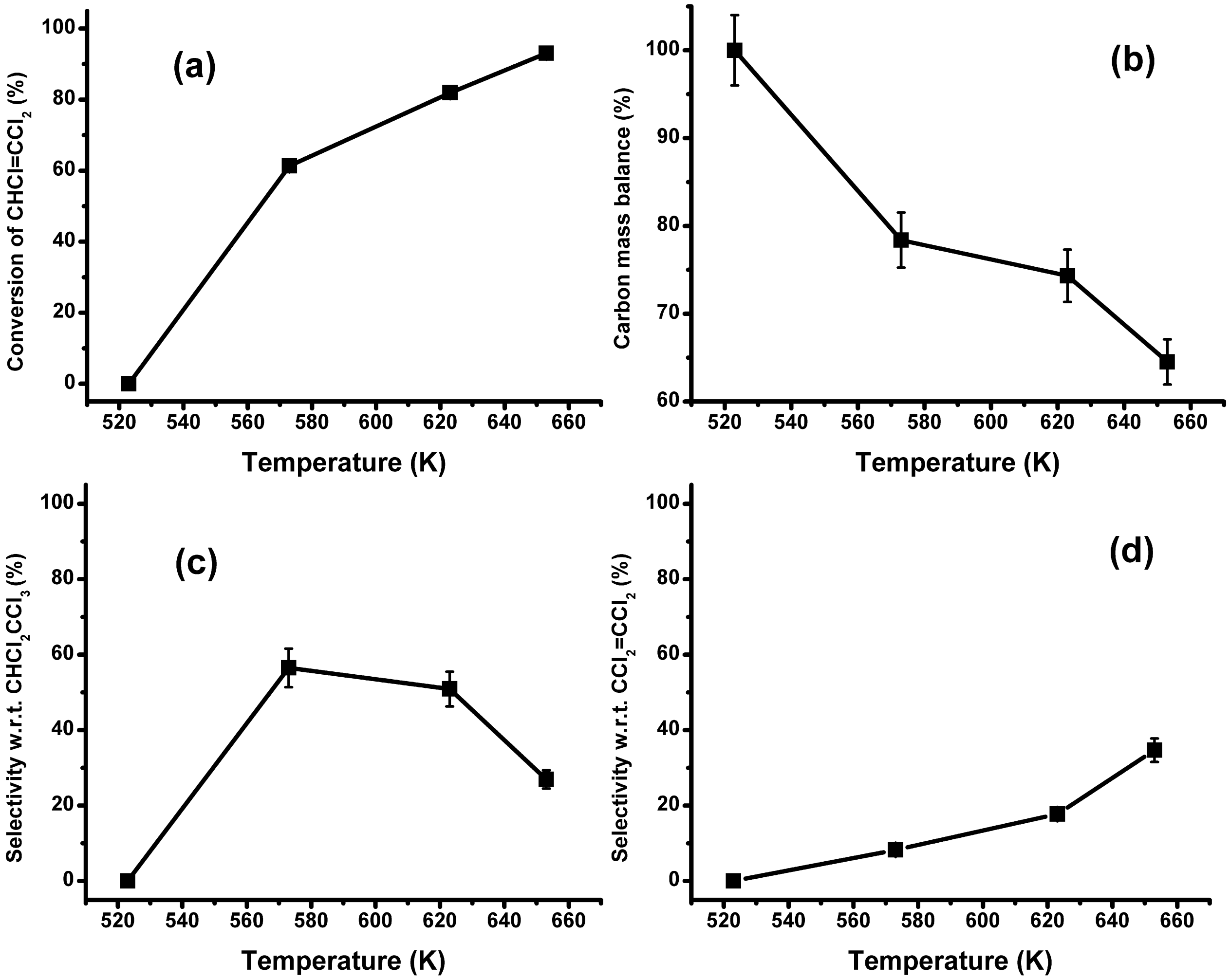

Fig. 4. Temperature relationships for (a) mean conversion of $CHCl{=}CCl_2$, (b) mean carbon mass balance, (c) mean selectivity with respect to $CHCl_2CCl_3$ and (d) mean selectivity with respect to $CCl_2{=}CCl_2$, for 1:3 $CHCl{=}CCl_2{:}Cl_2$ over 200 mg catalyst, total volumetric flow rate 25 $cm^3\ min^{-1}$, WHSV = 0.39 h^{-1}; over the temperature range 523–653 K. Error bars are standard deviations on the mean values of four or five measurements conducted at 10 min intervals.

Table 1 presents the product distributions at 653 K, which are also rather similar to those observed under chlorine-lean conditions [31]. Below 623 K, $CHCl{=}CCl_2$ is the only observable unsaturated product; a small quantity of $CHCl_2CCl_3$ is observed at 623 and 653 K. At the latter temperature $CCl_2{=}CCl_2$ is observed also (ca. 8% yield). No increase in $CHCl_2CCl_3$ is apparent with increasing temperature, since dehydrochlorination (reaction (4)) is facile under these conditions.

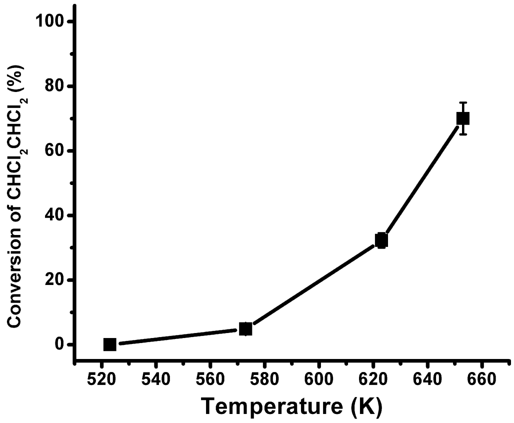

Fig. 5. Temperature relationship for mean conversions of $CHCl_2CHCl_2$ for 1:3$CHCl_2CHCl_2{:}Cl_2$ over 200 mg of catalyst, total volumetric flow rate 25 $cm^3\ min^{-1}$, WHSV = 0.42 h^{-1}; over the temperature range 523–653 K. Error bars are standard deviations on the mean values of five measurements conducted at 10 min intervals.

3.2. Catalytic conversion of hydrogen chloride to dichlorine

The Deacon reaction may be described in terms of the following reaction steps

$$2\,Cu^{II}Cl_2 \rightarrow 2\,Cu^{I}Cl + Cl_2 \qquad (7)$$

$$2\,Cu^{I}Cl + 1/2\,O_2 \rightarrow Cu^{II}{}_2OCl_2 \qquad (8)$$

$$Cu^{II}{}_2OCl_2 + 2\,HCl \rightarrow 2\,Cu^{II}Cl_2 + H_2O. \qquad (9)$$

Overall, this leads to the following chemical equation,

$$2\,HCl + 1/2\,O_2 \rightarrow H_2O + Cl_2. \qquad (10)$$

Firstly, conversion of HCl to Cl_2 was tested over three masses of catalyst, 200, 500 and 1000 mg and at two temperatures, 623 and 653 K, Fig. 6(a) and (b). No conversion of HCl to Cl_2 was observed below 623 K and the yield at that temperature over 200 mg catalyst was minimal, Fig. 6(a). This is consistent with previous work using similar KCl-doped Deacon catalysts [16,17].

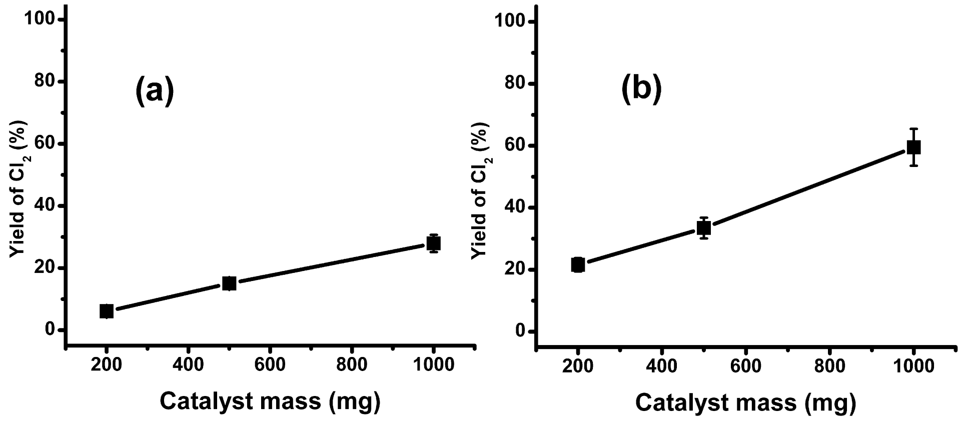

Fig. 6. Variation of dichlorine yield (%) from the Deacon reaction (feed mol ratio of 4:1HCl:O_2) as a function of catalyst mass; total volumetric flow rate 25 cm^3 min^{-1}; (a) at 623 K, (b) at 653 K, demonstrating approximate linear dependence.

Fig. 6 also shows an approximately first order dependence of dichlorine yield on catalyst mass at both temperatures and establishes that, under the flow conditions used here, that the catalyst can adequately recycle HCl in situ to produce dichlorine for subsequent reaction with a chlorocarbon. Further, comparing the dichlorine yields for 200 mg of catalysts (ca. 7% and 22% at 623 and 653 K, respectively, Fig. 6) with the conversion values for the chlorination of $CHCl_2CHCl_2$ over the same mass of catalyst (30% and 70% at 623 and 653 K, respectively, Fig. 5) suggests that the Deacon process is relatively slower than the chlorination reactions. This implies the possible presence of chlorine concentration gradients along the length of an oxychlorination reactor. Further kinetic studies are required to test the validity of this hypothesis but are beyond the scope of the current work.

3.3. *Oxychlorination reactions*

This section examines the oxychlorination of $CHCl_2CHCl_2$ over 500 and 1000 mg of catalyst in the presence of an HCl/O_2 feed. The conditions chosen enable two hypotheses to be tested: (a) that oxychlorination is an analogue of chlorination, with Cl_2 being supplied via the Deacon reaction (reaction (10)) rather than directly in the reactant feedstream and (b) that oxychlorination proceeds via a pathway where molecular chlorine is not an intermediate.

3.3.1. *Consideration of HCl as a reagent*

Flowing $CHCl_2CHCl_2$ plus anhydrous HCl (no O_2) over 500 mg catalyst for 200 min while ramping the catalyst bed temperature from 523 to 653 K resulted in no conversion of $CHCl_2CHCl_2$ (not shown); there was no evidence for product formation or for deviation from 100% carbon mass balance. Thus, it is concluded that (i) HCl alone does not behave as a reagent for chlorination under these conditions, (ii) tetrachloroethane does not dehydrochlorinate and (iii) that the equilibrium favours the reagents. Results presented below indicate molecular chlorine to be an intermediate in the molecular transformations associated with the oxychlorination process.

The conversion level of HCl to Cl_2 over a catalyst loading of 200 mg is too low to initiate reaction (Section 3.2), therefore 500 and 1000 mg charges of catalyst were used. With reference to Fig. 6, this will provide information on how, under oxy-chlorination conditions, catalyst mass can affect chlorine concentration in the reaction zone. The relative O_2 concentration in the feed is, in principle, another variable that could be investigated, however, in order to ensure that explosive mixtures were not encountered, this parameter was restricted in the studies reported here.

3.3.2. *Oxychlorination of 1,1,2,2-tetrachloroethane (mol ratio $CHCl_2CHCl_2$:HCl:O_2 = 3:2:4) over Cu^{II}/KCl/attapulgite, catalyst loadings of 500 or 1000 mg*

The mean conversion of $CHCl_2CHCl_2$ with change in temperature for the oxychlorination of 1,1,2,2-tetrachloroethane over 500 mg catalyst ($3CHCl_2CHCl_2 + 2HCl + 4O_2$, total volumetric flow 25 ml min^{-1}, WHSV = 0.17 h^{-1}) is shown in Fig. 7(a). In contrast to the chlorination reaction using Cl_2 (described in Section 3.1.3), there is no evidence for the chlorination of $CHCl_2CHCl_2$ or $CHCl{=}CCl_2$; the latter was the sole identified product at 623 and 653 K; this establishes dehydrochlorination (reaction (1), Fig. 1) to be the only reaction pathway accessible under these conditions. Whilst oxygen is primarily associated with the moderation of local chlorine supply via Eqs. (7)–(9), a possible role for oxygen-initiated dehydrochlorination cannot be excluded.

The behaviour observed resembles the homogeneous chlorination reactions; the lack of conversion at 573 K indicates that the Deacon reaction is inoperative; therefore no Cl_2 is present for the radical initiation step. The lack of any observable chlorination product at higher temperatures could indicate a restricted chlorine supply under these conditions. As shown below, extending the catalyst bed should enable some chlorination to be observed.

The carbon mass balance for the 500 mg catalyst run is effectively complete, which indicates that there is no significant oligomerization or, crucially, combustion. On a small, laboratory scale at least, it is possible to operate $CHCl_2CHCl_2$ oxychlorination for significant periods of time (ca. 24 h) without any significant loss of material to environmentally undesirable side reactions.

The differences in behaviour that result from a change in chlorine supply brought about by a change in catalyst mass are illustrated well by comparison of the mean feed conversion, Fig. 7(b) ($3CHCl_2CHCl_2 + 2HCl + 4O_2$, total volumetric flow 25 ml min^{-1}, WHSV = 0.08 h^{-1} over 1000 mg of catalyst) compared with Fig. 7(a), and by the product yields and selectivities given in Table 2.

Doubling the mass of catalyst to 1000 mg results in higher conversion of $CHCl_2CHCl_2$ at 623 K, although $CHCl{=}CCl_2$ remains the sole identified product (Table 2). At 653 K feed conversion is almost complete, Fig. 7(b), and the dehydrochlorination/chlorination chemistry, depicted in Fig. 1, is fully developed (Table 2). As a consequence, the yield of $CHCl{=}CCl_2$ is smaller than that using 500 mg catalyst. The yield of $CCl_2{=}CCl_2$ is comparable with that observed using 500 mg catalyst under Cl_2-rich conditions (Section 3.1.3, Fig. 6 and Table 1). In both situations, some conversion of $CHCl{=}CCl_2$ to $CHCl_2CCl_3$ and thence to $CCl_2{=}CCl_2$ is likely to occur. The oxychlorination sequence observed over 1000 mg of catalyst (Table 2) is rationalized as follows. As the reactant gases move

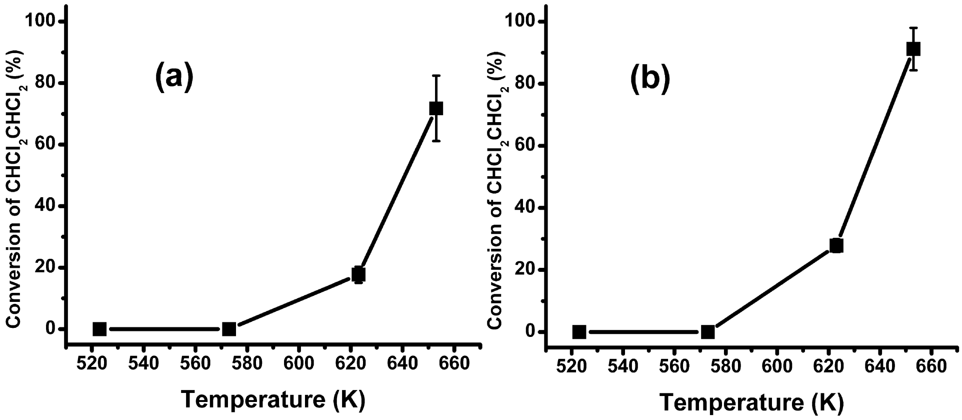

Fig. 7. Temperature relationships for mean conversions of $CHCl_2CHCl_2$ under oxychlorination conditions for 3:2:4 mol ratio $CHCl_2CHCl_2$:HCl:O_2: (a) over 500 mg catalyst, (b) over 1000 mg catalyst, total volumetric flow rate 25 cm^3 min^{-1}, WHSV = 0.17 and 0.08 h^{-1}, respectively; over the temperature range 523–653 K. Error bars are standard deviations on the mean values of five measurements conducted at 10 min intervals.

Table 2

$3CHCl_2CHCl_2 + 2HCl + 4O_2$: Mean values[a] of yields and selectivities with respect to the formation of $CHCl{=}CCl_2$, $CHCl_2CCl_3$ and $CCl_2{=}CCl_2$ obtained under oxychlorination conditions using 500 or 1000 mg of catalyst at 623 and 653 K[b].

Catalyst mass (mg)	Temp (K)	Product yield (%)			Selectivity (%) wrt		
		$CHCl{=}CCl_2$	$CHCl_2CCl_3$	$CCl_2{=}CCl_2$	$CHCl{=}CCl_2$	$CHCl_2CCl_3$	$CCl_2{=}CCl_2$
500	623	17.0 (0.5)	–	–	100	–	–
500	653	74.3 (1.8)	–	–	100	–	–
1000	623	24.9 (0.7)	–	–	100	–	–
1000	653	64.3 (0.9)	6.1 (0.5)	20.8 (0.7)	70.5 (1.0)	6.7 (0.6)	22.8 (0.8)

[a] Determined from five measurements; standard deviations in parentheses.

[b] Cu^{II}/KCl/attapulgite catalyst; feedstock mol ratio $CHCl_2CHCl_2$:HCl:O_2 = 3:2:4.

across the catalyst bed, HCl is converted to Cl_2, which can then initiate the dehydrochlorination of $CHCl_2CHCl_2$ to form $CHCl{=}CCl_2$ (reaction (1)). This is adsorbed at the catalyst surface and forms $CHCl_2CCl_3$ via heterogeneous chlorination (reaction (2)), possibly through reaction with $CuCl_2$. Surface catalytic or chlorine-initiated dehydrochlorination of $CHCl_2CCl_3$ leads to $CCl_2{=}CCl_2$, reaction (4) in Fig. 1, cf. [31].

In a study of this reaction, $3CHCl_2CHCl_2 + 2HCl + 4O_2$, over 1000 mg catalyst for an extended time, 18 h at 653 K, the mean feed conversions were in the range 90–92% with no evidence for the C mass balance deviating from 100%. The products observed are $CHCl{=}CCl_2$ (yield 65–72%) and $CCl_2{=}CCl_2$ (yield 20–23%). There was no evidence for the minor product, $CHCl_2CCl_3$; presumably its dehydrochlorination was rapid and complete under the conditions of the experiment. This set of measurements indicates sustained yields of unsaturated C_2 chlorocarbons to be attainable via the oxy-chlorination process.

3.3.3. *1,1,2,2-Tetrachloroethane with dichlorine and a dioxygen co-feed (mol ratio $CHCl_2CHCl_2$:Cl_2:O_2 = 3:1:4) in the presence of Cu^{II}/KCl/attapulgite catalyst*

The final reaction examined involved addition of an O_2 co-feed to a flow of $3CHCl_2CHCl_2$:Cl_2, i.e. chlorine-lean conditions, over 500 mg of catalyst. It might be expected that any HCl produced from chlorination of $CHCl_2CHCl_2$ would be oxidized to Cl_2 thus increasing the chlorine supply. This expectation was realized. Chlorination of $CHCl_2CHCl_2$ over 500 mg catalyst and in the presence of O_2 ($3CHCl_2CHCl_2 + Cl_2 + 4O_2$, total volumetric flow 25 cm^3 min^{-1},

Table 3

Sets of conditions required to observe the individual chlorination and hydrochlorination processes and formation of oligomer species.

Reaction	Reaction conditions [a]	Initiator/catalyst	Temperature (K)
1. $CHCl_2CHCl_2 \rightarrow CHCl{=}CCl_2 + HCl$	$CHCl_2CHCl_2$, Cl_2 (1:3)	Cl_2	573–653
	$CHCl_2CHCl_2$, HCl, O_2 (3:2:4)	Cu^{II}/KCl/attapulgite	623–653
2. $CHCl{=}CCl_2 + Cl_2 \rightarrow CHCl_2CCl_3$	$CHCl{=}CCl_2$, Cl_2 (1:3)	Cl_2	573–623
	$CHCl{=}CCl_2$, Cl_2 (1:3)	Cu^{II}/KCl/attapulgite	573–653
3. $CHCl_2CHCl_2 + Cl_2 \rightarrow CHCl_2CCl_3 + HCl$	$CHCl_2CHCl_2$, Cl_2 (1:3)	Cu^{II}/KCl/attapulgite	623–653
	$CHCl_2CHCl_2$, HCl, O_2 (3:2:4)	Cu^{II}/KCl/attapulgite	653
4. $CHCl_2CCl_3 \rightarrow CCl_2{=}CCl_2 + HCl$	$CHCl{=}CCl_2$, Cl_2 (1:3)	Cl_2 ?[b]	623–653
	$CHCl{=}CCl_2$, Cl_2 (1:3)	Cu^{II}/KCl/attapulgite	573–653
	$CHCl_2CHCl_2$, Cl_2 (1:3)	Cu^{II}/KCl/attapulgite	653
	$CHCl_2CHCl_2$, HCl, O_2 (3:2:4)	Cu^{II}/KCl/attapulgite	653
5. $CHCl_2{=}CCl_2 \rightarrow$ Oligomer formation	$CHCl_2CHCl_2$, Cl_2 (1;3)	Cl_2 ?[b]	623–653
	$CHCl{=}CCl_2$, Cl_2 (1:3)	Cu^{II}/KCl/attapulgite	573–653
6. $CCl_2{=}CCl_2 \rightarrow$ Oligomer formation	$CHCl{=}CCl_2$, Cl_2 (1:3)?	Cu^{II}/KCl/attapulgite	573–653
	$CHCl_2CHCl_2$, Cl_2 (1:3)	Cu^{II}/KCl/attapulgite	653

[a] Mol ratio presented in parentheses.

[b] A possible initiator/catalyst.

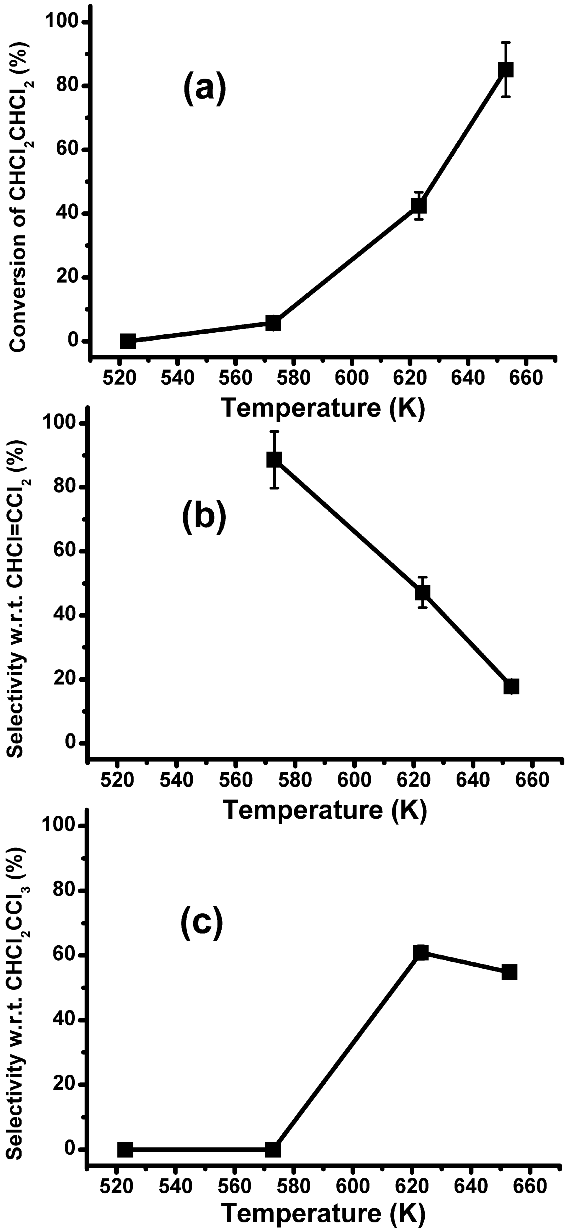

Fig. 8. Temperature relationships for (a) mean conversions of $CHCl_2CHCl_2$, (b) mean selectivity with respect to $CHCl{=}CCl_2$ and (c) mean selectivity with respect to $CHCl_2CCl_3$, for feed mol ratio 3:1:4 $CHCl_2CHCl_2$:Cl_2:O_2 over 500 mg catalyst, total volumetric flow rate 25 $cm^3\ min^{-1}$, WHSV = 0.17 h^{-1}; over the temperature range 523–653 K. Error bars are standard deviations on the mean values of five measurements conducted at 10 min intervals.

WHSV = 0.17 h^{-1}) resulted in mean feed conversions and product mean selectivities shown in Fig. 8.

At 573 K dehydrochlorination of $CHCl_2CHCl_2$ (conversion = 5.7%) yields $CHCl{=}CCl_2$ as the sole reaction product. At 623 K selectivity to $CHCl{=}CCl_2$ is decreased by the additional formation of $CHCl_2CCl_3$ (Fig. 8(b) and (c)). At 653 K $CCl_2{=}CCl_2$ is also observed in the product stream, occurring via the dehydrochlorination of $CHCl_2CCl_3$. (Fig. 1, Eq. (4)). There is no observable carbon mass deficiency over this temperature range. This indicates minimal oligomeric formation but also that there is no chlorine-initiated oxidation. The data indicate that the chlorine supply must be increased within the reactor, presumably via the operation of the Deacon reaction on the catalyst (Eqs. (7)–(9)), converting HCl produced from the formation of $CHCl{=}CCl_2$ from $CHCl_2CHCl_2$ (Fig. 1, Eq. (1)) to Cl_2.

4. Summary of the reactions

A range of reaction conditions, variation of reactant mole ratios, temperature and homogeneous (Cl_2) or heterogeneous (Cu^{II}/KCl/attapulgite) catalyst, has been used in the study of the three reaction types, dehydrochlorination, chlorination (including oxychlorination) and oligomer formation, which are shown in Fig. 1. Although formation of $CHCl{=}CCl_2$ can be achieved with high selectivity, this is not the case for formation of $CCl_2{=}CCl_2$ where its precursor, $CHCl_2CCl_3$, is normally a co-product. However, in both cases, conditions can be found where oligomerization, as evidenced by a deficiency in carbon mass balance, is absent or minimized. Sets of conditions which lead to, at least predominantly, the individual reactions (1)–(6) (Fig. 1) are given in Table 3.

The reactions are summarized in turn:

Reaction (1): Dehydrochlorination of $CHCl_2CHCl_2$ to give $CHCl{=}CCl_2$: This reaction is initiated homogeneously by Cl_2, the selectivity with respect to $CHCl{=}CCl_2$ being 100% at 573 K. Selectivity decreases at higher temperature due to material loss as a result of oligomerization (reaction (5)) but this can be avoided by working under chlorine-lean conditions [31]. In the presence of the Cu^{II} catalyst, selectivity to $CHCl{=}CCl_2$ decreases due to chlorination reactions (reactions (2) and (3)). In contrast, under chlorine-lean conditions the heterogeneous catalyst has little or no effect on mean selectivity with respect to $CHCl{=}CCl_2$ formation [31]. The use of an HCl/O_2 feed and the Cu^{II} catalyst results in behaviour that is highly selective towards $CHCl{=}CCl_2$ formation at 623 and 653 K; conversion of the $CHCl_2CHCl_2$ feed is substantial at the latter temperature (mean yield of $CHCl{=}CCl_2$ is 74.3%). The favourable selectivity of the oxychlorination reaction is attributed to a restricted chlorine supply that results from the Deacon reaction being relatively slow.

Reaction (2): Chlorination of $CHCl{=}CCl_2$ to $CHCl_2CCl_3$: This reaction is observed only under chlorine-rich conditions. In the presence of the Cu^{II} catalyst, $CHCl_2CCl_3$ yields are reasonable although HCl loss from $CHCl_2CCl_3$ to give $CCl_2{=}CCl_2$ is a competing process, which is observed at 573 K and above. Yields of the latter are substantial at 653 K.

Reaction (3): Chlorination of $CHCl_2CHCl_2$ to $CHCl_2CCl_3$: Under chlorine-rich conditions and in the presence of the Cu^{II} catalyst, the mean selectivity with respect to $CHCl_2CCl_3$ is moderate. Loss of HCl to give $CCl_2{=}CCl_2$ is observed at 653 K. However the major product at 623 and 653 K is $CHCl{=}CCl_2$ (reaction (1)). It appears that under this regime, there is competition between Cl_2 catalysed dehydrochlorination and Cu^{II} catalysed chlorination then dehydrochlorination. A similar competitive situation exists when HCl/O_2 feedstock is used instead of Cl_2.

Reaction (4): Dehydrochlorination of $CHCl_2CCl_3$: The final outcome of the processes described above is $CCl_2{=}CCl_2$, which is the thermodynamic sink of the whole system [31]. It is accessible via the intermediate, $CHCl_2CCl_3$, which in turn may involve the starting materials, $CHCl_2CHCl_2$ or $CHCl{=}CCl_2$ (Fig. 1). Chlorination of $CHCl{=}CCl_2$ over the Cu^{II} catalyst results in high conversions at 653 K but a decrease in selectivity to $CCl_2{=}CCl_2$ as $CHCl_2CCl_3$ is co-produced. Most seriously, loss of material is substantial, reactions (5) and (6). $CHCl_2CCl_3$ is observed as a product in the oxychlorination of $CHCl_2CHCl_2$ provided conditions favour the presence of chlorine in the reaction zone.

Reactions (5) and (6): Deficiencies in carbon mass balances are attributed to the loss of $CHCl{=}CCl_2$ and/or $CCl_2{=}CCl_2$ with subsequent oligomerisions. For convenience in Fig. 1 they are regarded as separate reactions, although it as likely that both depend on the presence of high concentrations of C-centred radicals formed under conditions of substantial feedstock conversions and high concentrations of Cl. As such, the reactions are more likely to occur under chlorine-rich conditions. For example, in the homogeneous reaction of $CHCl_2CHCl_2$ with $3Cl_2$, loss of material is substantial at 623 and 653 K, the sole identified product being $CHCl{=}CCl_2$. Loss of carbon in the reaction $CHCl{=}CCl_2 + 3Cl_2$ at 573 K and above in the presence of Cu^{II} catalyst, could indicate the occurrence of both reactions (5) and (6). Interestingly, there is no evidence for carbon loss in the oxychlorination reactions studied, presumably as the concentrations of radical species are likely to be smaller.

5. Conclusions

The relevance of relative chlorine supply in reactions connected with the synthesis of trichloroethene and tetrachloroethene over a commercial grade oxychlorination catalyst has been studied under homogeneous and heterogeneous conditions. The main conclusions from this investigation can be summarized as follows.

- Homogeneous processes are active at elevated temperatures, with increasing chlorine concentration seen to display a promotional effect. However, high conversions are linked to mass imbalances as a consequence of radical-mediated, oligomer-forming reactions.
- Product distributions indicate competition between chlorination and dehydrochlorination reactions. One of the roles of the catalyst is to facilitate surface chlorination reactions.
- The catalyst supports the Deacon process, i.e. the interconversion of hydrogen chloride to dichlorine. From comparisons between dichlorine yields and chlorination conversions at fixed temperature and contact times, it is deduced that the Deacon process is slow compared to the main organo-chlorine transformations.
- For temperatures up to 653 K, HCl alone does not act as a reagent for chlorination. However, in the presence of the catalyst, the Deacon process provides an in situ source of dichlorine.
- Under Deacon conditions, catalyst mass and reaction temperature are seen to moderate chlorine supply, which in turn may perturb product distributions. For instance, low catalyst mass and intermediate temperatures (i.e. 623 K) favour high selectivity to trichloroethene.
- The product distribution upon co-feeding oxygen in a chlorine-lean feedstream indicates that the Deacon reaction can supplement local chlorine supply by converting HCl produced from the formation of $CHCl{=}CCl_2$ from $CHCl_2CHCl_2$ to Cl_2.

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References

[1] (a) T.E. Graedel, B.R. Allenby, Industrial Ecology, Prentice Hall, Upper Saddle River, NJ, 1995;
T.E. Graedel, B.R. Allenby, Industrial Ecology and Sustainable Engineering, Prentice Hall, Upper Saddle River, NJ, 2009.
[2] N. Winterton, Chemistry for Sustainable Technologies: A Foundation, RSC Publishing, Cambridge, UK, 2011, pp. 290–298.
[3] F. Cavani, Catal. Today 157 (2010) 8–15.
[4] A.J. Rouco, J. Catal. 157 (1995) 380–387.
[5] E. Finocchio, N. Rossi, G. Busca, M. Padovan, G. Leofanti, B. Cremaschi, A. Marsella, D. Carmello, J. Catal. 179 (1998) 606–618.
[6] D. Carmello, E. Finocchio, A. Marsella, B. Cremaschi, G. Leofanti, M. Padovan, G. Busca, J. Catal. 191 (2000) 354–363.
[7] C. Lamberti, C. Prestipino, L. Capello, S. Bordiga, A. Zecchina, G. Spoto, S.D. Moreno, A. Marsella, B. Cremaschi, M. Garilli, S. Vidotto, G. Leofanti, Int. J. Mol. Sci. 2 (2001) 230–245.
[8] G. Leofanti, M. Padovan, M. Garilli, D. Carmello, A. Zecchina, G. Spoto, S. Bordiga, G. Turnes Palomino, C. Lamberti, J. Catal. 189 (2000) 91–104.
[9] G. Leofanti, M. Padovan, M. Garilli, D. Carmello, G.L. Marra, A. Zecchina, G. Spoto, S. Bordiga, C. Lamberti, J. Catal. 189 (2000) 105–116.
[10] G. Leofanti, A. Marsella, B. Cremaschi, M. Garilli, A. Zecchina, G. Spoto, S. Bordiga, P. Fisicaro, G. Berlier, C. Prestipino, G. Casali, C. Lamberti, J. Catal. 202 (2001) 279–295.
[11] G. Leofanti, A. Marsella, B. Cremaschi, M. Garilli, A. Zecchina, G. Spoto, S. Bordiga, P. Fisicaro, C. Prestipino, F. Villian, C. Lamberti, J. Catal. 205 (2002) 375–381.
[12] C. Lamberti, C. Prestipino, F. Bonino, L. Capello, S. Bordiga, G. Spoto, A. Zecchina, S. Diaz Moreno, B. Cremaschi, M. Garilli, A. Marsella, D. Carmello, S. Vidotto, G. Leofanti, Angew. Chem. Int. Ed. 41 (2002) 2341–2344.
[13] C. Prestipino, S. Bordiga, C. Lamberti, S. Vidotto, M. Garilli, B. Cremaschi, A. Marsella, G. Leofanti, P. Fisicaro, G. Spoto, A. Zecchina, J. Phys. Chem. B 107 (2003) 5022–5030.
[14] N.B. Muddada, U. Olsbye, L. Caccialupi, F. Cavani, G. Leofanti, D. Gianolio, S. Bordiga, C. Lamberti, Phys. Chem. Chem. Phys. 12 (2010) 5605–5618.
[15] N.B. Muddada, U. Olsbye, G. Leofanti, D. Gianolio, F. Bonino, S. Bordiga, T. Fuglerud, S. Vidotto, A. Marsella, C. Lamberti, Dalton Trans. 39 (2010) 8437–8449.
[16] C.N. Kenney, Catal. Rev. Sci. Eng. 11 (1975) 197–224.
[17] J. Villadsen, H. Livbjerg, Catal. Sci. Eng. 17 (1978) 203–272.
[18] H.Y. Pan, R.G. Minet, S.W. Benson, T.T. Tsotsis, Ind. Eng. Chem. Res. 33 (1994) 2996–3003.
[19] M.W.M. Hisham, S.W. Benson, J. Phys. Chem. 99 (1995) 6194–6198.
[20] M. Mortensen, R.G. Minet, T.T. Tsotsis, S.W. Benson, Chem. Eng. Sci. 54 (1999) 2131–2139.
[21] U. Nieken, O. Watzenberger, Chem. Eng. Sci. 54 (1999) 2619–2626.
[22] L. Xueju, L. Jie, Z. Guangdong, Z. Kaiji, L. Wenzing, C. Tiexin, Catal. Lett. 100 (2005) 153–159.
[23] N. López, J. Gómez-Segura, R.P. Marín, J. Pérez-Ramírez, J. Catal. 225 (2008) 29–39.
[24] A. Wolf, L. Mleczko, O.F. Schlülter, S. Schubert, EP No. 2026905, Assigned to Bayer MaterialScience, 2006.
[25] M.A.G. Hevia, A.P. Amrute, T. Schmidt, J. Pérez-Ramírez, J. Catal. 276 (2010) 141–151.
[26] C. Mondelli, A.P. Amrute, F. Krumeich, T. Schmidt, J. Pérez-Ramírez, ChemCatChem 3 (2011) 657–660.
[27] C. Mondelli, A.P. Amrute, T. Schmidt, J. Pérez-Ramírez, Chem. Commun. (2011) 7173–7175.
[28] A.P. Amrute, C. Mondelli, M.A.G. Hevia, J. Pérez-Ramírez, J. Phys. Chem. C 115 (2011) 1056–1063.
[29] H. Abekawa, Y. Ito, T. Hibi, U.S. Patent No. 5908607, Assigned to Sumitomo, 1999.
[30] H. Over, R. Schomäcker, ACS Catal. 3 (2013) 1034–1046.
[31] I.W. Sutherland, N.G. Hamilton, C.C. Dudman, P. Jones, D. Lennon, J.M. Winfield, Appl. Catal., A 399 (2011) 1–11.
[32] T. Kawaguchi, Y. Suzuki, R. Saito, Ind. Eng. Chem. 62 (1970) 36–41.
[33] A. Arcoya, A. Cortés, X.L. Seoane, Ind. Eng. Chem. Prod. Res. Dev. 19 (1980) 77,82–82,86.
[34] K. Weissermel, H.-J. Arpe, Industrial Organic Chemistry, fourth ed., Wiley-VCH, Weinheim, 2003, pp. 449–450.
[35] Ineos ChlorVinyls Ltd., Catalyst reference: Cu0951, Lot 31.