Total Oxidation of Chlorinated Hydrocarbons by Copper and Chlorine based Catalysts

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A new class of combustion catalyst containing copper and chlorine is described which has high activity for the total oxidation of chlorinated hydrocarbons such as CH_2Cl_2, CH_2ClCH_2Cl, CCl_4 and 1,2-dichlorobenzene (1% of gas stream) into carbon oxides, HCl and Cl_2, in the presence of excess air at 300–500 °C; no catalyst deactivation or loss of copper or chlorine is observed.

Chlorinated organics are highly toxic and their presence in the environment is most undesirable.[1–3] The current technology for the total oxidation of the chlorinated organic waste is incineration at extremely high temperatures (> 1000 °C).[4] Total oxidation refers to the oxidation of chlorinated hydrocarbons to carbon oxides (CO and CO_2) and HCl or Cl_2. The large energy input and the expensive construction materials required for the incinerator make this process expensive. Moreover, in these combustion flame processes, highly toxic byproducts such as dioxin or dibenzofurans can be formed by incomplete combustion. Therefore, the development of catalysts for the total oxidation of chlorinated hydrocarbons operating in mild conditions is of considerable interest. Patents claiming complete catalytic oxidation of chlorinated hydrocarbons have appeared on a regular basis in recent years.[5–7] The reported catalysts can be broadly divided into noble metal catalysts and oxide catalysts. A high intrinsic combustion activity of noble metal catalysts has been claimed but their relatively high cost and poor stability, especially in the presence of the HCl and Cl_2 produced in the reaction, limit their further development.[8] Supported transition metal oxides, such as oxides of chromium, copper, manganese, nickel and cobalt[9–12] and other acidic oxide materials such as zeolites and TiO_2/SiO_2[13] have also been studied for the total oxidation of chlorinated hydrocarbons, but generally they have low activity for catalytic combustion. Recently, an interesting catalyst system based on oxides of copper and manganese supported on sodium carbonate has been reported by Stenger *et al.*[14] and Drago and coworkers[15] reported that CrO_3 supported on porous carbon is very active for the decomposition of chlorinated hydrocarbons at low temperatures.

Here we present our work on copper and chlorine based catalysts which are very effective for *the decomposition of chlorinated hydrocarbons* into carbon oxides.

The catalysts were prepared on a high surface area silica by the incipient wetness method. For example, a solution of copper(I) chloride in 1 mol dm^{-3} HCl was added to the silica (Grace, plc), the water was removed and the residue was dried in an oven at 150 °C for 2 h and then at 500 °C for 8 h. A related catalyst $CuCl/KCl/SiO_2$ was prepared similarly by impregnating SiO_2 (60%) with 30% m/m CuCl and 10% KCl (described as $CuCl/KCl/SiO_2$ for simplicity). However, in the presence of air and high temperatures during calcination, a large proportion of copper may be in the higher oxidation state, some oxychloride $CuO{\cdot}CuCl_2$ is probably formed as reported.[16]

A DSC analysis of the $CuCl/KCl/SiO_2$ mixture showed an endothermic peak between 325 and 425 °C with a maximum at 384 °C. This indicates that the CuCl/KCl mixture was molten at these temperatures. For the purposes of comparison the silica supported metal oxide catalysts Cr_2O_3/SiO_2 (4% by weight of metal oxide), MnO_2/SiO_2 (4%), CuO/SiO_2 (8%) and Co_3O_4/SiO_2 (4%) were prepared by incipient wetness impregnation on silica using aqueous solutions of the nitrate salts.

The catalysts were tested for activity towards the total oxidation of CH_2Cl_2. The catalyst (2.0 g) was placed in a vertical silica tube reactor at 350 °C and the feedstock was a mixture of the chlorinated hydrocarbon in dry air (concentration of 10 000 ppm) at ambient pressure and at 10 ml min^{-1}. Table 1 shows the comparison of the performance of the catalyst $CuCl/KCl/SiO_2$ with the catalysts based on Cr_2O_3/SiO_2, CuO/SiO_2, Co_3O_4/SiO_2 and MnO_2/SiO_2. The transition metal oxide catalysts described in Table 1 are claimed to be among the most active oxides for the combustion of chlorinated hydrocarbons.[9–12] However, the supported molten catalyst $CuCl/KCl/SiO_2$ showed the highest activity and selectivity to total oxidation products, giving more than 98% conversion of dichloromethane to carbon oxides (CO and CO_2). The carbon input and output balance for the $CuCl/KCl/SiO_2$ catalyst was >95% at 350 °C. At 400 °C and with a feedstock of CH_2Cl_2 (10 000 ppm) in dry air at 18 ml min^{-1}, both $CuCl/KCl/SiO_2$ and Cr_2O_3/SiO_2 gave virtually 100% conversion of CH_2Cl_2.

We have compared the stability of the last two catalysts for 72 h at 400 °C and no apparent loss of activity and selectivity was observed in both cases during 70 h at 400 °C. The dichloromethane conversion was 100% with *ca.* 80% selectivity to CO_2 and 20% to CO (based on total carbon input) and 71% selectivity to HCl and 29% to Cl_2 (based on chlorine input). The atomic absorption analysis data in Table 2 shows there was no loss of copper whilst there was a significant decrease in chromium metal content in the supported chromium oxide catalyst after the reaction, probably due to the formation of the volatile compound CrO_2Cl_2.[9]

Analysis of the chlorine content of the $CuCl/KCl/SiO_2$ catalyst before and after use showed a slightly increased chlorine content in the used catalyst (Table 2). This might be due to partial oxidation of CuCl to $CuCl_2$ induced by the Cl_2 produced or the reaction of HCl with oxychloride species producing copper(II) chloride and water. Powder XRD spectra of the fresh and used $CuCl/KCl/SiO_2$ catalyst gave no evidence for phase segregation indicating that above 350 °C the active catalyst system operates in the molten phase.

The rate of CO_x (CO + CO_2) formation was found to be first order with respect to both CH_2Cl_2 and O_2 when the partial pressure of oxygen was below 0.15 atm. However, as the O_2 partial pressure increased (>0.15 atm) the order of reaction became zero with respect to O_2. Hence, under the reaction conditions (Table 1) the rate has zero order with respect to O_2. Comparative kinetic studies with CH_2Cl_2 and CD_2Cl_2 at 430 °C

Table 1 Catalytic combustion of methylene chloride at 350 °C[a]

Catalyst	% CH_2Cl_2 conv.	% CO_x[b]	% other[c]
$CuCl/KCl/SiO_2$	98.4	99.3	0.7
Cr_2O_3/SiO_2	96.7	90.8	9.2
CuO/SiO_2	87.9	96.3	3.7
Co_3O_4/SiO_2	54.3	90.0	10.0
MnO_2/SiO_2	71.6	88.9	11.1

[a] Catalyst 2.0 g, CH_2Cl_2 (10 000 ppm) 10 ml min^{-1} in air, 350 °C. [b] CO_x = CO + CO_2. [c] Other products: $CHCl_3$ and CCl_4 (GC–MS).

Table 2 Analysis of Cr, Cu and Cl for the catalysts Cr_2O_3/SiO_2, $CuCl/KCl/SiO_2$ before and after reaction at 400 °C for 72 h in the presence of CH_2Cl_2 (10 000 ppm) in dry air (18 ml min^{-1})

Element	Before reaction	After reaction
Cr/mmol (g catalyst)$^{-1}$	0.45	0.37
Cu/mmol (g catalyst)$^{-1}$	2.58	2.59
Cl/mmol (g catalyst)$^{-1}$	5.16	5.34

show a kinetic isotopic effect of k_H/k_D = *ca.* 1.5 for the rate of formation of CO_x and also for the formation of the byproduct $CHCl_3$. This suggests the rate controlling step involves C–H bond activation with an apparent activation energy of 26 kcal mol^{-1} (determined at conversions lower than 15%; 1 cal = 4.184 J). Experiments applying alternate pulses of O_2 and CH_2Cl_2 showed that the reaction products are only formed during the CH_2Cl_2 pulse. All these observations suggest the copper chloride system takes up oxygen at the higher partial pressure, probably forming the copper oxychloride complex $CuO{\cdot}CuCl_2$. These species are able to break the C–H bond in chlorinated hydrocarbons and oxidise the resulting surface intermediates into carbon oxides.

We have also studied the temperature profile for the oxidation of 1,2-dichloroethane in the presence of $CuCl/KCl/SiO_2$, as shown in Fig. 1. At temperatures around 300 °C, substantial amounts of chlorinated hydrocarbon products such as $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2H_5Cl, $C_2H_4Cl_2$ are observed (GC–MS). It appears that the catalyst surface is active for hydrogen and chlorine exchange reactions at these lower temperatures. However, when the reaction temperature was increased to >450 °C the carbon conversion of the 1,2-dichloroethane to carbon oxides reaches 100%. This observation suggests the copper–oxygen species are active at higher temperatures for the decomposition of these chemisorbed chlorinated hydrocarbons to carbon oxides.

We have also shown that chlorinated aromatic hydrocarbons, *e.g.* 1,2-dichlorobenzene (DCB) at 1000 ppm can be completely converted by $CuCl/KCl/SiO_2$, reaching 100% carbon balance at around 500 °C. Some condensation products may be formed at low temperatures. At 350 ppm in air, DCB can also be completely oxidised over $CuCl/SiO_2$ in the absence of potassium promoter, achieving 100% conversion to CO_x at 400 °C.

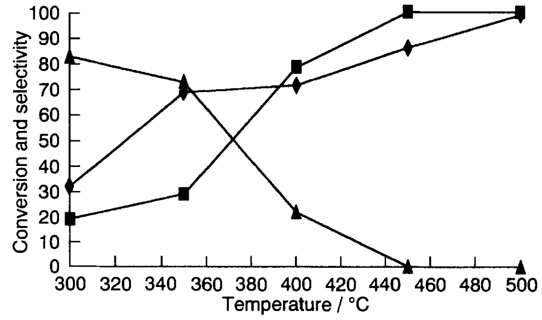

Fig. 1 Oxidation of 1,2-dichloroethane in the presence of $CuCl/KCl/SiO_2$ catalyst [$C_2H_4Cl_2$ (10 000 ppm) in dry air (18 ml min^{-1}), catalyst 2.0 g]. ▲ = byproducts, ♦ = $C_2H_4Cl_2$ conversion, ■ = CO_x.

Table 3 Temperatures required for the 100% combustion of chlorinated hydrocarbons and volatile organic compounds (VOC) into carbon oxides over supported copper chloride catalysts (catalyst 2.0 g, air 18 ml min^{-1})

Catalyst	VOC (concentration/ppm)	*T*/°C
$CuCl/KCl/SiO_2$	CH_2Cl_2 (10 000)	400
$CuCl/KCl/SiO_2$	CH_2ClCH_2Cl (10 000)	500
$CuCl/KCl/SiO_2$	CCl_4 (10 000)	375
$CuCl/SiO_2$	1,2-dichlorobenzene (350)	400
$CuCl/KCl/SiO_2$	$CH_2{=}CHC_2H_5$ (6 500)	400
$CuCl/KCl/SiO_2$	CH_4 (4 000)	500
$CuCl/KCl/SiO_2$	CO (280 000)	300
$CuCl/KCl/SiO_2$	C_2H_4O (10 000)	300

The data in Table 3 show that the supported copper chloride catalysts, with or without addition of KCl are very versatile for the total combustion of other chlorinated hydrocarbons. We note that the oxidation of CCl_4 proceeds stoichiometrically to carbon oxides and Cl_2 and there is no need for an additional hydrogen source such as H_2O.

The Cu–Cl catalysts are also very active for the complete combustion of non-chlorine containing reactants such as CO, ethene oxide and methane. Indeed, the initial activity of the catalyst $CuCl/KCl/SiO_2$ for methane combustion is comparable to the most active supported Pd, Pt and perovskite-type catalysts.[17] However, catalyst deactivation was observed and powder XRD analyses of the catalysts before and after methane oxidation revealed that phase segregation (*e.g.* CuO, KCl, K_2CuCl_4) from the molten catalyst occurs. This phase segregation and catalyst deactivation probably reflects the loss of chlorine from the catalysts as HCl, induced by hydrolysis, at the high reaction temperatures. The inclusion of KCl into the Cu–Cl-based catalyst reduces the rate of deactivation.

In conclusion, our results contrast with the well-known inhibition of the total oxidation of hydrocarbons in the presence of chlorine-containing species which enhances the partial oxidation products. For example, the ethylene oxide synthesis over silver catalyst[18] and the methane coupling reaction.[19] Copper chloride is also known to be an active catalyst for the *selective* oxidative chlorination of hydrocarbons, *e.g.* oxychlorination of ethene to vinyl chloride in the presence of HCl and O_2.[20]

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