# DECOMPOSITION OF 2-CHLOROPHENOL ON SURFACES OF NEAT ALUMINA AND ALUMINA SUPPORTED IRON (III) OXIDE CATALYSTS

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## Introduction

Chlorophenols constitute a group of the most important precursors for the formation of polychlorodibenzo-*p*-dioxin and polychlorinated dibenzofurans (PCDD/F, aka dioxins) in catalytic (250-400 °C)[1-4] and non-catalytic (550-700 °C)[5, 6] processes. Two catalytic processes exist[7], comprising the formation of PCDD/F from precursor molecules, such as 2-chlorophenol, and from oxidation of complex polycyclic soot matrices in the so-called de novo synthesis. In the former mechansim, chlorophenols react with the terminal hydroxyl groups of active sites on select surfaces, followed by an electron transfer from the chemisorbed molecule of chlorophenolate to an active site[8]. Subsequent reduction of the catalyst active site, and formation of physisorbed chlorophenoxy and chlorohydroxyphenoxy radicals[9], result in the formation of PCDD or PCDF via either Eley-Rideal (a reaction comprising an adsorbed radical and a gas-phase molecule) or Langmuir-Hinshelwood (a reaction involving two adsorbed radicals) mechanisms, respectively. Oxides of redox-active metals such as copper, nickel, iron, and zinc effectively catalyse the formation of PCDD/F from chlorophenols[1].

Iron oxide, alumina and silica occur in abundance in fly ash, with the latter two forming zeolites. These compounds catalyse generation of environmental pollutants under suitable conditions. In our earlier articles, we presented the decomposition of 2-chlorophenol (2-CPh) on the surface of silica-supported iron (III) oxide[10], and studied adsorption of hydrogen chloride gas on the surface of CuZSM-5 zeolite[11]. In this contribution, we report the formation of volatile organic compounds (VOC, such as higher chlorinated phenols and chlorobenzenes) as well as PCDD/F from oxidation of 2-CPh on the surface of neat alumina and alumina-supported iron (III) oxide at a reaction temperature of 350 °C. In particular, this study concentrates on gaining an understanding of the role of iron oxide and alumina on formation of PCDD/F and VOC and has direct application to emissions of these pollutants from combustion systems.

## Materials and Methods

We prepared 5 % iron (III) oxide catalyst on γ-alumina support by the method of incipient wetness[12], to serve as a model of the iron rich material, characteristic of fly ash. After applying a solution of $Fe(NO_3)_3$ to the alumina support, the sample was dried at 110 °C and then calcined in air at 450 °C for 5 h. The experiments involved catalyst particles of between 150 and 250 μm in size, further calcined in the reactor for 1 h, immediately before the start of the reaction. Each experiment comprised 89 mg of the catalyst with bulk density of 1.06 g/mL, charged inside a 4 mm ID quartz tube, with the catalyst immobilised in the tube by quartz wool. The contact time between the gas and the catalyst corresponded to 0.04 s. A syringe pump that introduced the reactant to the system operated at a constant rate to maintain the concentration of 2-CPh at 750 ppm, in a dilute stream of oxygen in nitrogen (10 % $O_2$). The product gases (containing VOC and PCDD/F) were passed through two XAD-2 resin cartridges (200 mg and 50 mg), positioned after the reactor tube, with the role of the second cartridge to confirm no VOC and PCDD/F breakthrough from the first. At the conclusion of each experiment, the resins were extracted with *n*-hexane for two hours using a sonicator. The reactor tube and packed catalyst were rinsed with dichloromethane, with the resulting solution added to that obtained from the extraction process. Finally, an Agilent 7200 quadruple time-of-flight GC/MS, operating in splitless mode, served to identify VOC and PCDD/F products. The GC oven housed a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm). The oven temperature was initially held at 40 °C for 2 min, then increased to 300 °C at 10 °C/min and finally held for 4 min. Helium flowed at 1.2 mL/min and the injection volume corresponded to 1 μL. The injector, the transfer line, and the source operated at 250 °C, 240 °C, and 230 °C, respectively and the electron impact source functioned at an ionisation energy of 70 eV.

We deployed the temperature-progamed desorption (TPD) technique to determine the acidity of the catalysts. This technique involves sample activation in a desorption cell at 450 °C for half an hour, followed by ammonia

adsorption at 150 °C and its desorption between 30 °C and 750 °C with a heating rate of 5 °C/min with a Pfeiffer Prisma quadrupole mass spectrometer set to record $m/z = 16$ for detection of the evolving ammonia. ZSM-5 zeolite (Si/Al=15) served as a calibration standard for quantitation of acid sites.

### Results and Discussion

In preliminary experiments with alumina supported iron (III) oxide catalysts, we observed the formation of a carbonaceous layer on the catalyst surface, with concurrent changes to conversion of 2-CPh and product selectivity. Until the carbonaceous layer fully covered the catalyst, which occurred at around four hours after the commencement of an experiment, the process consumed all 2-CPh and produced little PCDD/F. Following this four hour period, significant amounts of PCDD/F emerged. For the alumina supported iron (III) oxide catalyst, the results presented in Figures 1-3 arise from an experiment that lasted four hours (and hence produced PCDD/F but left some unconverted 2-CPh), and those illustrated in Figure 4 from a trial that lasted two hours (and hence generated little PCDD/F with all 2-CPh converted on the surface of the catalyst). A series of subsequent experiments, not presented in this paper, confirmed the formation of PCDD/F by the *precursor*, rather than de novo, pathway. Neat alumina exhibited incomplete 2-CPh conversion, even at the beginning of each experiment. Hence, experiments lasting two hours were of sufficient length to ascertain the product selectivity, as illustrated in Figures 1-3.

*Formation of volatile organic compounds (VOC)* The decomposition of 2-CPh on the surface of neat alumina and alumina-supported iron (III) oxide at temperature of 350 °C shows intriguing differences between the catalysts. Figures 1 and 3 illustrate that, the decomposition of 2-CPh on both catalysts produces chlorinated phenols, although only alumina-supported iron (III) oxide generates chlorobenzenes, whereas neat alumina catalyst results in the formation phenol and chlorinated phenols. These observations lead us to suggest that both catalysts exhibit capacity for dechlorination/chlorination (although alumina-supported iron (III) oxide exhibits less dechlorination efficacy), but only the alumina-supported iron (III) oxide catalyst can remove the hydroxyl groups via the surface-facilitated condensation reactions. In both experiments, we identified mono to tetra chlorinated phenols with the major isomers of 2,4-DCPh, 2,6-DCPh and 2,4,6-TriCPh, but mono to penta chlorinated benzenes, with 1,2-DCBz as the major congener, arise only on the surface of alumina-supported iron (III) oxide.
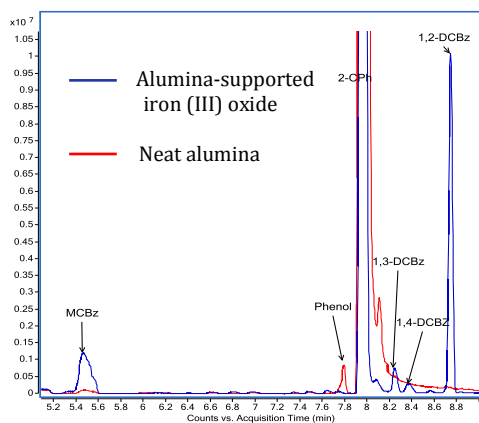


**Figure 1.** Formation of both chlorinated benzenes and phenols on the surface of alumina-supported iron (III) oxide and lack of formation of chlorinated benzenes on the surface of neat alumina. The large peak around 8.1 min is from benzofuran elution.

*Formation of dibenzo-p-dioxin and dibenzofuran (DD/DF)* As presented in Figure 2, both DF and DD form as a results of the decomposition of 2-CPh on the surface of a neat alumina catalyst. However, the surface of alumina-supported iron (III) oxide only promotes the generation of DD. Formation of DF on the surface of neat alumina and lack of identification of DF on the surface of alumina-supported iron (III) oxide illustrates the dechlorination capacity of the alumina catalyst, with iron (III) oxide merely reducing the dechlorination functionality of the alumina. According to Farquar et al.[9], the formation of DD requires coupling of a 2-CPh molecule in the gas phase with a surface bound chlorohydrophenoxy radical, accompanied with the loss of two HCl molecules. The results of our study also corroborate the findings of Schoonenboom et al.[13] who proposed an electrophilic substitution process to explain the dechlorination capacity of alumina. The formation of DF

requires two dechlorination steps of 4,6-DCDF, with 4-MCDF as an intermediate. Along the same line of enquiry, we suggest that the appearance of DD results from the dechlorination of 1-MCDD, the major product of the synthesis involving 2-CPh.
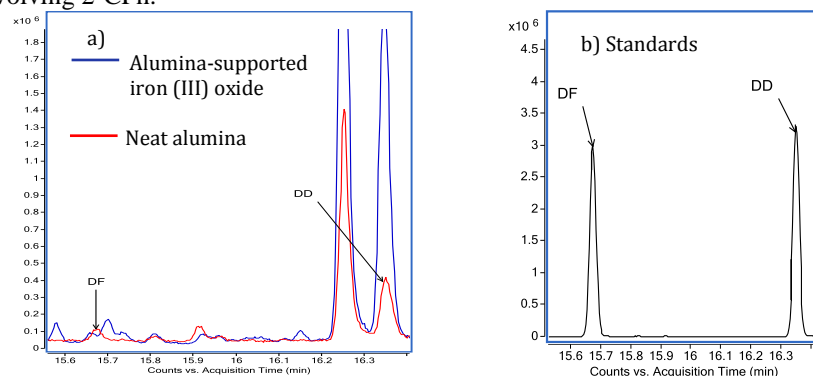


**Figure 2. a)** Identification of DD and DF on the surface of alumina (after two hours) and lack of detection of DF on the surface of alumina-supported iron (III) oxide (after four hours). **b)** Elution order of DD and DF by injection of standards. The peak at around 16.3 m is probably chlorochromone. (See text for explanatioin of the duration of the experiments.)

*Formation of polychlorinated dibenzo-p-dioxins and furans (PCDD/F)* Figure 3 presents the major products forming on the surface of the two catalysts. The result of the decomposition of 2-CPh on the surface of neat alumina disclose 1-MCDD, 4-MCDF, 4,6-DCDF, 1,6-DCDD, and 1,9-DCDD as the major products. According to Farquar et al.[9] for copper (II) oxide catalysts, 1-MCDD forms by coupling of one surface-bound chlorohydrophenoxy radical and one 2-CPh gas phase molecule, 1,6- and 1,9-DCDD arise by further chlorination of surface-bound 1-MCDD. On the other hand, 4,6-DCDF appears by direct coupling of two surface-bound chlorophenoxy radicals, with 4-MCDF created by dechlorination of 4,6-DCDF.

The major chlorinated DD/F product species from the decomposition of 2-CP on the surface of alumina-supported iron (III) oxide comprise 1-MCDD, 2-MCDD, 1,6-DCDD, 1,3-DCDD, 1,9-DCDD, 1,3,6-TriCDD, 1,3,9-TriCDD, 4,6-DCDF, and 4-MCDF. These products form in much larger quantities on the surface of alumina-supported iron (III) oxide than on that of neat alumina. Trace quantities of tetra and penta CDD/F also form on the surface of alumina-supported iron (III) oxide. Thus, iron, as one of the most abundant transition metals in fly ash, plays a vital role in the emission of PCDD/F.
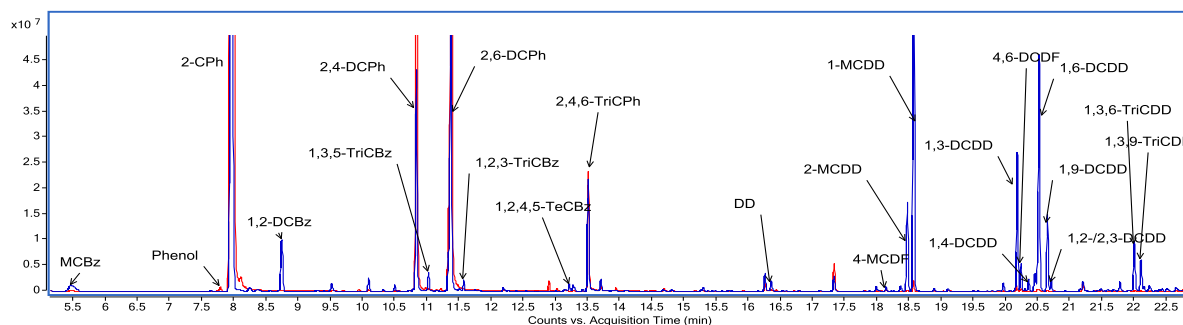


**Figure 3.** Formation of major VOC and PCDD/F species on the surface of neat alumina (red line, after two hours) and alumina-supported iron (III) oxide (blue line, after four hours).

*Catalysts acidity* Figure 4 presents the products of decomposition of 2-CPh on the surface of alumina-supported iron (III) oxide during the first two hours of the experiment; i.e., within the regime characterised by the conversion of the entire 2-CPh and negligible formation of chlorinated DD/F. The experimental conditions of decomposition of 2-CPh on the surface of alumina and alumina-supported iron (III) oxide are similar. The major products include chlorinated benzenes, the absence of phenolic products and complete conversion of 2-CPh. This indicates that 2-CPh has a higher affinity for adsorption/degradation on the surface of alumina-supported iron (III) oxide compared to neat alumina. We hypothesise that, this effect could be due to acidity of the catalyst and basicity of the feed. According to literature, 2-CPh displays proton affinity of 1408 kJ/mol[14] compared to

that of ammonia of 852 kJ/mol[15]. Thus, we performed the temperature-programed desorption of ammonia to measure the acidity of the two catalysts. Figure 5 shows the acidity of the two catalysts, and from Table 1 it is obvious that, the acidity of alumina-supported iron (III) oxide is significantly higher compared with neat alumina.
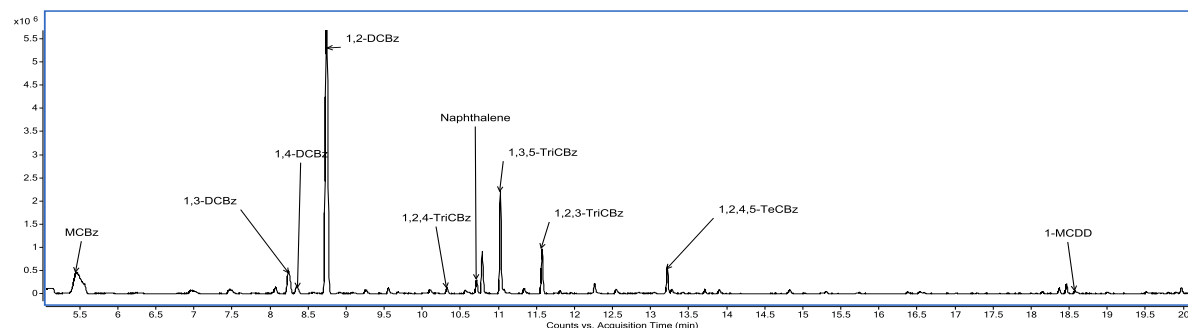


**Figure 4.** Formation of chlorinated benzenes on the surface of alumina-supported iron (III) oxide and adsorption/degradation of 2-CPh after two hours.
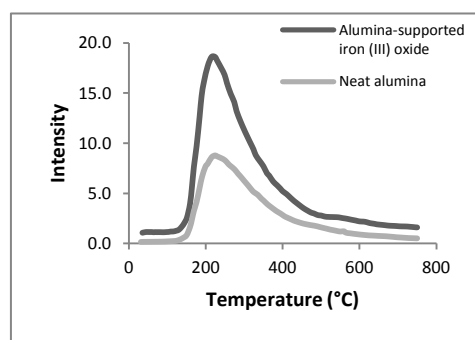


**Figure 5.** Ammonia desorption on the surface of two catalysts as measured for $m/z = 16$.

**Table 1.** Acid site density and concentration on the surface of two catalysts measured by ammonia-TPD

| Catalyst | Surface area $(m^2/g)$ | Desorption temp (°C) | Acid site density $(\mu mol/m^2)$ | Acid sites (mmol/g) |
|---|---|---|---|---|
| Neat alumina | 170.0 | 223 | 1.4 | 0.24 |
| Alumina-supported iron (III) oxide | 164.5 | 220 | 2.5 | 0.42 |

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