FORMATION OF PCDD/F FROM THE PYROLYSIS OF 2-CHLOROPHENOL ON THE SURFACE OF DISPERSED COPPER OXIDE PARTICLES

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The formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from 2-chlorophenol on supported copper oxide catalyst was studied over the temperature range 200–500 °C and a contact time of 0.17–0.5 s under pyrolytic conditions. It was found that despite the pyrolytic conditions, the majority of 2-chlorophenol undergoes oxidation to CO and CO_2. Approximately 0.5% of 2-chlorophenol was converted to PCDD/F. The results are consistent with a Langmuir-Hinshelwood mechanism for PCDF formation and an Eley-Rideal mechanism of formation of PCDD. Only one PCDF isomer was observed, 4,6-dichlorodibenzofuran, while substantial concentrations of highly chlorinated PCDD were detected. This observation can be explained by a mechanism of formation involving a surface-bound PCDD intermediate that can be further chlorinated. PCDFs are desorbed upon formation and are consequently not chlorinated.

Introduction

Emissions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from combustion and thermal processes is one of our most pressing environmental problems and is truly global in nature. Virtually any thermal process that contains a fuel, a source of chlorine, and a transition metal can form PCDD/F [1]. Purely homogeneous, gas-phase formation routes from specific precursors, that is, chlorophenols and chlorobenzenes, have been suggested, but are highly controversial [2–7]. Surface-mediated reactions over the fly ash [8,9] are generally considered to be more important routes of formation. The significant difference between these two models is that gas-phase processes occur at higher temperatures ($T > 500$ °C) in the combustion and postcombustion zone, while surface processes can result in PCDD/F formation at temperatures less than 500 °C in the air pollution control device and cool zone.

Among possible surface processes, two are of particular interest: transition-metal-catalyzed de novo synthesis of PCDD/F from carbonaceaous deposits/soot and catalytic condensation of PCDD/F precursors on fly ash surfaces [10]. For the de novo process, some progress has been made concerning the mechanism [11]. However, for the surface-catalyzed precursor condensation reactions, mechanistic details have not been experimentally elucidated.

Due to unknown interactions between the different ions present in the fly ash that affect catalytic properties as well as carbon presence, the use of fly ash or even a model fly ash complicates the mechanistic studies of PCDD/F formation [12–14]. Since available data indicate that copper and iron ions are probably the most active metals in PCDD/F formation over the fly ash, we use copper oxide supported on a silica matrix as a fly ash surrogate. This method will avoid the effect of other unknown cations present in fly ash. In addition, contrary to use of pure copper oxide, it will allow us to follow the reaction of small surface domains of well-dispersed copper oxide species, as would be the case for fly ashes that typically contain less than 1% copper [15,16].

Most of the research on the surface precursor reaction has been performed using polychlorinated phenols, in particular 2,4,6-trichlorophenol (2,4,6-TCP) [17,18], since this is the most abundant chlorophenol present in municipal waste incinerator exhaust [19]. However, due to the high degree of chlorination of 2,4,6-TCP and dechlorination reactions that form multiple PCDD/F congeners, it complicates the mechanistic interpretation of the results. Consequently, we have used 2-chlorophenol as a simple surrogate for more complex chlorinated phenols.

For meaningful mechanistic and kinetic studies, we must first determine the type of the interaction of the reacting molecules with the catalytic surface. Since it is established that the presence of oxygen influences the kinetics of the PCDD/F formation [20], we have divided our experiments into two parts: pyrolytic conditions and excess oxygen conditions. This manuscript presents the results of our studies of the pyrolysis of the 2-chlorophenol (MCP) reaction over a copper oxide/silica system. The experiments under pyrolytic conditions, although not
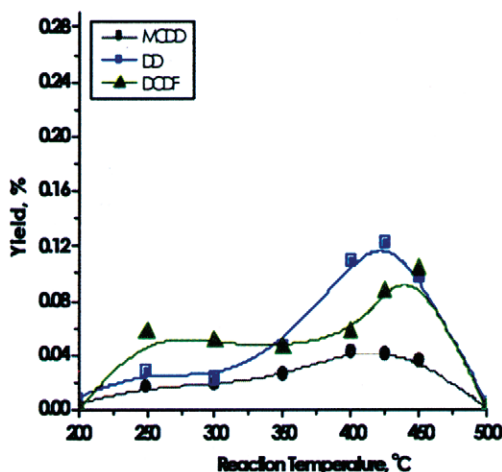
FIG. 1. Mole percent yields of DD, MCDD, and DCDF from pyrolysis of 88 ppmv of 2-chlorophenol over CuO/SiO$_2$ (3 mg).

consistent with the nominal conditions in a full-scale combustor, are important because they can reveal the nature of the surface interaction. Moreover, since the formation of PCDD/F from two chlorophenol precursors is accompanied by hydrogen elimination (or dehydrogenation), the process can be considered as a chemical oxidation, and surface redox processes are expected to be involved in the reaction. Therefore oxygen-deficient conditions can address the matter of oxygen involvement in the process: Is oxygen directly reacting with adsorbed molecules, or is its role rather to regenerate surface sites?

Experimental

The catalytic material (5% CuO/SiO$_2$) was prepared by the method of incipient wetness of the silica support. A water solution of copper (II) nitrate (Aldrich) of concentration chosen so as to obtain a 5% CuO/SiO$_2$ system was used as the active-phase precursor. Silica powder (Aldrich) was introduced into the equivalent amount of precursor solution for incipient wetness to occur. The suspension was then well mixed, and the samples were dried at 120 °C for 24 h. The surface area of catalyst used in the experiments was 500 m^2/g and was not changed after copper oxide deposition. With such high surface area, one can expect monolayer dispersion of copper oxide species.

For the catalytic studies, 1–3 mg of a CuO/SiO$_2$ sample was placed in a quartz reactor (1 mm i.d.) between quartz wool plugs. All transfer lines were isothermal at 225 °C. Before each experiment, the

samples were oxidized *in situ* at 500 °C for 1 h in a 20% O$_2$/He mixture at a flow rate of 5.5 cc/min.

2-Chlorophenol (Aldrich) was introduced into a helium stream by a syringe pump through a vaporizer maintained at 180 °C. The constant rate of the injection was selected so as to obtain a gas-phase concentration of 2-chlorophenol of 88 ppmv. The flow rate of the reacting mixture was 1–5.5 cc/min, depending upon temperature to obtain a contact time for the catalyst bed of 0.17–0.5 s. The reaction was performed over a temperature range of 225–500 °C. All presented results reflect 1 h on-stream experiments.

The effluent products from the reactor were trapped at the head of capillary column at −60 °C and analyzed after completion of the reaction using a GC-MS system (Varian saturn ion trap 2000). PCDD/F concentrations and yields were calculated based on the peak area counts of the chromatogram, based on the calibration made using standards (Cambridge Isotope Laboratory standards): 1-monochlorodibenzo-*p*-dioxin in a 50 µg/ml isooctane solution; 2,6-dichlorodibenzofuran in a 50 µg/ml in toluene, used as a standard for 4,6-dichlorodibenzofuran. The dibenzo-*p*-dioxin standard was prepared using a Chem-Service standard in methylene chloride solution. The 2-MCP breakthrough was calculated based on calibration using the reagent compound. Experiments with the empty reactor as well as with quartz wool stoppers were performed, and no activity was recorded.

Results

The results for pyrolysis of 2-MCP over 3 mg of catalyst at a contact time of 0.5 s are presented in Fig. 1. No PCDD/Fs were detectable in the catalyst bed; the only observable PCDD/Fs were in the gas-phase effluent of the reactor. Since PCDD/Fs were not observed without the catalyst bed under otherwise identical conditions, the observed PCDD/Fs result from desorption of PCDD/Fs formed on the catalyst surface.

Three PCDD/F congeners that are the direct product of condensation reactions of 2-MCP are observed: dibenzo-*p*-dioxin (DD), 1-monochlorodibenzo-*p*-dioxin (MCDD), and 4,6-dichlorodibenzofuran (DCDF). These are the same products predicted via gas-phase condensation reactions of the 2-chlorophenoxyl radical and MCP, the 2-chlorophenoxyl radical and its keto-mesomer, and two keto-mesomers of 2-chlorophenoxyl radical, respectively [3–7,20]. Initial experiments with 3 mg of catalyst and a longer contact time of 2.8 s resulted in complete oxidation of MCP with no observable products. The highest conversion to PCDD/F was observed at 400–450 °C versus greater than 550 °C and higher for the purely gas-phase reaction [3,21], clearly implicating the activity of the surfaces in the formation of PCDD/F.
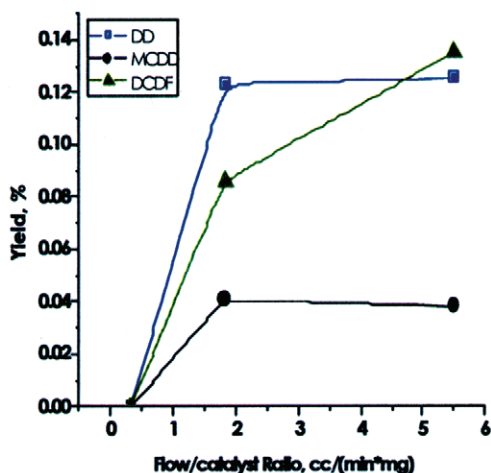
FIG. 2. Mole percent yields of DD, MCDD, and DCDF from pyrolysis of 2-chlorophenol over CuO/SiO$_2$ for various flow/catalyst ratios.
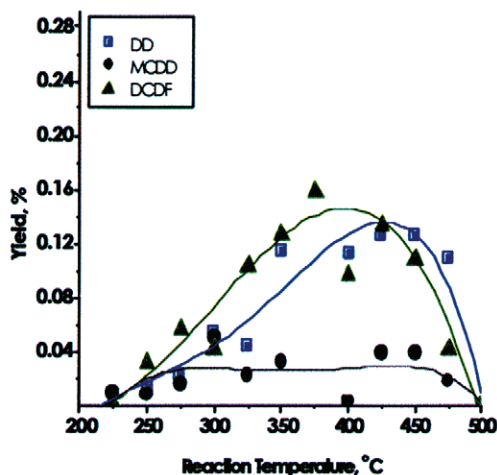

FIG. 3. Mole percent yields of DD, MCDD, and DCDF from pyrolysis of 88 ppmv of 2-chlorophenol over CuO/SiO$_2$ (1 mg).

The maximum total yield of DD, MCDD, and DCDF was 0.26 % at 425 °C; however, significant quantities were observed at temperatures as low as 250 °C and as high as 450 °C. Above 350 °C, the relative yields were DD > DCDF > MCDD. Below 350 °C, the relative yields were DCDF > DD > MCDD. The yield of MCDD was almost temperature independent over this range.

Since there were significant differences in the yields of PCDD/F formation for different reactant flows, another experiment was performed with a lower catalyst amount (1 mg) to ensure that there were no diffusion limitations. Fig. 2 presents the yields of DD, MCDD, and DCDF as a function of flow/catalyst ratio at 425 °C. The yields of DD and MCDD do not change above a ratio of 1.8; that indicates that our experiments, which were all performed at a ratio of greater than 1.8, were in the kinetic regime. In contrast, the yields of DCDF did vary, suggesting a different mechanism of formation of PCDF than PCDD.

Figure 3 presents the temperature dependence of the PCDD/F yields for the flow/catalyst ratio of 5.5 (5.5 cc/min, 1 mg catalyst). Compared to the reaction over 3 mg of catalyst, DCDF yields increased significantly, and the maximum yield shifted about 75 °C lower in temperature. In contrast, the yields of both DD and MCDD were unaffected by the change in reaction conditions over the entire temperature range. This result supports observations of mechanistic as well as kinetic differences between the formation of PCDDs and PCDFs.

Figure 4 presents the distribution of the higher chlorinated PCDD/Fs that were observed in addition to the three principal condensation products. It is notable that no PCDFs other than the principal condensation product, 2,6-DCDF was observed. In contrast, higher chlorinated PCDDs (mono- through octa-) were detected, with the degree of chlorination increasing up to 350 °C. Above 350 °C, only DDs, MCDDs, and DCDFs were observed. This is a curious result since one might expect the more volatile, less chlorinated congeners to volatilize as the temperature increases.

Discussion

Mechanism of Formation of DD, MCDD, and DCDF

The observed sharp decline in yields above 475 °C can be attributed to one of two origins: (1) oxidative destruction of formed PCDD/Fs or (2) desorption or surface-induced destruction of the precursors. Similar behavior has been previously reported for the reaction of various chlorinated phenol isomers on copper chloride [22] or fly ash surfaces [17,23]. These authors suggested that the decline of PCDD/Fs yields at higher temperatures is related to their destruction or the instability of the catalyst. To clarify this issue, a closer examination of the chlorophenol oxidation process is necessary.

Greater than 95% of the MCP was completely oxidized to CO/CO$_2$ at temperatures above 350 °C. (cf. Fig. 5) Since the reaction was performed under pyrolytic conditions (no oxygen in the gas phase), the surface of the copper oxide was the source of oxygen for oxidation processes. This suggests that MCP was
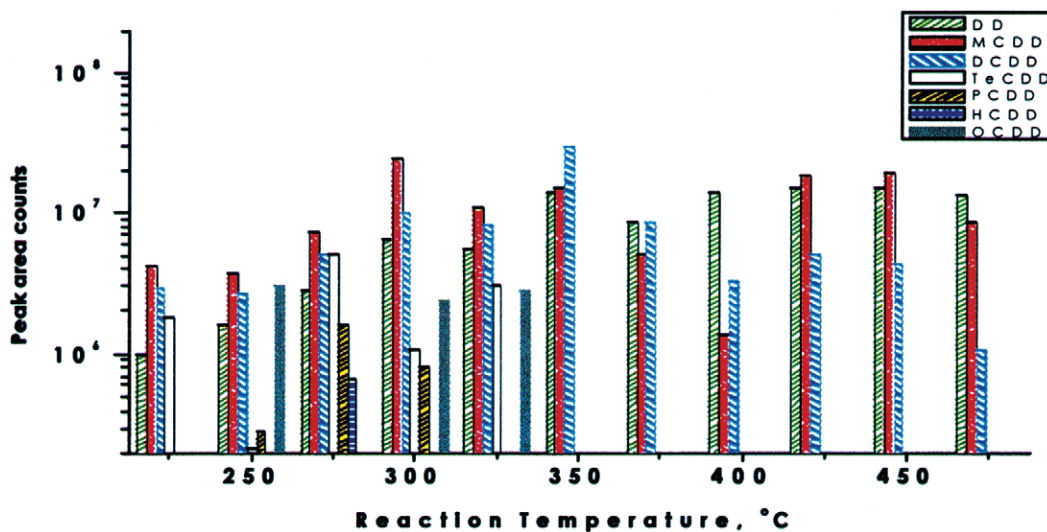
FIG. 4. PCDD homologue class distribution for 1 mg CuO/SiO$_2$. 4,6-DCDF was the only observed PCDF.
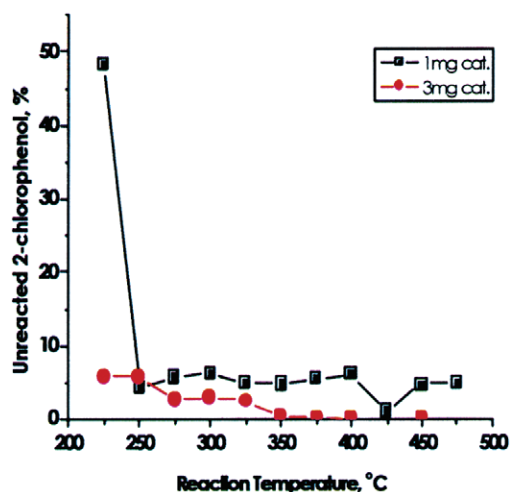

FIG. 5. Total conversion of 2-chlorophenol.

oxidized according to the Mars–van Krevelen reaction mechanism: surface oxygen atoms are consumed by the reagents, leaving oxygen vacancies on the surface. For the reaction performed over 3 mg of catalyst, a gradual decline of MCP breakthrough with increasing temperature was observed. However, when 1 mg of catalyst was used, the initial amount of unreacted 2-chlorophenol decreased sharply with increasing temperature and stabilized at 5% breakthrough. This interesting result indicates that when 1 mg of catalyst was used, surface oxygen deficiencies occurred that prevented the total oxidation of 2-chlorophenol at higher temperatures, namely, all available surface oxygens were consumed during the oxidation of adsorbed chlorophenol. As such, it is unlikely that the reduction in yields of PCDD/F at higher temperatures is due to their oxidation; consequently, desorption of precursors is the more likely source of the reduced yields above 450 °C.

Surface oxygen deficits result in a decrease in active oxidation sites. Thus, one can expect an increase in the number of adsorbed, unreacted MCP molecules. There are two general schemes for surface catalyzed reactions: Langmuir-Hinshelwood (LH), which assumes the reaction between two adsorbed surface species, and Eley-Rideal (ER), in which the reaction occurs between an adsorbed species and a gas-phase species. At high surface coverages, Θ, as in our experiments, the probability of the reaction between the two adsorbed species is increased. The mobility of the surface species is a function of temperature: the higher the temperature, the more rapid the migration of the species across the surface and the higher the collision frequency. However, the higher concentration of the surface species can compensate for their lower mobility at low temperature and result in the shift of the position of maximum yields of formation toward lower temperatures. This is exactly what was observed for the formation of DCDF, suggesting that it is formed by an LH mechanism. PCDD formation did not exhibit such a shift, and we suspect an ER mechanism.

Mechanism of Formation of Higher Chlorinated PCDDs

Higher chlorinated PCDDs were formed, while PCDFs were not. The degree of chlorination of
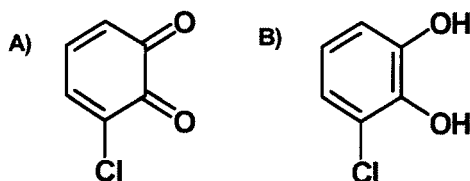
FIG. 6. Observed reaction by products/intermediates: a) 3-chloro-*o*-quinone; b) 3-chlorocatechol.

PCDDs increased up to 350 °C and decreased as the temperature increased. Clearly, there is surface-induced chlorination of dibenzo-*p*-dioxins, or its precursors, but not dibenzofurans.

It is possible that MCP is chlorinated before it reacts to form PCDD/Fs. In fact di-, tri- and even tetra-chlorinated phenols were observed. However, apart from the dichlorophenols, other polychlorinated phenols were in trace amounts. Taking into account the yield of MCDD formation from MCP (0.04%), it is unlikely that polychlorinated phenols can be precursors for the quantities of PCDD/F that were detected.

Since DD and MCDD concentrations did not decrease above 350 °C and the oxidizability of PCDDs decreases with increasing chlorination, it is unlikely that the that surface-induced oxidation is responsible for the reduction in tetra- through octa-CDDs above 350 °C [24]. Notably, there is an inverse correlation between the yield of DD and the yields of PCDDs, namely at 350 °C, where the tetra- through octa-CDDs disappear, the concentration of DD suddenly increases. This suggests that the

higher chlorinated PCDDs result from the chlorination of DD.

Thus, it appears that the desorption rate of DD increases significantly above 350 °C, resulting in increased yields of DD and decreased opportunity for chlorination and reduced yields of PCDDs. The yields of MCDD and DCDF do not exhibit a relationship with higher chlorinated PCDDs, suggesting that they are desorbed from the surface following their formation and are not susceptible to further surface-induced chlorination or dechlorination reactions.

We also note the formation of two reaction products which may play important roles in the formation of PCDD/F, 1,4-cyclohexadiene-4-chloro-5,6-one (or 3-chloro-*o*-quinone) and 3-chloro-1,2-benzendiol (or 3-chlorocatechol) (Fig. 6). These species, which have been partially oxygenated by reaction at the surface, were desorbed and were observable in the gaseous effluent of the reactor. Because they appear at lower temperatures than the PCDD/Fs, and their concentrations decrease as the concentrations of DD, MCDD, and DCDF increase, we believe that they may be reaction intermediates in the pathway to PCDD/F. They are also of considerable environmental interest as they are molecular derivatives of semiquinone radicals that can be very long lived, especially when associated with particulate matter [25–27]. As a class, semiquinone radicals are sufficiently long lived and powerful enough reducing agents to reduce molecular oxygen to the superoxide radical anion that can result in biological damage to exposed individuals [27,28].
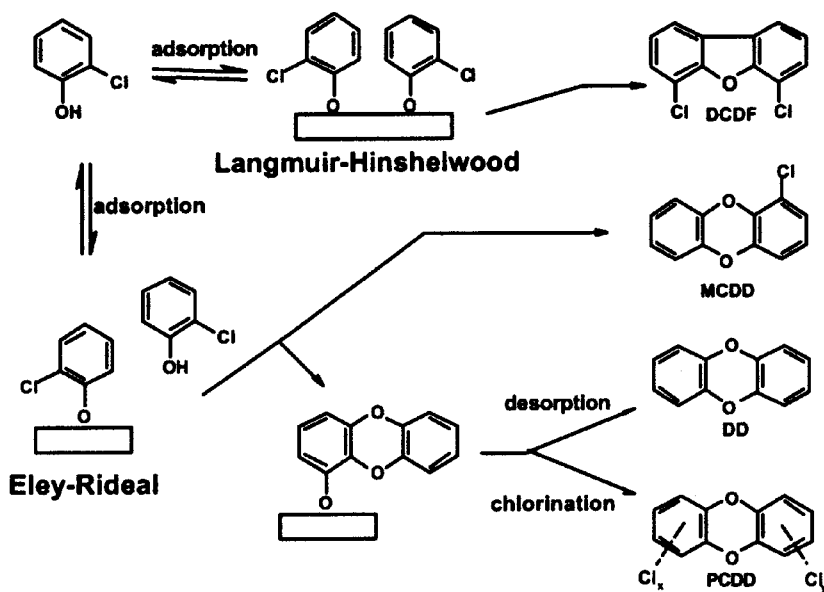

FIG. 7. Copper oxide–catalyzed formation of PCDDs and PCDF from pyrolysis of 2-chlorophenol.

Conclusions

PCDD/Fs were formed on the surface of supported copper oxide with significant yields. However, the main reaction pathway was MCP decomposition, even when the reaction was conducted under pyrolytic conditions. This indicates a Mars–van Krevelen–type of mechanism in which surface oxygen atoms are involved in PCDD/F formation.

The majority of the PCDD/Fs products were DCDF, DD, and MCDD, which are the possible direct condensation products of MCP. Formation of DCDF was found to be dependent on the surface species concentration, and we believe it is formed according to an LH mechanism. In contrast, this correlation was not observed for PCDDs, and the ER mechanism is proposed as the route of formation of DD and MCDD (Fig. 7).

DCDF and MCDD desorb from the surface immediately after formation, while DD remains adsorbed and is subject to chlorination to form higher chlorinated PCDDs. Higher chlorinated PCDFs are not observed due to the rapid desorption of DCDF prior to chlorination. This suggests that there are different routes of formation of DD, MCDD, and DCDF.

PCDD/Fs appear to be a side reaction of the oxidation process; and, consequently, MCP decomposition and condensation products are likely to have a common intermediate. If this is true, a surface other than copper oxide with a lower oxidative power (but still able to catalyze the oxidation process) could produce more PCDD/Fs.

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