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FTIR Investigation of 2-Chlorophenol Chemisorption on a Silica Surface from 200 to 500 °C

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The time-dependent chemisorption of 2-chlorophenol on a fumed silica surface was studied in situ from 200 to 500 °C using a temperature-controlled dosing cell and FTIR absorption spectroscopy. 2-Chlorophenol was found to chemisorb at isolated and geminal surface hydroxyl sites. 2-Chlorophenol chemisorption and subsequent surface oxidation resulted in a mixture of chlorophenolate and partial oxidation products, such as formates and acetates. The rates of chemisorption were measured, and the activation energy of adsorption was found to be 15 ± 4 kJ mol^{-1} for a fast, initial reaction and 22 ± 2 kJ mol^{-1} for a slower reaction at higher surface coverage. This work was motivated by the observation that combustion-generated fly ash mediates the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) at temperatures between 250 and 450 °C. Although transition metals such as copper are known to catalyze or mediate this reaction, silica is the major component of fly ash and chemisorption at higher concentration surface sites of silica must have a significant impact on the surface-mediated PCDD/F formation on fly ash surfaces.

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), or dioxins, are persistent, ubiquitous contaminants first discovered in the effluent of a municipal waste incinerator in 1977, and their emissions continue to be an important environmental issue.[1,2] Although emissions from municipal and hazardous waste combustors have received the most attention, PCDD/F appear to be formed and emitted from any thermal process with a source of chlorine and carbon.[3] Both gas-phase and heterogeneous formation pathways have been proposed to account for PCDD/F formation; however, it is generally accepted that surface-mediated formation is responsible for the majority of emissions.[2−7]

Surface-mediated formation occurs at temperatures between 250 and 450 °C and is accelerated by the presence of transition metals, with copper and iron being the most often studied and abundant metals in fly ash.[2,16,17] Chlorinated phenols are generally considered to be the dominant precursor to PCDD/F and have been identified as intermediates in de novo formation.[10,18]

Surface-mediated formation of PCDD/F from chlorophenols has been effectively studied using classical catalytic reaction models such as Langmuir−Hinshelwood (LH) and Eley−Rideal (ER) models.[17,19] The first step involved in these reactions is adsorption of chlorophenol to the catalytic surface site to yield chlorophenolate, where it then reacts with either an adjacent, adsorbed chlorophenol (LH) or gas-phase chlorophenol (ER) to form PCDD/F. There is evidence to suggest that surface-stabilized chlorophenoxy radicals form PCDD/F through reaction analogous to the gas-phase pathways.[17] These studies have proven to be very useful in describing global kinetics of dioxin formation, but in situ spectroscopic studies are needed to clarify the nature and mechanism of reaction of PCDD/F precursors at potentially active sites.

In this manuscript, we present the results of an FTIR spectroscopic study in which we explored the nature of chemisorption of 2-chlorophenol, a known dioxin precursor, on silica, which is a major component of fly ash. By limiting the surrogate fly ash to one component, we hoped to gain insight into the mechanisms of adsorption and measure rates of adsorption. Although the actual conversion of chlorinated phenols to PCDD/F is through redox reactions of transition metals such as copper, the reaction first requires the chlorophenol precursor to chemisorb to the surface. Because the concentration of reactive surface sites in combustion-generated fly ash is much higher for silica than for trace metal components, a significant fraction of the chlorophenols must adsorb at silica sites. Thus, this study is a necessary step in the study of more complex systems containing redox-active trace metals.

Experimental Section

Time-dependent adsorption of 2-chlorophenol on silica was monitored in situ from 200 to 500 °C with Fourier transform infrared (FTIR) spectroscopy using a temperature-controlled dosing cell. All FTIR spectra were collected using a Midac M2000 series Fourier transform infrared spectrometer. Spectra were collected in the absorbance mode from 4000 to 1100 cm^{-1} with 2 cm^{-1} resolution. The region below 1275 cm^{-1} could not be examined due to strong absorption by the silica.

Dosing Cell. A detailed description of the dosing cell has been given elsewhere,[20] and the dosing cell used is similar to a system described by Basu et al.[21] Briefly, the cell consists of a stainless steel cube with six ports that accept 2.75 in. conflat flanges. The dimensions of the cell are such that it can be placed directly into the FTIR sample compartment. In the center of the cell is a 2.5 cm^2 square of tungsten mesh fastened across two copper posts that extend from a high current electrical/thermocouple feedthrough. The silica sample is supported on

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the grid and resistively heated. The surface temperature is measured with a 0.08 mm type K thermocouple spot-welded to the top center of the grid. Surface temperatures from ambient to 900 °C can be achieved. The cell is equipped with CaF_2 transmission windows embedded in conflat flanges.

Dosant vapor is introduced to the cell from an evacuated sidearm dosing port containing liquid 2-chlorophenol. The gas-phase concentration of the dosant is limited to that of its vapor pressure. For 2-chlorophenol, this is ca. 1.42 Torr, which is sufficient to ensure pseudo-first-order reaction conditions, with respect to 2-chlorophenol, in which the surface is exposed to an excess 2-chlorophenol during the entire course of the reaction. The cell is connected to a rotary vane/turbomolecular pump combination that permits evacuation to 10^{-6} Torr. All experiments were conducted under oxygen-free conditions unless stated otherwise.

Sample Preparation and Data Collection. The silica substrate chosen for the experiments was Cabosil, a high purity, fumed silica with a surface area of approximately 250 m^2/g. An acetone slurry containing 0.25 g of Cabosil in 125 mL of solvent was prepared using an ultrasonic bath. An atomizer was used to evenly coat the entire tungsten mesh with a fine mist of the suspension. By heating the grid surface to ~70 °C, the solvent was flash-evaporated leaving behind a uniform layer of the substrate over the voids in the grid.[21] The total amount of powder deposited on the grid was typically 10−15 mg. Once supported on the grid, the silica was held at 375 °C for 20 min in air to remove any remaining solvent and organic impurities in the material.

Prior to dosing with 2-chlorophenol, the silica sample was heated under vacuum at 800 °C for 20 min. This procedure removes all bound and molecular water and converts all hydrogen bonded, surface hydroxyl groups to siloxanes. Isolated, freely vibrating hydroxyl groups remain on the surface and give rise to a sharp absorption band at 3747 cm^{-1}. Shoulders on each side of this absorption band at 3743 and 3751 cm^{-1} are due to freely vibrating geminal hydroxyl groups that are spaced far enough apart as not to mutually hydrogen bond; thus they are not converted to siloxanes during the thermal pretreatment.[22] This method of surface pretreatment facilitates kinetic measurement, as the rate of 2-chlorophenol chemisorption will be determined by measuring the rate of disappearance of surface hydroxyl groups. This technique has been used to measure the rate of adsorption of chlorosilanes on Cabosil.[22]

The substrate temperature was raised to reaction temperature, and 2-chlorophenol vapor was introduced into the cell to initiate the reaction and held for the desired reaction interval. One significant feature of the dosing cell is the ability to rapidly heat and cool the sample, because of the low heat capacity of the tungsten grid. The sample can be heated or cooled in less than 5 s, thus allowing one to rapidly initiate and quench the reaction. This allows for time-dependent spectral studies because chemisorption of the 2-chlorophenol can be stopped at a known reaction time and a spectrum can be acquired.

Before collecting spectra, the supply of 2-chlorophenol was isolated and the cell evacuated to 5×10^{-6} Torr and held for 10 min. The surface temperature was held at 150 °C during cell evacuation. This ensures that all free and physisorbed chlorophenol was removed from the cell, thus leaving only chemically adsorbed species on the surface. The standard for an adsorbate to be chemisorbed is that it remains on the surface after evacuation, and control experiments demonstrated this to be the case for our system. Additionally, when physisorbed 2-chlorophenol is present on the surface, an absorption band due to phenolic O−H bending is observed at 1338 cm^{-1}. This band is not observed after cell evacuation. After collecting the spectrum, the dose/evacuate/acquire spectrum cycle was repeated until the reaction was at or near equilibrium surface coverage.

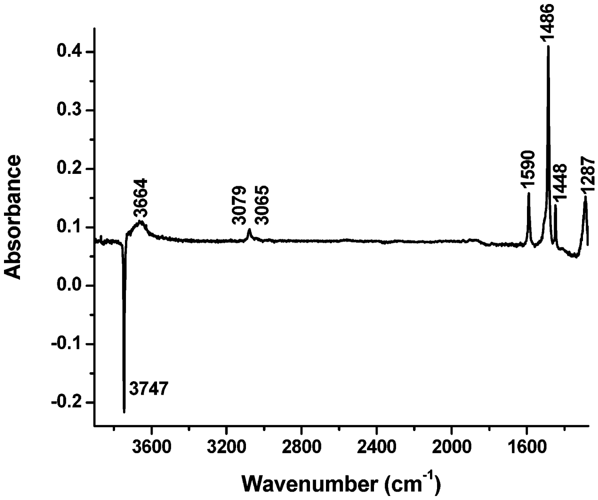

Figure 1. An FTIR difference spectrum of silica after 30 min exposure to 2-chlorophenol at 325 °C. The negative peak at 3747 cm^{-1} is due to the loss of silica surface hydroxyl groups, indicating that they are sites of chemisorption. The labeled positive peaks are from 2-chlorophenol chemisorbed as chlorophenolate (see text). These features persist on the surface after evacuating the sample to 10^{-6} Torr at 150 °C, indicating that the responsible species is chemisorbed to the surface.

Because 2-chlorophenol vapor was introduced to the cell from the bulk, and the cell was evacuated prior to collecting each IR spectrum and fresh 2-chlorophenol admitted to the cell before proceeding to the next time point, the concentration of 2-chlorophenol was essentially constant throughout any given run. Additionally, it has been estimated that a silica surface dehydroxylated at 800 °C will have a hydroxyl surface coverage of less than 1.2 OH groups/100 Å^2.[23] For our purposes, this corresponds to approximately 4×10^{18} available surface hydroxyl groups, which are shown to be the sites of adsorption, while our 2-chlorophenol molecular density remains constant and an order of magnitude higher, ensuring pseudo-first-order conditions.

Results and Discussion

FTIR Characterization of Adsorbed Species. Figure 1 presents an FTIR difference spectrum resulting from exposure of Cabosil to 2-chlorophenol after 30 min of reaction at 325 °C. As this is a difference absorption spectrum, with the FTIR background taken over the undosed silica, the negative peak at 3747 cm^{-1} indicates a loss of surface hydroxyl groups on the silica, indicating that they are the sites of chemisorption. For kinetic measurements, difference spectra are not employed because the peak height at 3747 cm^{-1} at a known reaction time relative to that of the undosed sample is used to monitor uptake of 2-chlorophenol (vide infra). Peaks at 3079 and 3065 cm^{-1} are due to aromatic C−H stretching vibrations of chemisorbed 2-chlorophenol and are shifted 7 and 15 cm^{-1} lower in energy, respectively, from their gas-phase values. Peaks at 1590, 1486, and 1448 cm^{-1} are attributed to the aromatic ring-breathing modes of chemisorbed chlorophenolate and are shifted 3−10 cm^{-1} from the gas phase. The C−O stretch of the adsorbed chlorophenolate is observed at 1287 cm^{-1}, which is shifted 8 cm^{-1} from the gas phase. Because these features persist after

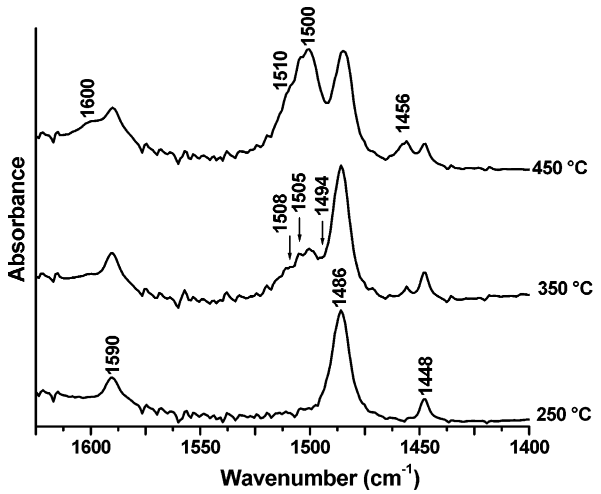

Figure 2. Temperature-dependent IR spectra of 2-chlorophenol adsorption and oxidation after 10 min of reaction. For clarity, peaks attributed to chemisorbed 2-chlorophenolate are labeled in the 250 °C trace. Peaks attributed to chlorophenol bound in the bidentate form are depicted in the 350 °C trace. The carboxylate and carbonate partial oxidation products are labeled in the 450 °C trace.

the cell had been evacuated to 10^{-6} Torr and held 10 min at 150 °C, the absorbing species are determined to be chemisorbed to the surface and not physically bound. These assignments are in close agreement with other 2-chlorophenol adsorption studies reported in the literature.[24,25] The broad absorption band at 3664 cm^{-1} is most likely due to hydrogen bonding between chlorine ring substituents of surface-bound 2-chlorophenol and neighboring silica hydroxyl groups. Absent from the spectrum is a peak at 1338 cm^{-1} due to 2-chlorphenol O−H bending. This peak is present when 2-chlorophenol is physisorbed and is an indication that 2-chlorophenol chemisorbs though its hydroxyl substituent.[25] There is also no evidence of 2-chlorophenol O−H stretching, which is observed at 3570 cm^{-1} when physisorbed, further indicating that 2-chlorophenol chemisorbs at silica surface hydroxyl groups via its hydroxyl group.

At a reaction temperature of 300 °C, features begin to appear in the spectra that are not assigned to adsorbed 2-chlorophenol. As will be discussed, these additional features are due to surface-bound carboxylates and possibly other reaction products, as well as 2-chlorophenol chemisorbed to the surface through both its hydroxyl and its chlorine substituent as a catecholic-type intermediate. These features are shown in Figure 2, which depicts the spectral region of 1625−1400 cm^{-1} for selected temperatures after 10 min of reaction.

The peak at 1600 cm^{-1} is assigned to the asymmetric $-\mathrm{COO}^-$ vibration of a surface carboxylate of the formate type, while the peak at 1456 cm^{-1} is due to asymmetric $-\mathrm{COO}^-$ stretching due to a surface-bound carboxylate of the acetate type.[26−30] The shoulder at 1510 cm^{-1} is most likely due to the presence of surface-bound carbonate.[29] The very intense peak at 1500 cm^{-1} is not conclusively assigned, but it is most likely also due to a surface carboxylate species,[31] probably of the formate type, as the adsorbing species responsible for this peak is more stable upon air oxidation versus the chlorophenolate or acetate species (vide infra). Surface-bound carboxylates are commonly formed partial oxidation products and have been detected with FTIR in the catalytic oxidation of 1,2-dichlorobenzene over vanadia doped Al_2O_3, during the conversion of 2-chloropropane with SCR-DeNOx catalysts, and in surface-mediated methanol oxidation.[28,29,32] It has also been reported that carboxylate species are the dominant surface-mediated partial oxidation product of substituted benzenes.[32]

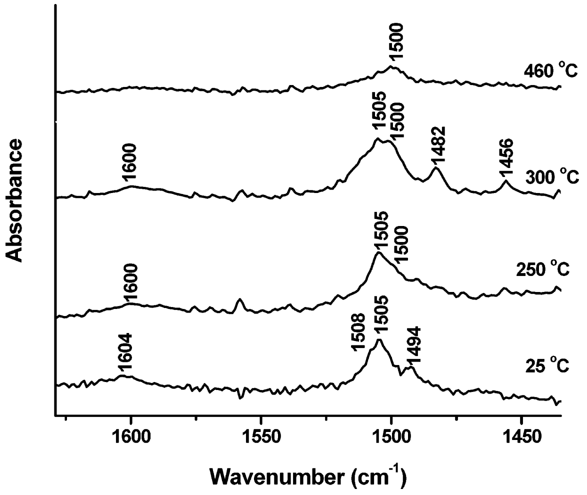

Figure 3. Temperature-dependent spectra of catechol adsorbed onto cabosil at 25 °C and heated in 21% O_2 for 2 min at 250, 300, and 460 °C.

Even though the absorption of 2-chlorophenol was carried out in the absence of gas-phase oxygen, oxidation products are still formed due to the uptake of surface oxygen.[26,29] Utilization of surface oxygen has been proposed to take place for trichlorophenol oxidation though a Mars−van Krevelen type of mechanism.[33]

Catecholic Reaction Intermediate. It has been proposed that carboxylates are formed heterogeneously from aromatic species through a dihydroxy, or catecholic, type intermediate.[34] To this end, we elected to adsorb catechol vapor from the finely ground solid onto pretreated Cabosil at room temperature. Following this procedure, adsorption bands were noted at 1604, 1508, 1505, and 1493 cm^{-1}. These peaks are also evident in our spectra generated from 2-chlorophenol chemisorption and are most prevalent in the 300−350 °C range and are labeled on the 350 °C trace of Figure 2. When adsorbed catechol is heated in air (2 min, 21% O_2), the peaks attributed to catecholic species reduce in intensity and are completely removed at 460 °C. This behavior is shown in Figure 3. During this thermal oxidation process, new peaks appear that are in excellent agreement with those we previously assigned to surface carboxylates. This is further evidence that formation of carboxylate partial oxidation products from 2-chlorophenol and catechol proceeds though a common intermediate, that is, a bidentate bound aromatic ring structure. Again, the most stable peak with respect to air oxidation of adsorbed catechol is the peak at 1500 cm^{-1}.

When 2-chlorophenol, chemisorbed at 325 °C, is exposed to 20% oxygen and held at 400 °C for 6 min, approximately 33% of adsorbed 2-chlorophenol is removed from the surface, based on loss of the chlorophenolate ring-breathing peak at 1486 cm^{-1}. The peaks at 1500 and 1505 cm^{-1} become more resolved and are shown to be more stable toward oxidation than 2-chlorophenolate, which is the expected behavior of surface carboxylates. This may indicate that the peak observed at 1505 cm^{-1} after catechol adsorption is due to a partial oxidation product, formed at room temperature. However, another explanation is that both an oxidation product and a catecholic ring-breathing mode coexist at this frequency. Oxidation at longer times caused increasing removal of surface species, both phenolate and carboxylates, with the peak at 1500 cm^{-1} being the most persistent. Concurrent with the removal of surface-bound

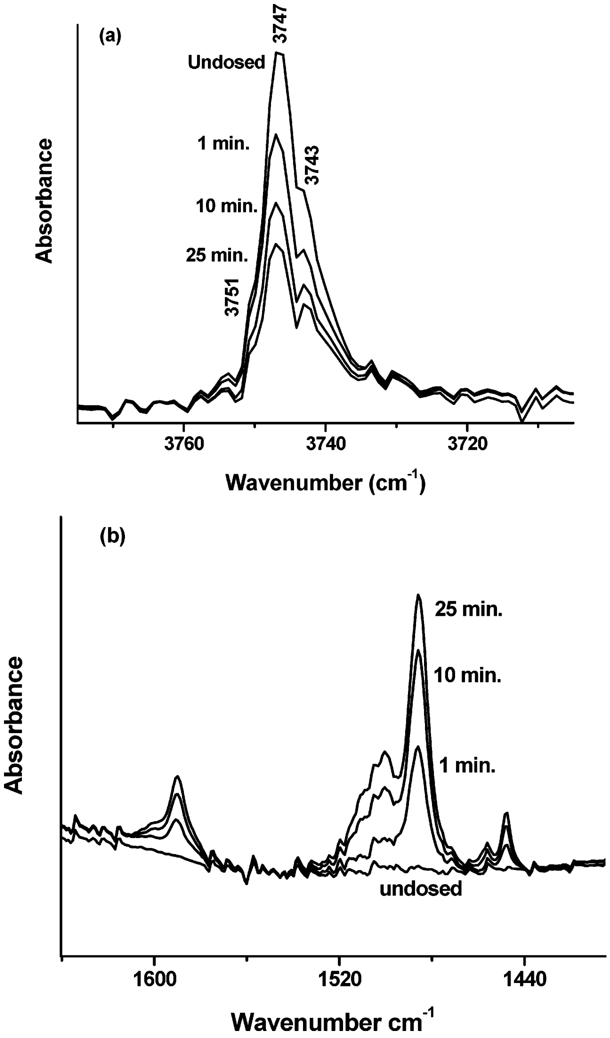

Figure 4. (a) Loss of hydroxyl stretching due to adsorption of 2-chlorophenol at 350 °C for the selected times indicated in the figure. (b) Growth of phenolate and partial oxidation products.

phenolate and carboxylate due to air oxidation is the reformation of surface hydroxyl groups.

Rate of 2-Chlorophenol Chemisorption. Figure 4a depicts the expanded spectrum of the IR band due to freely vibrating surface hydroxyl groups and the time-dependent loss of intensity of the peak after exposure to 2-chlorophenol at 350 °C. Only a few of the time points measured are shown to reduce congestion in the figure. The central peak at 3747 cm^{-1} is due to O−H stretching of isolated hydroxyl groups, and the shoulders at 3751 and 3743 cm^{-1} are due to geminal hydroxyl groups that are sufficiently spaced as to not mutually hydrogen bond. This characteristic of Cabosil has been reported by Hair and Hertl, and their observations suggest that a Cabosil surface heated to 800 °C will have approximately 60% isolated hydroxyl groups and 40% geminal groups.[22] As the reaction progresses, there is loss of intensity for all bands, which means isolated and geminal hydroxyl groups participate in adsorption of 2-chlorophenol. The geminal bands become increasingly resolved as the reactions proceeds. The behavior depicted in Figure 4a is representative for all temperatures examined, which ranged from 200 to 500 °C, in 50 °C increments. For completeness, the time-dependent growth of phenolate absorption and carboxylate partial oxidation products is shown for same time points in Figure 4b.

Because the undosed peak height is proportional to the number of available surface sites, the surface coverage, θ, at any time can be determined on the basis of the degree of reduction of the surface hydroxyl stretching peak at 3747 cm^{-1}. We can assume that all surface sites are available for 2-chlorophenol chemisorption because long reaction times at high temperature results in the complete disappearance of silanol stretching peak. The surface coverage was determined according to eq 1.

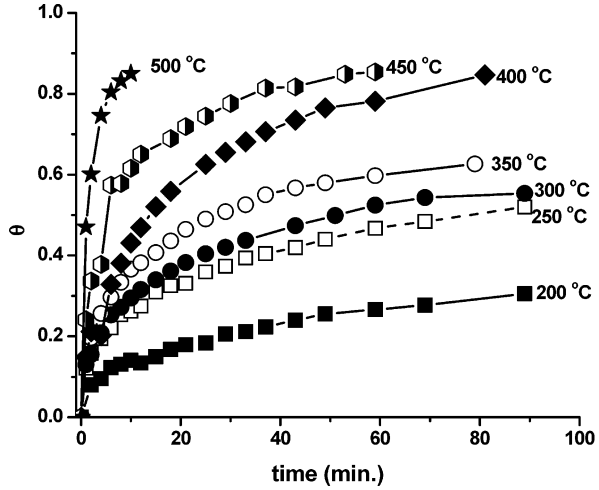

Figure 5. Surface coverage as a function of temperature as determined by the loss of surface hydroxyl groups after 2-chlorophenol chemisorption on Cabosil.

$$\theta(t) = \frac{\text{peak height}(0) - \text{peak height}(t)}{\text{peak height}(0)} \qquad (1)$$

Figure 5 depicts the surface coverage with respect to time for all temperatures measured. For each temperature, the reaction is initially fast, and then begins to slow as equilibrium surface coverage is approached. After approximately 30 min of reaction at 500 °C, the surface hydroxyl sites are nearly completely removed, making a precise determination of the degree of reduction difficult.

Chemisorption kinetics were determined on the basis of the following:

$$\mathrm{A} + \mathrm{S} \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\longleftrightarrow}} \mathrm{AS}$$

where A is vapor phase 2-chlorophenol and S is the silica surface and AS is 2-chlorophenol chemisorbed to the surface.

The rate of chemisorption is then:

$$\frac{\mathrm{d[AS]}}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{A}][\mathrm{S}] - k_\mathrm{d}[\mathrm{AS}]$$

For pseudo-first-order conditions, $[\mathrm{A}] = [\mathrm{A}_0]$ and $k_{\mathrm{a}'} = k_\mathrm{a}[\mathrm{A}]_0$; therefore,

$$\frac{\mathrm{d[AS]}}{\mathrm{d}t} = k_{\mathrm{a}'}[\mathrm{S}] - k_\mathrm{d}[\mathrm{AS}]$$

Because $[\mathrm{S}] = [\mathrm{S}]_0 - [\mathrm{AS}]$,

$$\frac{\mathrm{d[AS]}}{\mathrm{d}t} = k_{\mathrm{a}'}([\mathrm{S}]_0 - [\mathrm{AS}]) - k_\mathrm{d}[\mathrm{AS}] = k_{\mathrm{a}'}[\mathrm{S}]_0 - (k_{\mathrm{a}'} + k_\mathrm{d})[\mathrm{AS}]$$

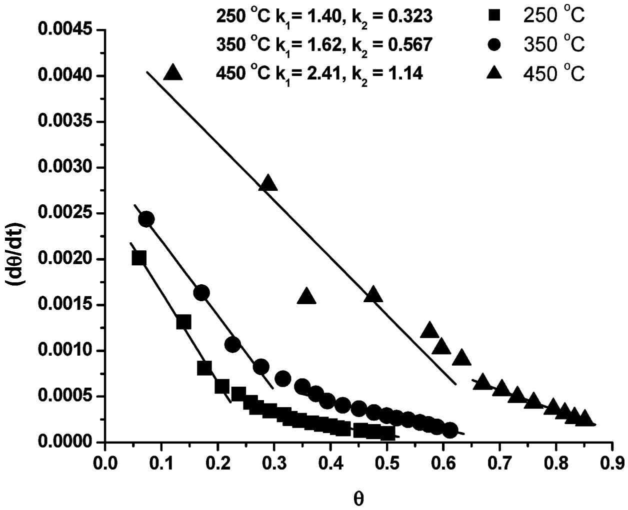

Figure 6. Pseudo-first-order kinetic plots for the chemisorption of 2-chlorophenol on silica shown at selected temperatures. The *y*-intercept corresponds to the pseudo-first-order rate constant. k_2 indicates the fast, initial reaction, and k_2 indicates the slower reaction that occurs at higher surface coverage.

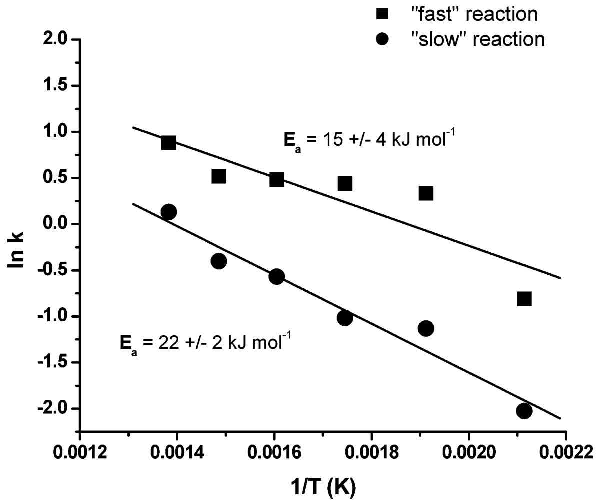

Figure 7. Arrhenius behavior of 2-chlorophenol chemisorption on Cabosil. The fast initial reaction has an activation energy of 15 kJ mol^{-1}, while the slower reaction has an activation energy of 22 kJ mol^{-1} over the 200−450 °C range.

Dividing though by $[S]_0$ and defining

$$\theta = \frac{[AS]}{[S]_0}$$

yields

$$\frac{d\theta}{dt} = k_{a'} - (k_{a'} + k_d)\theta$$

Plotting dθ/dt versus θ will yield a straight line with a slope of $-k_{a'} + k_d$ and an intercept of $k_{a'}$.

Figure 6 depicts these kinetic plots for a few selected temperatures. Adsorption occurs at a fast initial rate and a slower rate at higher surface coverage. The fast reaction extends to greater surface coverage with increasing temperature. For instance, at 250, 350, and 450 °C, this fast initial reaction rate occurs up to $\theta = 0.21$, 0.28, and 0.63, respectively. It is possible the two rates are observed due to the presence of two different adsorption sites, the geminal and vicinal hydroxyl groups. The Arrhenius behavior is depicted in Figure 7 for both the “fast” and the “slow” reaction. The data were fit to eq 2.

$$k = Ae\frac{-B}{T}$$

where

$$B = \frac{E_a}{R} \tag{2}$$

The fast reaction exhibits an activation energy of 15 ± 4 kJ mol^{-1} and B = 1804 K , while the slower reaction has an activation energy of 22 ± 2 kJ mol^{-1} and B = 2646 K in the 200−450 °C range.

Possible Implications for the Formation of PCDD/F. The formation of PCDD/F when associated with combustion-generated fly ash is a marginal process of chlorophenol oxidation, evidenced by the fact that yields of PCDD/F from reaction of chlorophenols on fly ash and surrogate fly ash are typically less than 1%.[9,17] However, the heterogeneous oxidation of chlorophenols to their most thermodynamically stable end-products, that is, CO_2 and HCl, and their incomplete oxidation to form such species as PCDD/F involves chemisorption at

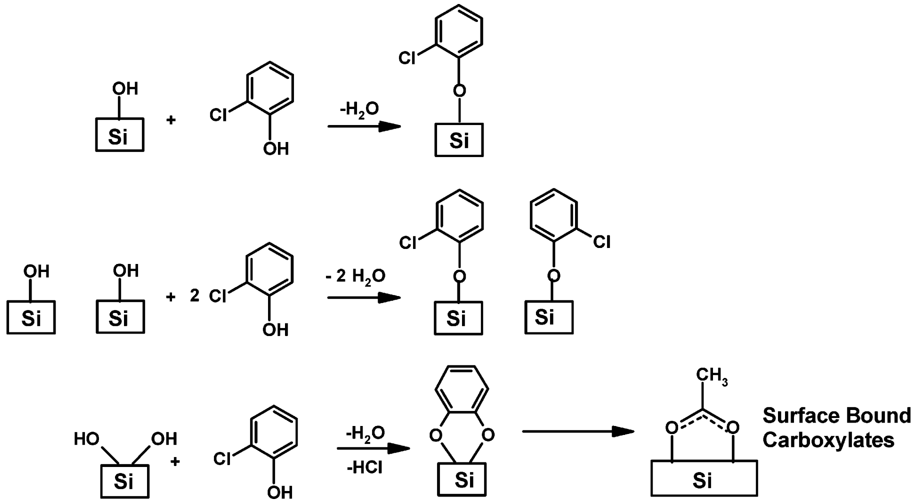

Figure 8. Chemisorption of 2-chlorophenol onto silica. The upper pathway illustrates chemisorption of 2-chlorophenol at an isolated hydroxyl via H_2O elimination to form 2-chlorophenolate. The middle pathway depicts adsorption at neighboring isolated sites. The lower pathway illustrates 2-chlorophenol adsorbed at a geminal site through both the phenolic hydroxyl and the chlorine substituent resulting in a bidentate bound diphenolate, which is believed to be an intermediate in the formation of carboxylate partial oxidation products.

active surface sites. Therefore, knowledge of the rates and geometries of precursor adsorption at potentially active sites is beneficial in developing a detailed model of PCDD/F formation from chlorinated phenols. In this study, we have demonstrated that 2-chlorophenol chemisorbs at isolated and geminal surface hydroxyl groups to form surface-bound phenolates. Proposed mechanisms for these pathways are depicted in Figure 8.

In the upper pathway of Figure 8, we depict the chemisorption of 2-chlorophenol at a single isolated surface hydroxyl site to form the surface-bound 2-chlorophenolate, as was observed experimentally. In the middle pathway in Figure 8, chemisorption of 2-chlorophenols at two neighboring isolated sites is depicted. In the lower pathway of Figure 8, 2-chlorophenol reacts with geminal, surface hydroxyl sites to form a surface-bound catecholate species. Oxidation of the catecholate results in the formation of the observed carboxylates. However, free catechols have previously been observed in the CuO/silica-catalyzed oxidation of 2-MCP, which suggests that they participate in other reactions or are desorbed from the surface.[17]

We have not included transition metals, for example, copper oxides, in this study, which are known to catalyze the formation of PCDD/F from chlorophenols. However, both silica and transition metal surface contain surface hydroxyl sites at which 2-chlorophenol can chemisorb. The moderately high surface area silica used in this study is readily amenable to study by FTIR because the different types of surface hydroxyl sites are well resolved. This is not true for copper oxide or actual incinerator fly ash. However, reaction with silica can be considered a model, especially with respect to adsorption geometries, for reaction with transition metal oxides and fly ash.

One interesting trend revealed by our data is that the degree of 2-chlorophenol chemisorption continually increases within the temperature range studied, whereas maximum PCDD/F formation from chlorophenols is typically near 350 °C. It is not surprising that typical maximum PCDD/F formation does not correlate with our observed chemisorption behavior. Factors such as surface-mediated PCDD/F destruction and increasing complete and/or partial oxidation of chlorophenol (thus making it unavailable for PCDD/F formation) most likely account for the decrease in PCDD/F formation above 350 °C, even though we have demonstrated, at least in our case, that the extent of chemisorption of the dioxin precursor increases. However, this behavior needs to be characterized further using more representative fly ash surrogates.

One of the suggested roles of transition metal species in the formation of PCDD/ F is that of an electron acceptor, in which upon chemisorption of the chlorophenol to a metal cation site (M^{n+}) an electron is transferred from chlorophenolate to the metal, resulting in the formation of a surface associated chlorophenoxyl radical and a $(M^{n+})^{-1}$. Evidence of this has been provided using EPR[17] and X-ray adsorption spectroscopy.[20] Because reactions of chlorophenols on both catalytic copper oxide surfaces and silica surfaces involved initial chemisorption of chlorophenols, future studies will focus on the differences in the distributions and reactivities of isolated, vicinal, and geminal hydroxyl sites associated with mixed copper oxide/ silica surfaces. This distribution may well control the absolute and relative yields of PCDD and PCDF by determining whether they are oxidized, react with another surface-bound PCDD/F precursor, or react with a gas-phase precursor.

At this point, it is unclear if chemisorption to silica ties up potential PCDD/F precursors and permanently removes them from further reactions that form PCDD/F, or whether initial chemisorption at silica sites facilitates further reaction. Chemisorption on silica requires slightly higher temperatures than chemisorption on copper that could affect the distribution of PCDD/F precursors on transition metals and silica sites, the former leading to PCDD/F and the latter leading primarily to oxidation products. Thus, slow cooling of the fly ash as it passes from the combustion zone to the cool zone of combustors can result in preferential binding to the higher concentration silica sites, while rapid cooling could prevent chemisorption to high activation energy silica sites and increase chemisorption to low activation energy metal sites that lead to PCDD/F formation.

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