

## FORMATION OF DIBENZO-*p*-DIOXINS AND DIBENZOFURANS IN OXIDATION OF 2-CHLOROPHENOL OVER IRON OXIDE/SILICA SURFACE

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### Introduction

Chlorophenols constitute one of the most important precursors for formation of polychlorodibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F, dioxins), both under pyrolytic and oxidative conditions<sup>1,2</sup>. PCDD/F emerge from condensation of chlorophenol, chlorophenoxy and chlorohydrophenoxy species, in catalytic (250 to 400 °C) and non-catalytic (550 - 700 °C) processes. The catalytic process involves reaction of chlorophenols with the terminal hydroxy groups on the active surfaces, followed by an electron transfer from the chemisorbed molecule of chlorophenolate to an active site<sup>3</sup>, subsequent reduction of the active site on the catalyst with concurrent formation of physisorbed chlorophenoxy and chlorohydroxyphenoxy radicals<sup>4</sup>, to conclude with either Langmuir-Hinshelwood (i.e., a reaction involving two adsorbed radicals) or Eley-Rideal (i.e., a reaction comprising an adsorbed radical and a gas-phase molecule) type formation of PCDF and PCDD, respectively. Oxides of redox-active metals such as copper, nickel, iron, and zinc effectively catalyse the formation of PCDD/F from chlorophenols<sup>5</sup>. In this contribution, for convenience, the term PCDD/F also includes monochlorinated and nonchlorinated dibenzo-*p*-dioxins and dibenzofurans.

Although iron represents the most abundant transition metal found in the fly ash produced in combustion systems<sup>6</sup>, the role of its oxides on the formation of PCDD/F remains unresolved. Some experimental studies have reported the destruction of PCDD/F on surfaces of iron oxides<sup>7</sup>, whereas the recent study by Nganai et al. described significant yields of PCDD/F from chlorophenols<sup>8,9</sup>, including dibenzo-*p*-dioxin (DD), 1-monochlorodibenzo-*p*-dioxin (1-MCDD), dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), in addition to large amounts of highly chlorinated benzenes. Nganai et al.'s detection of non-chlorinated DF (which was undetected in other studies), no detection of 4-MCDF, 2-MCDD and dichlorinated DD, and lower ratios of CDD/CDF comprise the most intriguing differences between their results and the measurements of the previous investigators, in particular Born et al.<sup>10</sup> and Ryu<sup>11</sup> who studied, respectively, the oxidation of 2-CP on fly ash and CuCl<sub>2</sub> surfaces. Hence, different reaction pathways might operate on surfaces of Cu and Fe catalysts.

The present study was aimed at investigating the formation of volatile organic compounds (VOC, such as chlorophenols and chlorobenzenes) as well as PCDD/F from oxidation of 2-CP on silica-supported iron (III) oxide catalyst, under experimental conditions nearly similar to those of Nganai et al.<sup>9</sup>, to gain insight into the role of iron-rich fly ash on pollutant emissions from combustion systems. In particular, we intended to confirm Nganai et al.'s findings of significantly different effects of copper and iron surfaces on the formation of dibenzo-*p*-dioxins and dibenzofuran congeners from 2-CP. We used a more sensitive mass spectrometer than that featured in the work of Nganai et al., affording identification of additional reaction products. Our results indicate a similar distribution of PCDD/F products to those reported by Born et al.<sup>10</sup> and Ryu<sup>11</sup>; in other words, we are unable to confirm the measurements of Nganai et al. The reason for the observed discrepancy remains unclear. We also carried out the density functional theory calculations involving a cluster of iron oxide to elucidate the energetics of the formation of the initial phenoxy radicals on Fe<sub>2</sub>O<sub>3</sub> surfaces. Although these calculations are preliminary, they indicate profound similarities in the roles of copper and iron surfaces in formation of PCDD/F from 2-CP, supporting the experimental findings reported in this contribution.

### Computational methods

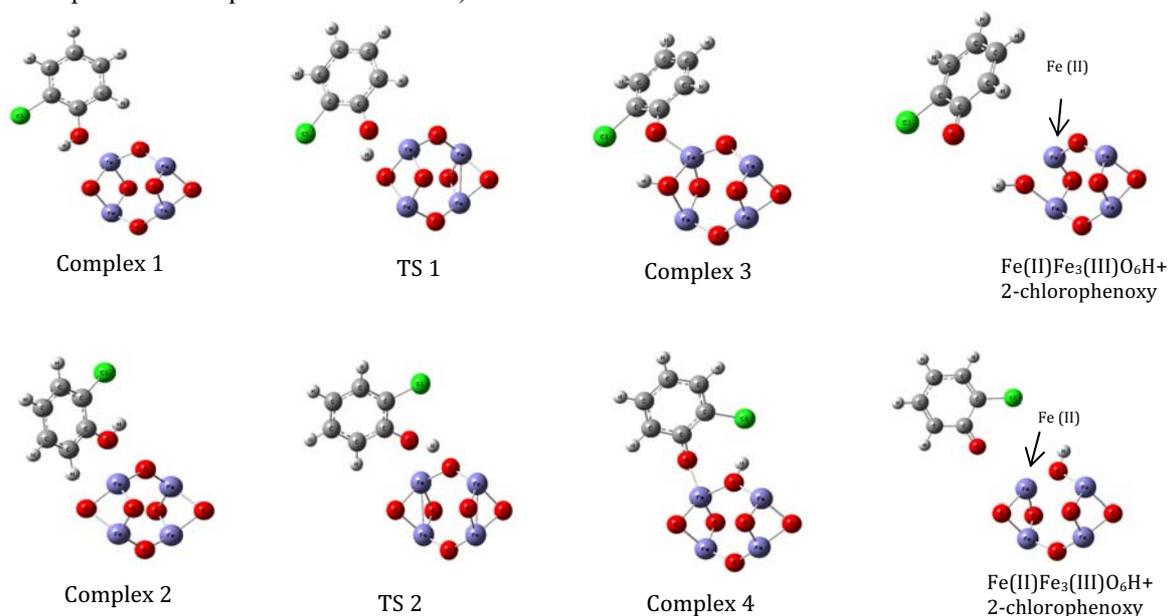
All calculations involved B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p) level of theory as implemented on the Gaussian 09 package<sup>12</sup>, with intrinsic reaction coordinate (IRC) analysis carried out to link transition state structures to their related reactants and products.

## Experimental methods

We prepared 5 % iron (III) oxide catalyst on silica support by the method of incipient wetness<sup>8</sup>, to serve as a model of the iron rich material, in subsequent experiments. After applying the solution of  $\text{Fe}(\text{NO}_3)_3$  to silica gel, we allowed the sample to dry at 110 °C and then calcined it in air at 450 °C for 5 h. The experiments involved catalyst particles of between 150 and 250  $\mu\text{m}$  in size, further calcined in the reactor for 1 h immediately before the start of the reaction. In each experiment, we placed an amount of 50 mg of the catalyst with bulk density of 0.59 g/mL inside a 4 mm i.d. quartz tube, with the catalyst immobilised in the tube by quartz wool. The contact time between the gas and the catalyst was 0.04 s. We used a syringe pump for introducing the reactant to the system operated at a constant rate to keep its concentration at 75 ppm, in a dilute stream of oxygen in nitrogen (10 %  $\text{O}_2$ ). Experiments lasted for 1 h, with the product gases (PCDD/F and VOC) passing through two XAD-2 resin cartridges (200 mg and 50 mg), positioned after the reactor's tube. At the conclusion of each experiment, the resin was extracted with *n*-hexane for 2 h using a sonicator. We rinsed the reactor tube and the packed catalyst with dichloromethane and added the eluted solution from the reactor to the solution obtained from the extraction process. Finally, 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  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$ ). The oven temperature for PCDD/F identification started at 80 °C (held for 1 min), then followed isothermal increase to 150 °C at 20 °C/min and then to 280 °C at 3 °C/min. Helium flowed at 1.2 mL/min and the sample size corresponded to 1  $\mu\text{L}$ . The injector, the transfer line, and the source operated at 250 °C, 240 °C, and 230 °C, respectively. The electron impact source functioned at 70 eV ionisation energy.

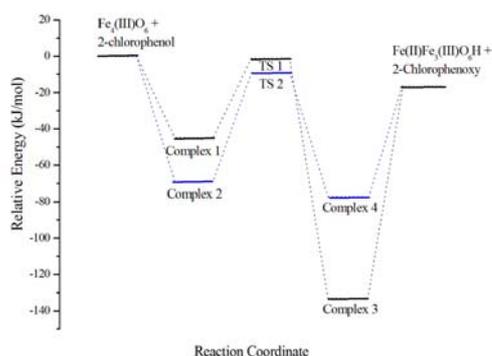
## Results and discussion

Formation of chlorophenoxy and chlorohydroxyphenoxy radicals from chlorophenol represents a crucial step in the production of PCDD/F via the precursor pathway. For the gas-phase reactions, this step may involve either the homogenous dissociation of the O-H bond requiring 362.7 kJ/mol, or bimolecular reactions between chlorophenols and radical pool necessitating modest reaction barriers, e.g., 12.5 kJ/mol for OH, and 54.8 kJ/mol for  $\text{H}^{13,14}$ . An example of our computations involving iron oxide clusters (Figures 1 and 2) highlights the exothermic nature of the catalytic dissociation of the O-H bonds. The size of the iron oxide cluster does not allow the initial termination of surface iron molecules by hydroxyl group, but, as illustrated in Figure 1, the initial reaction between 2-CP and iron entails the formation of surface-bound OH groups (which engender chemisorption of subsequent 2-CP molecules).



**Figure 1.** Optimised geometries of the complexes formed in reaction of 2-CP with  $\text{Fe}_4\text{O}_6$

The resulting chlorophenoxy radicals react on the catalyst's surface via the Langmuir-Hinshelwood mechanism to produce PCDF. From the seminal work of Dellinger's group, we know that chlorophenoxy radicals may also generate hydroxyphenoxy radicals that combine with a gas-phase chlorophenol molecules, leading to formation of PCDD via an Eley-Rideal mechanism<sup>15</sup>. Present calculations indicate that these steps remain essentially unchanged for iron surfaces. Figure 2 illustrates the potential energy surface (PES) for the formation of a 2-chlorophenoxy radical from 2-CP on an iron oxide cluster, and Table 1 presents the total and relative energies of complexes and their related transition states. The last step yields the formation of 2-chlorophenoxy radical and iron cluster that involves a reduced iron atom and an iron atom terminated by OH, with both products located 16.3 kJ/mol below the separated reactants. Clearly, in the process, iron (III) reduces to iron (II) by electron transfer from chlorophenolate to the iron, as it is also the case for copper catalyst. For comparison, Sun et al. reported the exothermicity of 97.9 kJ/mol for the formation of chlorophenoxy radical as a result of the interaction of the 2,4,5-TriCP molecule with a CuO cluster<sup>16</sup>.

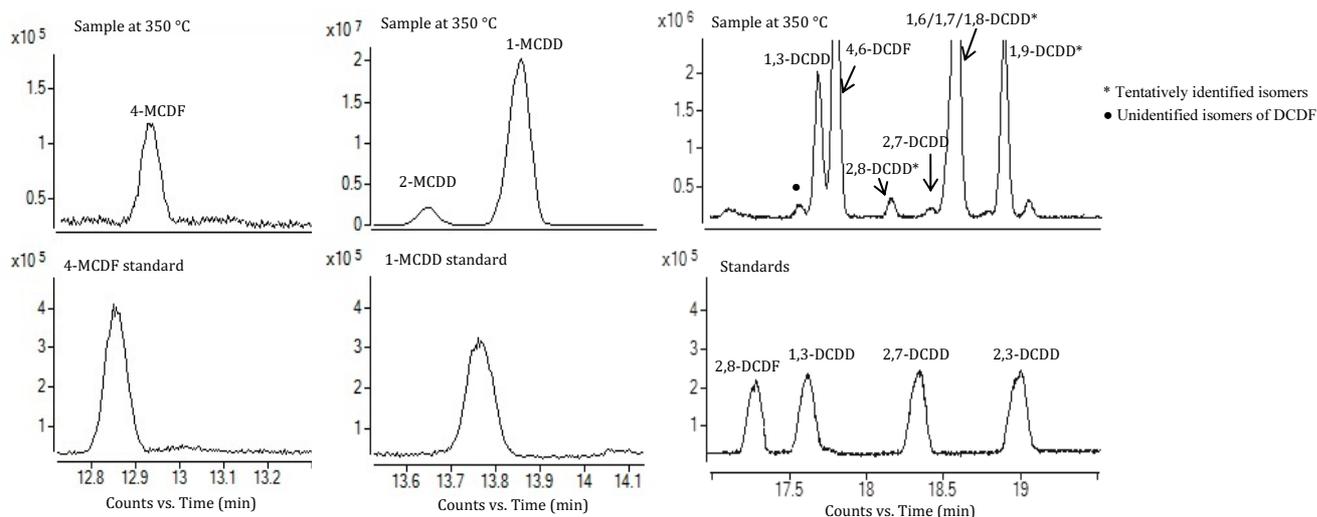


**Figure 2.** The potential energy surface (PES) at 0 K for the reaction of 2-CP and  $\text{Fe}_4\text{O}_6$

**Table 1.** The total energies (a.u.), zero-point energies (a. u.) and relative energies (kJ/mol) at 0 K

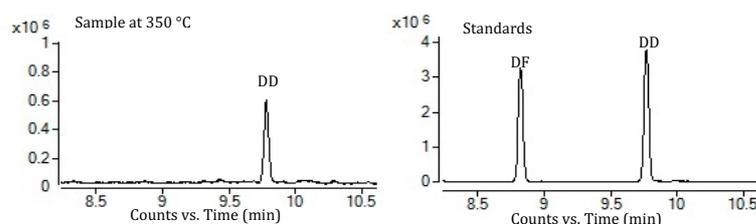
	6-311G(d,p)	ZPE	6-311+G(3df,2p)	$\Delta E$
$\text{Fe}_4(\text{III})\text{O}_6$	-5506.08	0.02	-5506.28	
$\text{Fe}(\text{II})\text{Fe}_3(\text{III})\text{O}_6\text{H}$	-5506.75	0.04	-5506.94	
2-chlorophenol	-767.08	0.10	-767.21	
2-chlorophenoxy	-766.45	0.08	-766.55	
Complex 1	-6273.18	0.12	-6273.51	-44.8
Complex 2	-6273.19	0.12	-6273.52	-69.0
Complex 3	-6273.22	0.12	-6273.54	-132.9
Complex 4	-6273.20	0.12	-6273.52	-77.1
TS 1	-6273.17	0.12	-6273.49	-1.2
TS 2	-6273.18	0.12	-6273.49	-9.7

The experimental results indicate the primary DD/F products as 1-MCDD, followed by 4,6-DCDF and two isomers of DCDD, which we tentatively identified as 1,6-DCDD and 1,9-DCDD (Figure 3). The 4,6-DCDF forms by direct coupling of two surface-bound chlorophenoxy radicals (4,6-DCDF), whereas 1-MCDD is produced by one surface-bound chlorohydrophenoxy radical and one gas-phase molecule of chlorophenol, in processes established by Farquar et al. for copper surfaces<sup>4</sup>. Formation of dichlorinated DD requires coupling of two-surface bound chlorohydrophenoxy radicals, making it a less preferred route to that leading to 1-MCDD.



**Figure 3.** The identification of MCDD/F and DCDD congeners. Slight mismatch in residence time between samples and standards is due to different solvents used (hexane/DCM vs nonane).

Production of 4-MCDF requires dechlorination of 4,6-MCDF, resulting in minor emissions of 4-MCDF (Figure 3), as  $\text{Fe}_2\text{O}_3$  is not a chlorination/dechlorination catalyst. In spite of the 99 % recovery of DF from XAD-2, we have not detected DF (Figure 4), which would have to form by further dechlorination of 4-MCDF. This very characteristic result for catalytic oxidation of 2-CP has been also reported by Born et al.<sup>10</sup> and Ryu<sup>11</sup> for experiments involving fly ash and  $\text{CuCl}_2$  surfaces. Similarity of products formed on Cu and Fe catalysts is expected in light of the results from our DFT computations (Figures 1 and 2). From this perspective, a high yield of DF and no formation of 4-MCDF observed by Nganai et al. for  $\text{Fe}_2\text{O}_3$  surface remain unexplained<sup>8,9</sup>.



**Figure 4.** Lack of detection of DF and identification of minor amounts of DD

Preference for chlorination of 1-MCDD in positions 3, 7 and 8 leads to the formation of minor amounts of 1,3-DCDD, 1,7-DCDD and 1,8-DCDD (Figure 3). Other DCDD (2,7 and 2,3-DCDD) products form only in trace amounts, as they require chlorination of 2-MCDD, a product which is much lower in concentration in comparison to 1-MCDD. By the same token, we observed production of trace amounts of only two TriCDD, as expected due to lack of chlorination/dechlorination functionality of  $\text{Fe}_2\text{O}_3$ . This observation is supported further by detection of small amounts of 2,4-DCP, 2,6-DCP, 2,4,6-TriCP, 1,2-DCBz and 1,2,3-TriCBz in the present experiments. These species form by electrophilic halogenations of 2-CP and MCBz, in a process that could be facilitated by impurities in our  $\text{Fe}_2\text{O}_3$  catalyst. The appearance of elevated amounts of polychlorinated phenols and benzenes, especially PCBz and HCBz, in the measurements of Nganai et al.<sup>8,9</sup> is again inconsistent with the present results. Rather, one would expect enhanced emissions of these species in experiments involving fly ash and  $\text{CuCl}_2$  (or other Lewis acids such as  $\text{FeCl}_3$ ), as is evident in the data collected by Born et al.<sup>10</sup> and Ryu<sup>11</sup>.

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#### References

1. Altwicker ER, Milligan MS. (1993); *Chemosphere* 27(1–3): 301-7.
2. Addink R, Cnubben P, Olie K. (1995); *Carbon* 33(10): 1463-71.
3. Dellinger B, Lomnicki S, Khachatryan L, Maskos Z, Hall RW, Adoukpe J, McFerrin C, Truong H. (2007); *Proc Combust Inst.* 31(1): 521-8.
4. Farquar GR, Alderman SL, Poliakoff ED, Dellinger B. (2003); *Environ. Sci. Technol.* 37(5): 931-5.
5. Qian Y, Zheng M, Liu W, Ma X, Zhang B. (2005); *Chemosphere* 60(7): 951-8.
6. Cains PW, McCausland LJ, Fernandes AR, Dyke P. (1997); *Environ. Sci. Technol.* 31(3): 776-85.
7. Wang HC, Chang SH, Hung PC, Hwang JF, Chang MB. (2009); *J. Hazard. Mater.* 164(2–3): 1452-9.
8. Nganai S, Lomnicki S, Dellinger B. (2008); *Environ. Sci. Technol.* 43(2): 368-73.
9. Nganai S, Lomnicki S, Dellinger B. (2012); *Chemosphere* 88(3): 371-6.
10. Born JGP, Mulder P, Louw R. (1993); *Environ. Sci. Technol.* 27(9): 1849-63.
11. Ryu J-Y. (2008); *Chemosphere* 71(6): 1100-9.
12. Frisch MJ, Trucks GW, Schlegel HB. *Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.*
13. Altarawneh M, Dlugogorski BZ, Kennedy EM, Mackie JC. (2008); *J. Phys. Chem A* 112(16): 3680-92.
14. Altarawneh M, Dlugogorski BZ, Kennedy EM, Mackie JC. (2009); *Prog. Energy Combust. Sci.* 35(3): 245-74.
15. Lomnicki S, Dellinger B. (2003); *J. Phys. Chem A* 107(22): 4387-95.

16. Sun Q, Altarawneh M, Dlugogorski BZ, Kennedy EM, Mackie JC. (2007); *Environ. Sci. Technol.* 41(16): 5708-15.