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A Detailed Mechanism of the Surface-Mediated Formation of PCDD/F from the Oxidation of 2-Chlorophenol on a CuO/Silica Surface

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The formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) via a Cu(II)O-mediated reaction of 2-chlorophenol (2-MCP) has been studied in a packed bed reactor over a temperature range of 200−500 °C. Under oxidative conditions, the principle PCDD/F products were 1-monochlorodibenzo-*p*-dioxin (MCDD) > 4,6-dichlorodibenzofuran (DCDF) > dibenzo-*p*-dioxin (DD). EPR studies indicated the presence of a carbon-centered phenoxyl radical on the surface, which is attributed to chemisorption of 2-MCP at a copper oxide site followed by electron transfer to Cu(II) to form Cu(I) and a phenoxyl radical. The presence of a surface bound phenoxyl radical and the formation of MCDD, DCDF, and DD, which were also observed as the principle products of the gas-phase oxidation of 2-MCP, strongly suggest a surface-mediated mechanism involving many of the same radical and molecular species involved in the gas-phase formation of PCDD/F from 2-MCP. Reaction orders of 0.5−1.0 were observed for MCDD and DD formation, indicating an Eley−Rideal formation mechanism. Negative reaction orders were observed for DCDF formation, indicating a Langmuir−Hinshelwood formation mechanism. No highly chlorinated PCDFs were observed, suggesting a mechanism in which DCDF is desorbed from the surface before it can undergo additional chlorination. Highly chlorinated PCDDs were observed, which were consistent with a mechanism in which DD remained adsorbed to the surface and underwent additional chlorination. Chloro-*o*-quinone and chlorocatechol, which are precursors to semiquinone radicals, were also observed products. A detailed reaction mechanism accounting for all reported products is proposed.

I. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated furans (PCDD/F or “dioxins”) are among the most toxic known environmental pollutants. It is well established that combustion and other thermal processes are the principal origin of PCDD/F,[1−6] yet a detailed chemical mechanism that can account for the majority of their formation has eluded researchers even though it has been the subject of extensive research for the past two decades.[7−11] This research has resulted in different proposed theories on how dioxins are formed: (i) gas-phase formation from molecular precursors at temperatures >600 °C, (ii) condensation reactions of precursors catalyzed by transition metal oxides in “fly ash” at temperatures between 200 and 600 °C, and (iii) de novo oxidation and chlorination of elemental carbon in soot between 200 and 600 °C.[12−15]

Although considerable progress has been made on the gas-phase mechanism, it only accounts for about 30% of dioxin emissions.[16,17] Generally, it is accepted that dioxins can be formed from identifiable precursors such as chlorophenols and chlorobenzenes [18] through the reactions of the keto and enol forms of phenoxyl radicals.[19−21] These radicals can combine with other phenoxyl radicals, molecular chlorobenzenes, or phenols to form PCDD/F.

With respect to the surface-mediated processes, which are believed to account for on the order of 70% of all dioxin formation, it is known that transition metal oxides and chlorides play a significant role in dioxin formation.[11] Transition metals are present in the fly ashes in the exhaust and air pollution control devices of most combustion systems,[22,23] with copper and iron ions believed to be the most active. However, for surface-mediated processes, only semiglobal Eley-Rideal and Langmuir-Hinshelwood mechanisms have been proposed.[9,15,24,25] Because detailed reactions are not included in these mechanisms and the PCDD/F forming reactions are side-reactions of other surface process, there has been great confusion concerning the role and implications of surface-catalyzed dioxin formation. Does the surface-mediated reaction involve the same species as the gas-phase reaction, with the surface sites being only a medium for a low-temperature radical formation? Or, is the mechanism entirely different, involving different reactants and intermediates? This is one of the most intriguing questions remaining unanswered.

In an attempt to clarify some of these issues, we have performed a detailed study of the copper-catalyzed reaction of chlorinated phenols. Chlorinated phenols have been demonstrated to be the predominant precursors in the surface-catalyzed formation schemes of PCDD/F and are implicated as key intermediates in the de novo pathway.[14] Previous studies of surface-catalyzed reactions of chlorinated phenols have answered some questions but have also raised many issues due to the selection of highly chlorinated congeners for experimental study.[9,26−29] In some cases, complex surfaces, including real fly ash, were used.[15,26,30,31] Consequently, we chose to study the reaction of one of the simplest PCDD/F precursors, 2-chlorophenol, and use copper oxide supported on silica as a surrogate for fly ash.[32] In this paper, we present the reaction kinetic results of the transformations of 2-chlorophenol over a

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bed of copper oxide/silica under oxidative conditions and propose detailed surface-mediated mechanisms that account for the observed reaction products.

II. Experimental Section

The catalytic material (5% CuO/silica, m/m) was prepared by the method of incipient wetness. A water solution of copper(II) nitrate (Aldrich) of concentration chosen so as to obtain 5% CuO/SiO2 system was used as the active phase precursor. Silica powder (Aldrich, 500 m^2/g) was introduced into the equivalent volume of precursor solution for incipient wetness to occur. The suspension was then well mixed and dried at 120 °C for 24 h.

For the catalytic tests, 1 or 3 mg of a sample was placed between the quartz wool plugs in a fused-silica reactor (1 mm i.d.) in a well-characterized flow-reactor system setup. All transfer lines were maintained at isothermal conditions at 225 °C. Prior to each flow-reactor experiment, the samples were oxidized in situ at 500 °C for 1 h in 20% O_2/He mixture at a flow rate of 5.5 cm^3/min to convert the copper nitrate to CuO. 2-Monochlorophenol (2-MCP) (Aldrich) was introduced into 20% O_2/He reaction stream by a syringe pump through a vaporizer maintained at 180 °C. The constant rate of the injection was selected to obtain gas-phase concentration of 2-MCP of 88 ppm (v/v) to facilitate comparison of the results to previous gas-phase experiments.[32] The flow rate of the reacting mixture was 5.5 cm^3/min. For separate experiments in which the contact time was varied, the flow rate of the reactant was 1 cm^3/min. The reaction was studied over a temperature range of 225−500 °C. In some additional experiments, the 2-MCP concentration was varied from 29 to 177 ppm (v/v). All reported results reflect 1-h on-stream experiments.

The effluent products from the reactor were trapped at the head of capillary column (CP-Sil 8 phase 30 m, 0.25 mm i.d., 0.25 film thickness and analyzed after completion of the reaction using a GC-MS system (VARIAN SATURN 2000). The column was temperature programmed from −60 to 290 C at 15 °C/min. Mass spectra were obtained by running on full scale mode (10 to 650 amu) for 26 min.

The spent catalyst bed was subjected to extraction with methylene chloride in Micro Soxhlet extraction apparatus (Ace Glass) for 24 h. The extract was then condensed and analyzed via GC-MS for adsorbed reaction products. However, no PCDD/F were detected in the extract, chlorinated naphthalenes and phenols being the only compounds detected. Since no PCDD/F were found to be present on the spent catalyst bed, we can presume that all the products of interest were desorbed into the gas phase.

PCDD/F concentrations were calculated based on the peak area counts of chromatogram, based on the calibration made using CIL (Cambridge Isotope Lab) standards. 2-MCP breakthrough amounts were calculated based on the calibration using reagent compound. The yields of PCDD/F were calculated using the formula as follows:

$$Y = \left(\frac{C_{\mathrm{PCDD/F}}^{\mathrm{out}} \cdot 2}{C_{2-\mathrm{MCP}}^{\mathrm{in}}}\right) 100\%$$

where $C_{\mathrm{PCDD/F}}^{\mathrm{out}}$ is concentration of particular PCDD/F congeners formed (in moles) and $C_{2-\mathrm{MCP}}^{\mathrm{in}}$ is inlet amount of 2-MCP (in moles)

Experimental reaction rates were calculated assuming a simple power law-type expression ($R = kC^n$). Since the catalyst bed was very small and the kinetic analyses were performed at 250 °C where the 2-MCP conversion was low, we could assume a differential mode of operation of the reactor. Thus, the expression for the reaction rate is

$$R = \frac{C_{2-\mathrm{MCP}} \cdot x}{W \cdot t}$$

where $C_{2-\mathrm{MCP}}$ is the amount of 2-MCP (moles) introduced to the system, x is a molar fractional conversion toward a particular product, W is weight of catalyst (g), t is time on stream (h), and R is the reaction rate (mol g^{-1} h^{-1}). Studies to determine whether the reactions are kinetically controlled or diffusion controlled have been reported in a previous paper[32] and indicated that the reactor operates in the kinetic regime for the conditions reported in this manuscript.

Electron Paramagnetic Resonance (EPR). EPR spectra of 2-MCP dosed CuO/silica powder were obtained using a VARIAN E-109 EPR spectrometer. Samples were prepared as follows: CuO/silica powder was placed in quartz tubes connected to vacuum line and treated at 500 °C in air for 2 h. The temperature was then decreased to 200 °C and samples were evacuated to 1×10^{-2} atm. A reference sample was then sealed under vacuum. The CuO/silica sample was exposed to 4 Torr of 2-MCP at 200 °C for 2 min, evacuated to 1×10^{-2} atm and sealed under vacuum. The EPR parameters were set at 100-kHz, X-band; microwave frequency, 9.345 GHz; attenuation, 7 dB; modulation amplitude, 0.50 G; time constant, 0.032 s; receiver gain 5−500, and scan time, 4 min (10 Hz). For the g values/spin counts solid 1,1-diphenyl-2-picrylhydrazyl (DPPH, $\sim$50 μg) was used as a centerfield standard. EPR measurement was performed at room temperature.

III. Results

In a previous paper,[32] we reported the copper oxide catalyzed condensation of 2-MCP to form PCDD/F under pyrolytic conditions. We found that PCDD/F formation is a side reaction of 2-chlorophenol oxidation via the Mars-van Krevelen mechanism which involves transfer of oxygen atoms from the surface to the adsorbate. Moreover, the data presented therein indicated significant differences between the formation of PCDDs and PCDFs, which in turn resulted in the conjecture that they are formed according to two different mechanisms, Eley−Rideal (E−R) and Langmuir−Hinshelwood (L−H), respectively. The E−R mechanism involves the reaction between the adsorbed species and a gas-phase molecule, while L−H is the reaction between two surface-adsorbed species. However, on the basis of the pyrolysis data alone, we could not construct a detailed reaction mechanism. In combination with the following oxidation data, a detailed mechanism can be proposed (vide Discussion).

Figure 1 presents product data obtained with 1 mg of catalyst (3 mg resulted in complete oxidation of 2-MCP and condensation products). The main PCDD/F products detected were the same as under pyrolytic conditions: dibenzo-*p*-dioxin (DD), 1-monochloro dibenzo-*p*-dioxin (MCDD), and 4,6-dichlorodibenzofuran (DCDF). These are the same products expected based on gas-phase radical−molecule and radical−radical reactions.[13,20,21,33−35] However, the gas-phase reactions only occur above 600 °C.[20,21] In our study, PCDD/F formation occurred in the 200 to 500 °C range, which indicates the surface mediated process. Between 300 and 500 °C, significant quantities of more highly chlorinated PCDD/F are formed; however, MCDD is the dominant congener with a yield more than twice

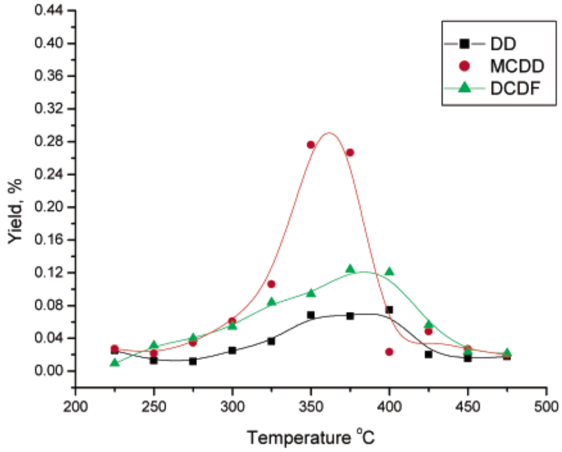


Figure 1. Gas-Phase PCDD/Fs products from oxidation of 2-MCP over CuO(5%)/SiO$_2$.

as high as other PCDD/F. Above 400 °C, MCDD yield dramatically drops below those of DD and DCDF. For reaction at >450 °C both DD and DCDF concentrations also decline significantly.

To obtain more information on the kinetics of the PCDD/F formation processes, experiments with varying feed stream concentration were performed. Figure 2 presents the natural logarithmic relation of reaction rates versus concentration of reactant (2-MCP) at 250 °C. Since PCDD/F formation is a marginal process of chlorophenol oxidation, this particular reaction temperature was chosen to avoid the effects of oxidation/decomposition of both reaction products and 2-MCP while preserving noticeable rates of PCDD/F formations. The observed scattering of the data is a result of very low concentration of analyzed products (ppb). The slope of the regression is the reaction order for formation of each of the products.

For the same reaction conditions (250 °C), the increase of fuel/catalyst ratio (F/C) resulted in a significant change in the product distribution (cf. Figure 3). With increasing F/C, a significant decrease in DCDF yield can be observed, while DD and MCDD show a moderate dependence. Simultaneously, another product, 1′,2-dichloro-1-hydroxy-diphenyl ether (DCH-DPE), appears whose yield gradually increases with F/C ratio, slowly reaching a plateau for high F/C values.

Figure 4 presents the temperature dependence of the congener distribution of PCDDs for both pyrolytic and excess oxygen conditions. Significant is the fact that for both conditions, no other PCDF congeners than 4,6-DCDF were detected. On the other hand, PCDDs are detected over the entire range of chlorination, i.e., from non-chlorinated to octachlorinated. Under pyrolytic conditions, higher chlorinated congeners disappear at temperatures above 350 °C. In contrast, for excess oxygen conditions, even more highly chlorinated PCDDs are detected above 350 °C than below that temperature and the total PCDD concentration is higher.

Figure 5 presents the yield of the reaction products, chloro-*o*-quinone (CQ) and chloro-catechol (CC) as a function of reaction temperature for both pyrolytic and excess oxygen conditions. CC yields initially increased with increasing reaction temperature and drastically decreased above 350 °C for both pyrolytic and oxidative conditions. In contrast, CQ varies significantly with reaction conditions. Under pyrolysis conditions, only small changes with temperature are observed up to 450 °C, while under oxidative conditions the CQ yield steadily increase with reaction temperature up to 400 °C before declining again. The yields of CQ under oxygen rich conditions are significantly higher than under pyrolysis.

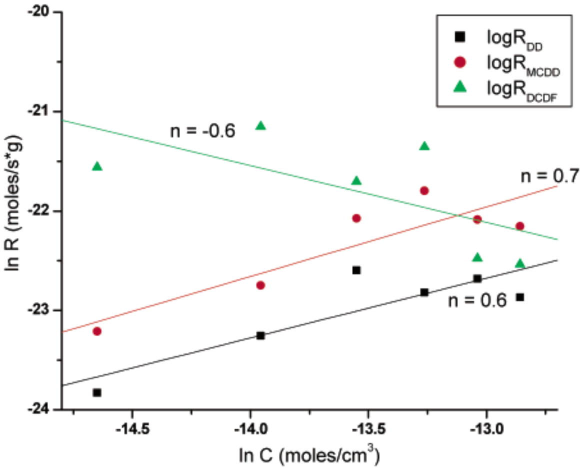


Figure 2. Kinetic rate order plot at 250 °C: 1 mg of CuO(5%)/SiO$_2$, 88 ppm 2-CPh, 20% O$_2$.

The results of EPR experiments of 2-chlorophenol adsorption over copper oxide/silica catalyst are presented in Figure 6A,B. The CuO/Silica sample shows a broad signal originating from Cu(II) complexes. When the sample was exposed to 4 Torr of 2-MCP at 200 °C for 2 min, trace A, sharp signal with a *g*-value of 2.0028 appeared superimposed on the broad Cu(II) signal.

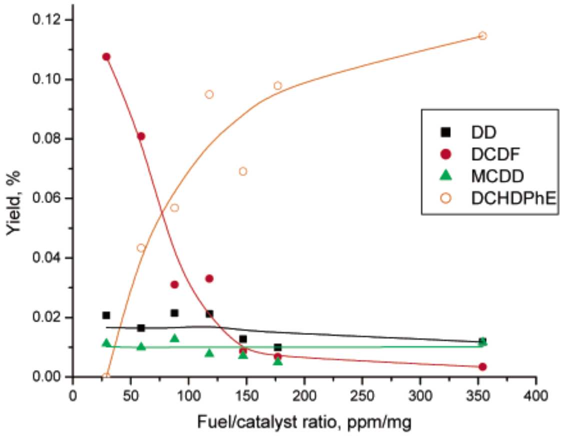


Figure 3. Conversion as a function of the catalyst load, 250 °C, 20% O$_2$

IV. Discussion

Eley−Rideal vs Langmuir−Hinshelwood Formation of PCDD and PCDF? In our previous paper concerning the CuO-catalyzed pyrolysis of 2-MCP, we discussed the differences in mechanism of PCDD and PCDF formation.[32] Pyrolytic conditions resulted in a significant surface oxygen deficit. This resulted in 2-MCP remaining adsorbed on the surface rather than being oxidized. Since the DCDF yield increased as the catalyst mass was decreased, we concluded that the DCDF yield directly correlated with the concentration of surface species. This argument is supported by the observation that the DCDF maximum shifted ∼100 °C lower in temperature when the catalyst mass was decreased by a factor of 3. This correlation between the surface concentration of adsorbed phenolic species and increased yield of DCDF was a foundation of the thesis that PCDFs are formed according to Langmuir−Hinshelwood mechanism under pyrolytic conditions. In contrast, the lack of a similar dependence for PCDDs suggested that they may be formed by an Eley−Rideal mechanism.

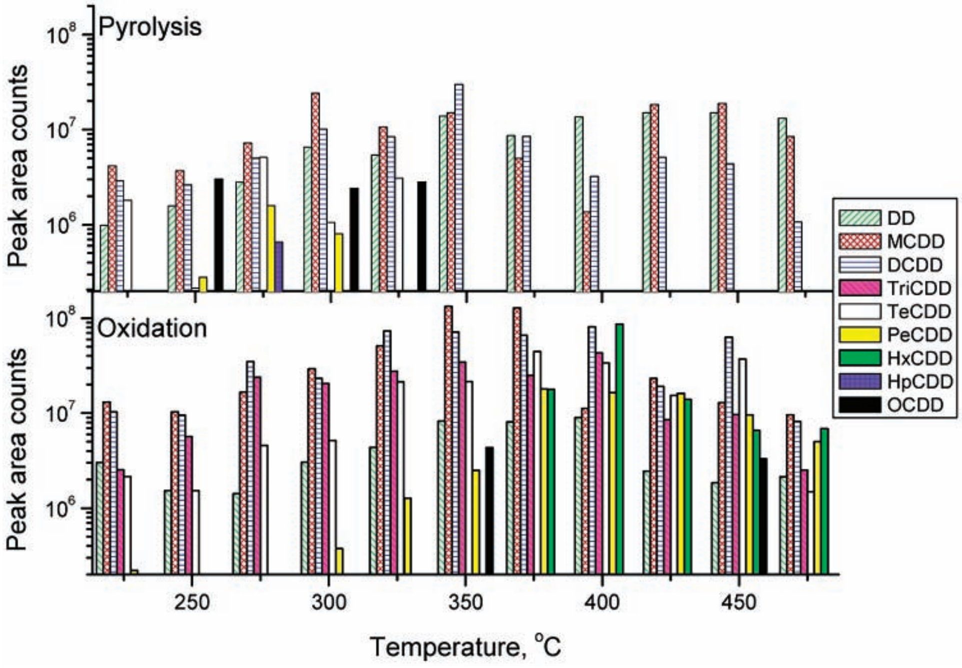


Figure 4. PCDD Congener distribution under pyrolytic and oxidative conditions. 1 mg of CuO(5%)/SiO_2, 88 ppm 2-CPh.

The data presented for excess oxygen conditions in this paper further underline the differences in PCDD and PCDF formation, as the PCDD/F yields presented in Figure 1 are very different from those reported earlier under pyrolytic conditions. A comparison of results under oxidative and pyrolytic conditions is presented in Table 1. While the DCDF yield decreased by only 25% with the addition of oxygen to the reaction system, both DD and MCDD yields show significant variation. In particular, the MCDD yield increased by a factor of 10. It is interesting that, contrary to pyrolytic conditions, where no specific maximum was found for MCDD on the temperature dependence curve, a narrow window of high yields is present under oxidative conditions. In contrast, the DD yields decreased by a factor of 2 under oxidative conditions and the maximum yield shifted 50 °C lower in temperature.

The significant differences in PCDD and PCDF formation are also reflected in the reaction kinetic parameters (cf. Figure 2). The rate orders of MCDD and DD formation are in the range of 0.5−1.0, which indicate the involvement of an adsorbed species in the reaction mechanism. In contrast, the rate order of the DCDF formation reaction is (−0.6). Negative rate orders of catalytic reactions may occur if the Langmuir−Hinshelwood mechanism is involved, i.e., when both reacting species are adsorbed on the surface. The negative rate orders have been observed previously for surface-catalyzed reaction of two reagents[36,37] and generally are a result of strong and competitive adsorption effects. However, our situation is somewhat different in that there is only one reactant in the gas phase and the product is a result of condensation of the same two species. A reasonable alternative explanation is a competitive reaction between the adsorbed species and a gas-phase molecule (eq 1)

$$A + A^* = B \tag{1}$$

$$A^* + A^* = AA \tag{2}$$

where A* represents the adsorbed surface species and A is the gas phase molecule. In this case, increasing concentration of the gas phase species A will reduce the concentration of the surface (adsorbed) species A* due to an increase in the rate of formation of B by reaction 1. Consequently, the rate of reaction 2 and formation of AA will decline because of the competitive loss of A* due to reaction 1. This phenomenon has been previously observed[25] for the phenyl coupling reaction.

In our study, the formation curves of DCHDPE (cf. Scheme 1) and DCDF are mirror images (cf. Figure 3). This indicates a competitive character of these two products and supports our

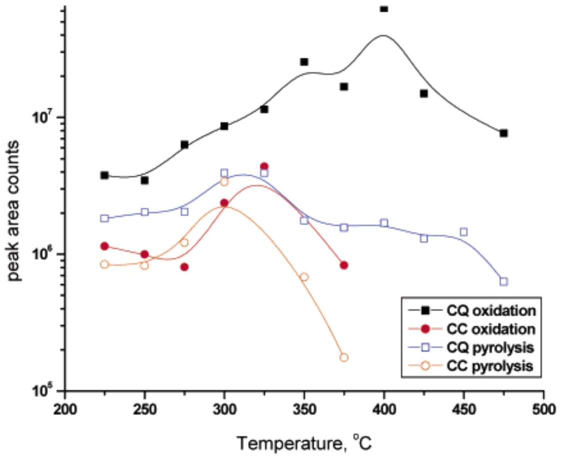
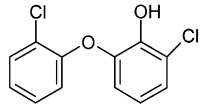


Figure 5. Chloro-quinones and chloro-catechols formation as a function of temperature and reaction conditions.

TABLE 1: Comparison of Maximum PCDD/F Yields at Pyrolytic and Oxidative Conditions

	pyrolysis		oxidation	
product	max yield (%)	*T* (°C)	max yield (%}	*T* (°C)
DD	~0.13	425−450	0.07	400
MCDD	~0.03	225−475	0.28	325−350
DCDF	0.16	375	0.12	375

SCHEME 1: 1,2′-Dichloro-1′-hydroxy-diphenyl Ether (DCHDPhE)



earlier conjecture that DCDF is formed by a Langmuir–Hinshelwood mechanism. At higher chlorophenol concentrations, a competitive reaction occurs with gas phase 2-MCP resulting in DCHDPE formation. This type of behavior is not observed for PCDDs. Under pyrolytic conditions, we reported that unlike the DCDF, whose yield increased and formation maximum shifted toward lower temperatures with a decrease of catalyst load, PCDD formation was not dependent on the concentration of the surface sites.[32] These two observations suggest an Eley–Rideal mechanism for DD and MCDD formation.

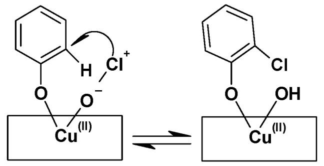
The differences between the L–H and E–R mechanisms should result in significant differences in the rate orders, i.e., the L–H reactions generally have lower reaction orders for similar reactions,[38] which is observed in our studies. These mechanistic differences can explain observed differences between the PCDF and PCDD formation. An Eley–Rideal mechanism was recently proposed for de novo formation of PCDDs, where partially oxidized polynuclear aromatic hydrocarbons (PAH) bonded to the carbon matrix reacted with a gas-phase chlorophenol forming PCDDs.[14]

Surface Catalyzed Chlorination Reactions. Since the MCDD formation rate order is slightly higher than for DD, we expect stronger adsorption effects for DD formation. In fact, our previous experiments suggested that DD remains adsorbed on the surface, while MCDD is desorbed immediately after it is formed.[32] Accordingly, DD is more prone to additional surface reactions such as chlorination. This conclusion may also well be applied to explain the observed, unexpected differences in MCDD and DD yields under oxidative conditions (Figure 1, Table 1).

MCDD is not subject to subsequent surface reactions and its yield increases compared to pyrolytic conditions, which directly reflects the effect of oxygen on the rate of formation. The addition of oxygen could also increase DD formation; however, since it remains adsorbed on the surface it can undergo a series of additional surface-catalyzed oxidation reactions. This thesis is supported by the observation that DD has a maximum yield under pyrolytic conditions at 450 °C, but has an almost undetectable yield at the same temperature under oxidative conditions. Moreover, the chlorination process can contribute to the decline of the DD yield. In fact, formation of higher chlorinated congeners through the chlorination process is associated with the adsorbed DD (vide infra), and a significant increase in the total PCDD yield compared to pyrolytic conditions (Figure 4) is observed. The majority of the PCDD congeners are highly chlorinated PCDDs. These effects can justify the observed “formal” decrease of DD yield under oxidative conditions.

The effect of oxygen on the degree of chlorination of PCDD/F needs more attention. Higher chlorinated PCDFs were not detected under oxidative or pyrolytic conditions which we attribute to immediate desorption of the initially formed DCDF. In contrast, more highly chlorinated PCDDs were formed under oxidative than pyrolytic conditions (cf. Figure 4). However, formation of highly chlorinated PCDDs is suppressed above 350 °C under pyrolytic conditions in which the rate of desorption is higher than the rate of chlorination.[32] Conversely, under oxidative conditions, the chlorination process is even more effective above 350 °C than below this temperature. Considering that, under pyrolytic conditions, DD desorption becomes significant at 350 °C (sharp increase of DD yield), it can be concluded that under oxidative conditions the rate of chlorination of PCDDs is greater than the rate of desorption. This explains the decrease in DD under oxidative conditions, viz., it is being chlorinated to form highly chlorinated PCDDs. The presence of oxygen is also affecting the chlorination of other products, i.e., significantly more polychlorinated phenols (PCPs) are formed under oxidative conditions up to 375 °C. Above this temperature PCP concentrations are comparable for both oxidative and pyrolytic conditions. Dechlorination of reactants, intermediates, or products was not observed, i.e., we have not observed non-chlorinated phenols, benzenes, or dibenzofuran in the gas-phase products of the process.

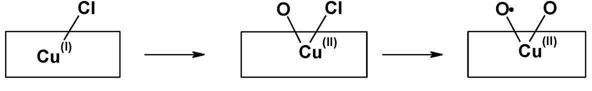
SCHEME 2: Chlorination by Surface Hypochlorite Ion



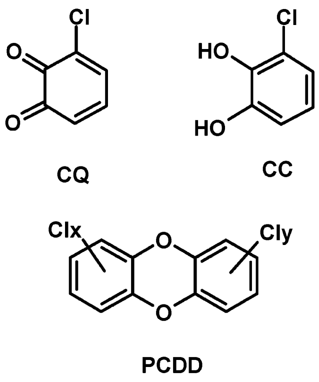
Various mechanisms of PCDD/F chlorination have been proposed,[15] including chlorination by Cl_2 formed either in the Deacon reaction, surface chloride decomposition, or direct chlorination by metal chlorides.[39] Recent studies have shown that the surface chloride ions are very effective chlorinating agents and exchange between the organic phase and surface chlorides is fast.[30,40] The presence of surface, metal chloride species in our experiments are the result of reaction between the surface hydroxides and oxides with HCl which is present as a result of oxidation of 2-MCP.

The effect of oxygen is explained in terms of reoxidation of surface copper (or other metal ion) since the lower oxidation state of cations are retarding the chlorination process.[41] However, this explanation does not agree with the results obtained in our experiments. Since 95% of the 2-MCP is completely oxidized to CO and CO_2 under pyrolytic conditions, there are enough Cu(II) surface sites for 2-MCP oxidation such that chlorination should not be limited. Under oxidative conditions, significant chlorination is observed above 350 °C. Surface bound DD is subject to two competitive processes: desorption and chlorination. With increasing reaction temperature, the rate of desorption is fast enough to prevent chlorination above 350 °C. However, under oxidative conditions, highly chlorinated PCDDs are detected, and, above 350 °C, their concentration is even higher, suggesting that the rate of chlorination is higher in the presence of oxygen than pyrolysis. These two observations indicate that in the presence of oxygen, other reagents may be formed with more chlorinating power than chloride ions, e.g., surface hypochlorite ions (cf. Scheme 2). In fact, it has been reported[42] that the *ortho*- to *para*-chlorophenol ratio observed during the chlorination of phenol over fly ash surfaces in the presence of oxygen was exactly the same as those observed for chlorination of phenol with *tert*-butyl hypochlorite. The formation of surface hypochlorite species could explain the differences between the degree of chlorination with and without oxygen present. In such a case, surface-catalyzed chlorination of the adsorbed aromatic species would proceed via electrophilic substitution of the aromatic hydrogen atom (Scheme 3). The chlorinated aryl compound can further undergo isomerization forming different isomers. Additional experiments are indicated concerning the

SCHEME 3: Formation of Surface Hypochlorite Species



SCHEME 4: Chloro-quinone (CQ), Chloro-catechol (CC), and PCDD



identification and nature of the species responsible for chlorination under oxygen-rich conditions.

Intermediates. Under pyrolytic conditions, two possible intermediates in the formation of PCDD/F were recognized, i.e., 3-chloro-1,2-benzendiol (3-chlorocatechol or CC) and 1,4-cyclohexadiene-4-chloro-5,6-one (chloro-*o*-quinone or CQ). Similar products have been previously reported as intermediates of the phenol oxidation processes. In particular, during the photocatalytic oxidation of phenols in solution, catechols and quinones were detected.[43−45] Because CQ and CC both contain ortho oxygens atoms, they are likely intermediates in the formation of oligomers of 2-MCP (Scheme 4). The data obtained under pyrolytic conditions indicate a correlation between the CC and PCDD formation, i.e., both DD and CC increase with temperature until 350 °C, where significant increase in DD and drastic decline in CC yields are observed.

CQ may be a product of further oxidation of CC, or they may share a common precursor.[46] Figure 5 presents a comparison of CC and CQ formation as a function of temperature under pyrolytic and oxidative conditions. The yield of CC is slightly increased in the presence of oxygen, while the overall shapes of the pyrolysis and oxidation curves are otherwise similar. In contrast, the presence of molecular oxygen increases the CQ yields almost 2 orders of magnitude in the low-temperature region and a factor of 10 above 350 °C. Since CQ is a product of either CC oxidation or they share a common precursor, one might anticipate that CC would be also formed at a higher rate when oxygen is present in the stream and therefore have a higher concentration. However, the lack of a significant increase in the CC concentration in the effluent indicates that it can undergo further transformations. PCDD yields increase significantly under oxidative conditions (contrary to PCDF which are not affected by the presence of oxygen). Thus, we conclude that CC is indeed involved in the formation of the PCDDs, which is supported by the fact that at temperatures where PCDD yields increase sharply (above 350 °C), the CC concentration drops drastically.

Detailed Reaction Mechanism. The first step of every catalytic reaction requires adsorption of the reactant on the catalytic surface. Phenol and chlorophenol adsorption has been studied extensively. It is generally believed that phenols adsorb on the surfaces through H_2O elimination at surface oxide and hydroxyl sites resulting in surface phenolate formation.[31,47−50] However, the subsequent steps in their surface reaction are not well understood. Some authors propose that phenolates withdraw electrons from the metal site leading to carbanion formation.[51] However, since chlorophenols are known to be electron donors,[52] it is more likely that the electron transfer is from chlorophenolate to the metal cation site (M^{n+}) forming surface-associated chlorophenoxyl radical and $M^{(n+)-1}$ site. Such interaction was proposed [48] for the phenol adsorption over a Co−Fe−O system.

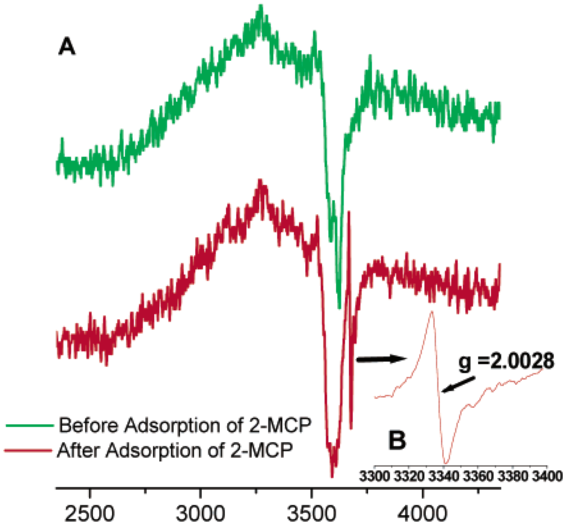


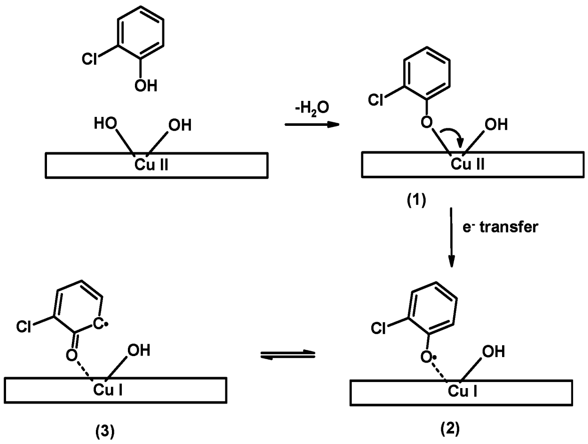
Figure 6. EPR spectra of CuO(5%)/SiO_2 before and after 2-MCP adsorption.

The results of our EPR studies on 2-MCP adsorption over copper oxide/silica catalyst are presented in Figure 6. The CuO/silica sample displays a broad signal originating from Cu(II) complexes. When the sample was exposed to 4 Torr of 2-MCP at 200 °C for 2 min, a new, sharp signal with a *g*-value of 2.0028 appeared superimposed on the broad copper signal (cf. Figure 6b), which we attribute to a radical formed as a result of chlorophenol interactions with copper oxide surface. Similar interaction was reported earlier for various chlorophenol isomers.[53,54] Signals with similar parameters were observed for adsorption of 4-, and 3-chlorophenol, DD and 4-chloroanisole over Cu(II) smectites.[54−56] The authors of the latter have attributed this signal to the formation of the keto form of a radical with the electron delocalized on the ortho and para positions of the ring. This explanation is also plausible in our case, since oxygen centered radicals easily convert to their respective keto forms,[8,13,21,34] and they have much higher *g*-values.[57]

This experiment confirms that upon adsorption of 2-chlorophenol over copper oxide, the interaction of adsorbed phenolate species with the surface results in formation of phenoxyl radical. This type of radical is resonance stabilized with the radical center delocalized. The most favorable positions for the electron to be localized are the oxygen atom and the ortho and para positions in the ring.[8,13] Taking into the account the above discussion, the proposed adsorption mechanism is presented in Scheme 5.

A very interesting conclusion can be drawn by comparison of our results with the EPR studies of 2,4,6-trichlorophenol adsorbed on copper oxide.[58] The authors of this work have detected a radical signal with $g = 2.0063$ and attributed it to adsorbed phenoxyl radical species. This is in contrast with our case, where the *g*-value was 2.0028. On the basis of the *g*-value we attribute our signal from 2-MCP to a carbon centered radical, while the signal observed for 2,4,6-TCP was attributed to an oxygen-centered radical. This difference suggests that if ortho and para positions in the ring are substituted (this is true at least for chlorine) the equilibrium between different mesomers is shifted toward the oxygen-centered phenoxyl radicals. When ortho or para positions are not substituted, the carbon centered,

SCHEME 5: Adsorption of 2-MCP on Copper (II) Oxide



keto form of the radical appears to be more stable on the surface (cf. Scheme 5).

This finding has implications for the mechanism of formation of PCDDs and PCDFs. Two different surface mechanisms are involved in PCDD/F formation (vide supra); PCDFs are formed according to a Langmuir−Hinshelwood pathway and PCDDs are produced as a result of an Eley−Rideal mechanism. The surface species (3) presented in Scheme 5 is a surface equivalent for the gas-phase, carbon-centered radical that is a PCDF precursor.[21,34] We can expect that reaction of two surface keto-, carbon-centered radicals will result in the formation of PCDFs (cf. Scheme 6). As a result of surface radical−radical interaction they undergo recombination and tautomerization leading to species.[4] The adsorbed species eliminates a hydrogen to form species [5] as one of the Cu(I) ions is oxidized back to Cu(II). Ring closure then occurs via a cyclic transition state that results in regeneration of the surface hydroxyl group on Cu(II) in a catalytic cycle. The desorption of 4,6-PCDF from the surface as it is formed explains the lack of observation of more highly chlorinated PCDFs.

CC and CQ are also formed from species 3, but by a parallel reaction pathway. Species 3 reacts with the terminal oxygen ion of the copper oxide surface (cf. Scheme 7) forming species 7. A similar surface process has been previously reported;[48] however, the proposed mechanism involved bonding between a carbon center and reduced metal. Since the metal sites are coordinated to more than one terminal oxygen ligand, we believe that the reaction involves the latter. This species can further react via two pathways: desorption followed by hydrogen elimination as copper is reduced to Cu(0) and form CQ, or tautomerization to surface species.[8] Species 8 results in the formation of CC, and Cu(0) is again formed. Species 8 can also be subject to chlorination. In fact, trace quantities of dichlorocatechol were detected in the gas phase effluent. However, since the concentration of the latter is very low, it is reasonable to assume that species 8 transforms rapidly to other surface associated structures, preventing chlorination of surface-bound catechol.

CC is an intermediate in PCDD formation, which is reflected in correlation of CC and DD yields. Species 8 can react with gas-phase 2-MCP (cf. Scheme 8). There are two possible modes of attack, each of them leading to different surface species (9 and 11) and, as a consequence, different reaction products. In Scheme 8a, MCDD is formed as it is desorbed from the surface following hydrogen transfer to the surface via the same cyclic pathway proposed in Scheme 5. In contrast in Scheme 8b, the formation of DD involves ring closure via HCl elimination, and DD remains attached to the surface. The attachment of DD to the surface explains its lower concentration than DCDF or MCDD as well as the presence of higher PCDDs (but not higher chlorinated PCDFs), i.e., DD is chlorinated, while it is chemisorbed to the surface. At temperature >350 °C the C−O−Cu bond is likely to rupture, producing gas-phase DD (after hydrogen insertion), which explains the drastic increase in DD yield above this temperature.

It is interesting to note that DCHDPE formation increases as DCDF concentrations decrease. We believe this is the result of the reaction between the surface bound radical (3) with the gas-phase chlorophenol (Scheme 9).

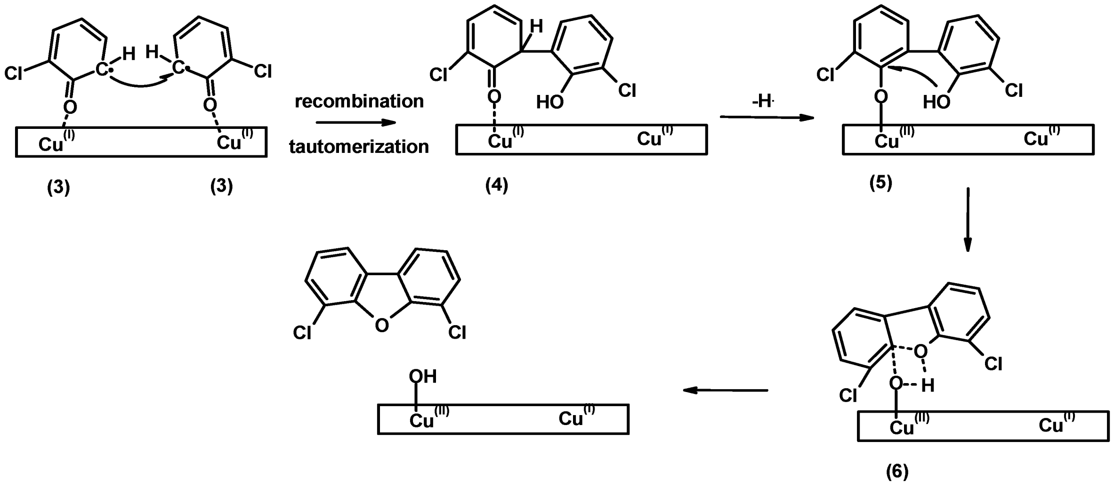
V. Conclusions

The results of this study have multiple implications for copper-catalyzed PCDD/F formation from chlorinated phenols.

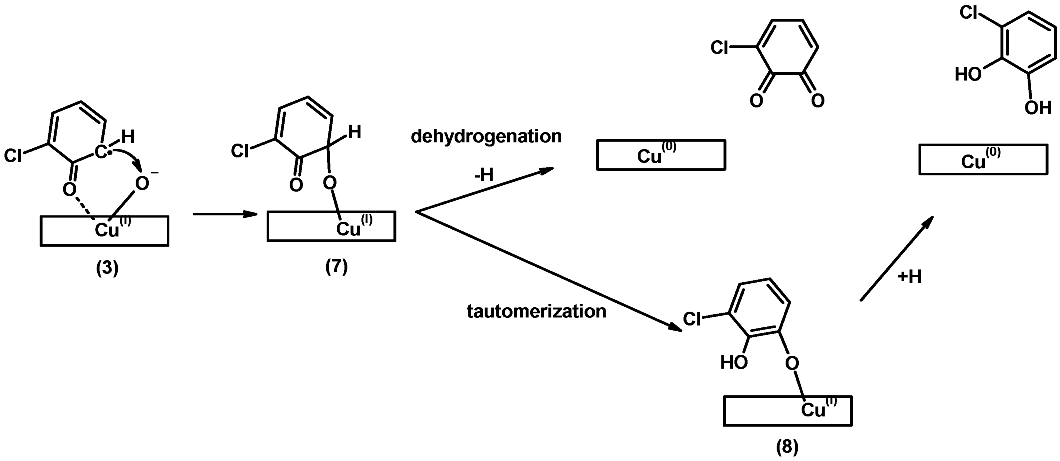
(i) The major PCDD/F products are the same as those predicted and observed for the gas-phase reaction of 2-MCP, i.e., MCDD > DCDF > DD. This is attributable to a general transferrability of the gas-phase radical−radical and radical−molecule mechanisms of formation to the surface. PCDD/F were formed as low as 225 °C and reached a maximum in the 325−475 °C temperature range.

(ii) Upon 2-monochlorophenol adsorption on CuO/silica catalyst, an EPR signal with a *g*-value of 2.0028 was observed.

SCHEME 6: Surface-Mediated Formation of DCDF



SCHEME 7: Surface-Mediated Chloro-catechol and Chloro-quinone Formation



On the basis of comparison to other studies in the literature, it is assignable as the carbon-centered, keto-mesomer of phenoxyl radical. This further supports the contention that surface-assisted radical reactions are active in PCDD/F formation.

(iii) A negative reaction order was observed for DCDF formation, indicating a Langmuir−Hinshelwood mechanism of formation that involved two surface adsorbed chlorophenols. Positive reaction orders were observed for MCDD and DD formation. For the latter two, an Eley−Rideal mechanism involving one surface adsorbed and one gas-phase chlorophenol molecules can explain the observed product distribution.

(iv) Increasing the concentration of 2-MCP reduced the yield of DCDF. This is attributable to the more rapid rate of the competing reaction of the surface adsorbed chlorophenoxyl with gas phase 2-MCP than the reaction between two surface bound species. As a result dichloro-hydoxy diphenyl ether (DCHDPE) is formed.

(v) The only observed PCDF was 4,6-dichloro-dibenzofuran. This was attributed to a mechanism of formation in which DCDF was immediately desorbed from the surface upon formation such that no additional chlorination could occur.

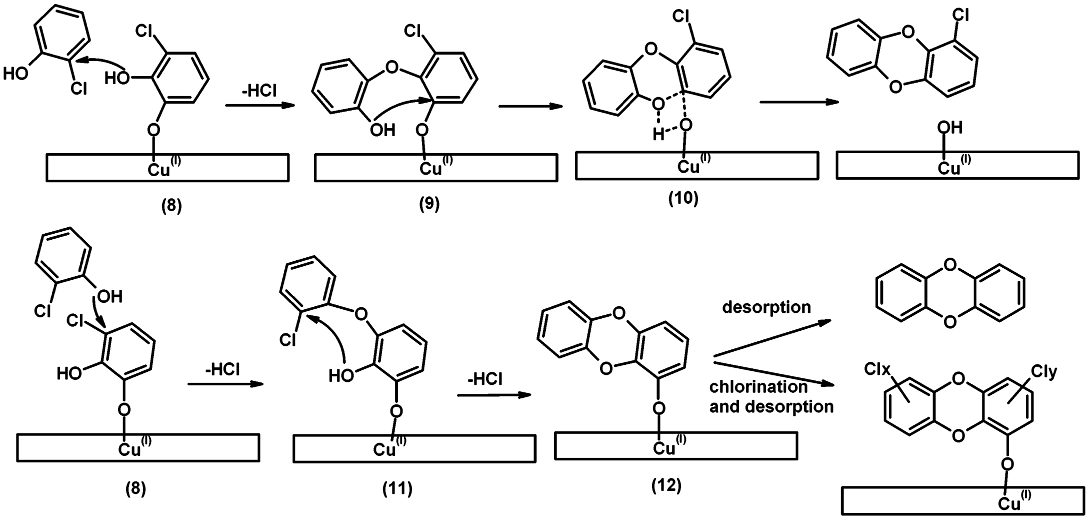
(vi) Highly chlorinated congeners of PCDD were observed in addition to MCDD and DD. Two different pathways of their formation were proposed. Like DCDF, MCDD is immediately desorbed upon formation. DD remains chemisorbed and undergoes chlorination. In contrast, at higher temperature (>350 °C) under pyrolytic conditions, highly chlorinated PCDDs were not observed due to DD desorption prior to chlorination.

(vii) Chlorination is enhanced in the presence of oxygen (versus pyrolysis) due to the formation of surface hypochlorite species.

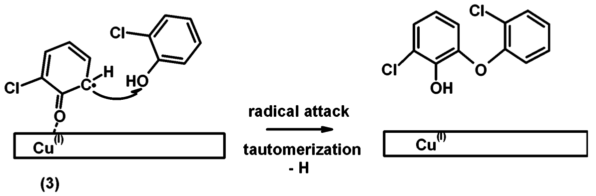
(viii) Chlorinated catechol and chlorinated quinone are formed via competitive side reactions. Adsorbed catechol is an intermediate in formation of PCDDs. Both catechols and quinones are precursors to semiquinone type radicals that are known to reduce molecular oxygen to superoxide.

This work also has implications for the possible involvement of other species, i.e., chlorinated benzenes, in the formation of PCDD/F. It is reasonably well established that the exhaust of incinerators contain higher concentrations of chlorinated benzenes than chlorinated phenols.[59−61] On the basis of our proposed mechanism of formation, this suggests significant consequences. It is possible, even likely, that chlorobenzenes will adsorb on transition metal surfaces by HCl elimination to again form surface phenoxyls. If gas-phase chlorophenols are also present, surface-catalyzed PCDF formation is limited by the competition with the fast reaction of surface bound phenoxyls with gas-phase chlorophenols that lead to side-products such as DCHDPE. However, if chlorobenzenes are the dominant gas-phase species, there will be minimal competition with the Langmuir−Hinshelwood surface reaction to form PCDFs because the reaction of surface-bound chlorophenoxyl

SCHEME 8: Surface-Mediated MCDD and DD Formation



SCHEME 9: Competitive Reaction of DCDF Precursor with Gas-Phase 2-MCP



with gas-phase chlorobenzenes is slower than with gas-phase chlorophenols. This results in increased yields of PCDFs. This can explain the difference between laboratory studies of chlorinated phenols, which result in very high PCDD to PCDF ratios, and full-scale measurements that indicate low PCDD to PCDF ratios.

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