

FORMATION OF PCDD/F ON THE SURFACE OF IRON OXIDE PARTICLES VIA A PRECURSOR PATHWAY

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Introduction

Iron represents the most abundant transition metal in fly ash,¹ but its role in the condensation and chlorination/dechlorination reactions of PCDD/F from precursor molecules still remains unclear. Previous studies reported the destruction of PCDD/F on surfaces of iron oxides,^{2,3} however, the studies of Nganai et al.⁴⁻⁶ identified large quantities of highly chlorinated phenols and benzenes, in addition to significant yields of dibenzo-p-dioxin (DD), dibenzofuran (DF), 1-MCDD and 4,6-DiCDF, from 2-chlorophenol (2-CPh), with the ratio of PCDD: PCDF (including DD and DF) less than unity. These results indicate strong chlorination/dechlorination activity of iron oxide surfaces. The dechlorination seems more favoured on the surface of the catalyst by the formation of DF from 4,6-DiCDF. Also, the previous studies of 2-CPh oxidation on the surface of fly ash⁷, CuO⁸ and CuCl₂⁹ show a high affinity of these surfaces for the formation of highly chlorinated dioxins with PCDD:PCDF ratio greater than unity. Meanwhile, the investigators did not identify all the isomers of the detected PCDD/F. To this end, the present study aims to investigate the formation of PCDD/F from the oxidation of 2-CPh on surfaces of iron oxide supported on silica to gain a detailed understanding of the role of iron-rich fly ash on the yield and species distribution of chlorinated pollutants in combustion systems. In addition, we are interested in determining the isomers of produced PCDD/F to illustrate their mechanism of formation.

Materials and Methods

We prepared 5 wt % iron (III) oxide catalyst on silica gel (Aldrich, grade 645) support by the method of incipient wetness, to serve as a model for iron-rich fly ash. We explained the catalyst preparation methodology in more detail in ref 10.

Figure 1 illustrates the experimental apparatus. Each experiment comprised 50 mg of the catalyst with a bulk density of 0.59 g/mL, charged inside a 4 mm ID quartz tube and remained immobilised in that by quartz wool. The contact time between the gas and the catalyst varied between 0.03 – 0.06 s at a temperature range of 250 to 550 °C. A syringe pump introduced a constant concentration of 2-CPh (70 ppm) to the reactor in a dilute stream of oxygen in nitrogen (10 % O₂). During 1 h, the product gases were captured in two XAD-2 resin cartridges (200 mg and 50 mg) positioned downstream of the reactor, with the role of the second cartridge to confirm no PCDD/F products breakthrough from the first. At the end of each experiment, *n*-hexane served to extract the resins for two hours using a sonicator. Furthermore, we rinsed the reactor tube and packed catalyst with dichloromethane, and then added the resulting solution to that obtained from the extraction process.

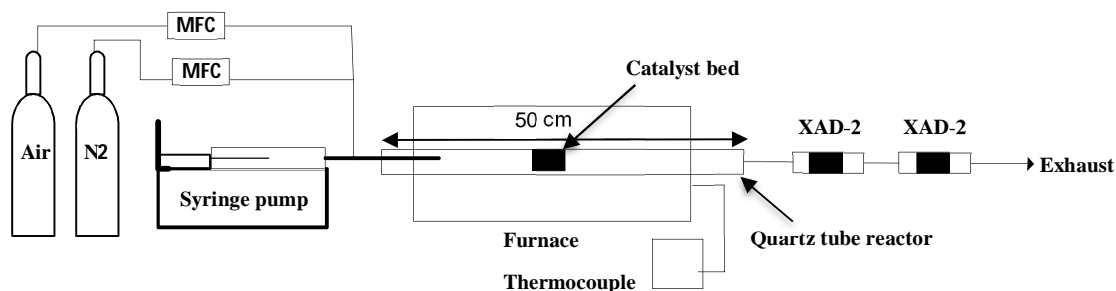


Figure 1. Schematic of the experimental apparatus.¹¹

We analysed the final solutions in two parts, in Newcastle, using Agilent 7200 quadruple time-of-flight GC/MS with a HP-5MS column (length 30 m, inner diameter 0.25 mm and film thickness 0.25 µm) and, in Japan, deploying a GC/HRMS with a SP-2331 column (length 60 m × inner diameter 0.32 mm and film thickness 0.2 µm). We quantitated all detected PCDD/F, in addition to DD with the first column. We used the second column to confirm the distribution of PCDD/F isomers, as, in past studies, this column was found particularly helpful for this purpose.^{12,13} The GCs were operated in a splitless mode for analysing the species and the temperature program of the ovens, which housed the HP-5MS, and the SP-2331 column, imposed 40 °C → (6 °C/min) → 270 °C and 120 °C → (30 °C/min) → 190 °C → (2 °C/min) → 250 °C, respectively. The injector temperature was kept at 250 °C.

Helium, as the carrier gas flowed through the HP-5MS and SP-2331 at a constant rate of 1.2 mL/min and 1.5 mL/min, respectively.

Results

The volatile organic compounds (VOCs) identified in our reactions mainly consist of phenol, benzene, chlorophenols (2,4-, 2,6-DiCPh and 2,4,6-TriCPh) and chlorobenzenes (MCBz, 1,2-, 1,3-, 1,4-DiCBz, 1,3,5-, 1,2,4-, 1,2,3-TriCBz and 1,2,3,4-, 1,2,3,5-TeCBz). In our previous studies we established that, the same isomers of CPhs and CBzs formed on the surface of iron oxide (although at different ratios) regardless of the support used.^{10,14,15} We confirmed the formation of DD and Mono-TriCDD/F in the reaction of 2-CPh on the surface of iron oxide on silica support and quantitated majority of the species. Previously, we showed that contrary to the results of Nganai et al.⁴⁻⁶, we see no formation of DF and detect the appearance of 4-MCDF¹⁶ with both observations agreeing with the findings of other researchers.⁷⁻⁹ Table 1 lists the yields of quantitated species and Figures 2-5 present GC traces of Di-TriCDD/F for the reaction products collected in experiment conducted at 350 °C with the product gases analysed on the SP-2331 column.

We detected 1-MCDD and 4,6-DiCDF, as the prevalent PCDD/F condensation products, with other major condensation species comprising DD, 1,6-, 1,9-, 1,3-DiCDD, 1,3,6- and 1,3,9-TriCDD. The remaining species detected in the exhaust gases originated from either condensation of VOCs or chlorination/dechlorination reactions of the major condensation products. Strong electrophilic substitution of DD yields 2-MCDD and weak acidic activity of the catalyst facilitated limited surface chlorination reactions of 1-MCDD, 2-MCDD, 1,6-DiCDD and 1,9-DiCDD, yielding 1,8-DiCDD with smaller amounts of 1,2-/2,3-, 2,7-/2,8-, 1,4-/1,7-DiCDD, and 1,3,7-, 1,3,8-1,2,4-, 1,2,3-, 1,7,8-, 1,2,8- 1,2,6- and 1,2,9-TriCDD. Dechlorination of 4,6-DiCDF produced 4-MCDF and other species, such as 1,6-, 2,6- and 3,6-DiCDF appeared from the condensation of 1,2,3- and 1,2,4- trichlorobenzene radicals with 2-chlorophenoxy radical on the surface, respectively. Further chlorination of 1,6-, 2,6- and 3,6-DiCDF resulted in appearance of 1,2,6-, 1,3,6- and 2,3,6-/3,4,7-TriCDF. In addition, 1,4,6-, 2,4,6- and 3,4,6-TriCDF results from further chlorination of 4,6-DiCDF.

Comparing the dioxins and furans form on the surface of iron oxide in this study to those generated on the surfaces of CuO⁸ and CuCl₂⁹ indicates lower affinity of iron oxide for chlorination/dechlorination but the same congeners profile with different yields. As Table 1 displays, unlike Nganai et al.⁴⁻⁶ studies, the PCDD:PCDF ratio in this study is greater than unity concurring with similar results of the previous investigations⁷⁻⁹.

Table 1. Yields of DD and Mono-TriCDD/F forming on the surface of iron oxide supported on silica support.

Congeners	Yield [mol %]						
	250 °C	300 °C	350 °C (±SD)	400 °C	450 °C	500 °C	550 °C
DD	0.006	0.012	0.044 (±0.026)	0.020	0.053	0.035	0.024
1-MCDD	0.056	0.41	0.83 (±0.15)	0.74	1.33	0.83	0.32
2-MCDD	0.010	0.031	0.10 (±0.07)	0.041	0.078	0.071	0.028
4-MCDF	0.0087	0.011	0.012 (±0.003)	0.0097	0.011	0.012	0.016
1,3-DiCDD	0.0089	0.025	0.11 (±0.03)	0.034	0.072	0.042	0.021
1,7-/1,4-DiCDD	0.0084	0.011	0.019 (±0.007)	0.013	0.021	0.022	0.014
2,7-/2,8-DiCDD	0.0085	0.011	0.014 (±0.011)	0.010	0.011	0.019	0.011
1,6-DiCDD	0.0676	0.381	0.425 (±0.141)	0.136	0.157	0.145	0.051
1,9-DiCDD	0.023	0.150	0.202 (±0.110)	0.059	0.0702	0.0482	0.0116
1,2-/2,3-DiCDD	0.0087	0.012	0.019 (±0.076)	0.013	0.020	0.032	0.016
1,6-DiCDF	0.0002	0.0021	0.011 (±0.001)	0.0058	0.0081	0.0113	0.0112
3,6-DiCDF	0.0000	0.0013	0.016 (±0.004)	0.0076	0.0074	0.0098	0.0067
2,6-DiCDF	0.0005	0.0038	0.011 (±0.004)	0.0063	0.0084	0.011	0.0070
4,6-DiCDF	0.0507	0.232	0.329 (±0.051)	0.148	0.139	0.113	0.176
1,3,6-TriCDD	0.0082	0.010	0.029 (±0.005)	0.011	0.016	0.014	0.0083
1,3,9-TriCDD	0.0083	0.0093	0.023 (±0.006)	0.011	0.016	0.014	0.0080
1,3,6-TriCDF	0.0000	0.0000	0.0015 (±0.0005)	0.0009	0.0012	0.0013	0.0006
1,4,6-TriCDF	0.0000	0.0000	0.0004 (±0.0008)	0.0007	0.0009	0.0020	0.0038
2,4,6-TriCDF	0.0000	0.0009	0.0032 (±0.0005)	0.0024	0.0028	0.0038	0.0053
1,2,6-TriCDF	0.0000	0.0000	0.0003 (±0.0002)	0.0004	0.0005	0.0015	0.0012
2,3,6-/3,4,7-TriCDF	0.0000	0.0000	0.0015 (±0.0011)	0.0012	0.0011	0.0020	0.0012
3,4,6-TriCDF	0.0000	0.0013	0.006 (±0.002)	0.0036	0.0027	0.0030	0.0038
Yield Σ PCDD*	0.21	1.06	1.8	1.09	1.84	1.27	0.51
Yield Σ PCDF**	0.06	0.25	0.39	0.19	0.18	0.17	0.23
Yield Σ PCDD/F	0.27	1.31	2.84	1.27	2.03	1.44	0.75
PCDD/PCDF	3.55	4.21	4.61	5.83	10.07	7.45	2.20

*Including DD and MCDD **Including DF and 4-MCDF

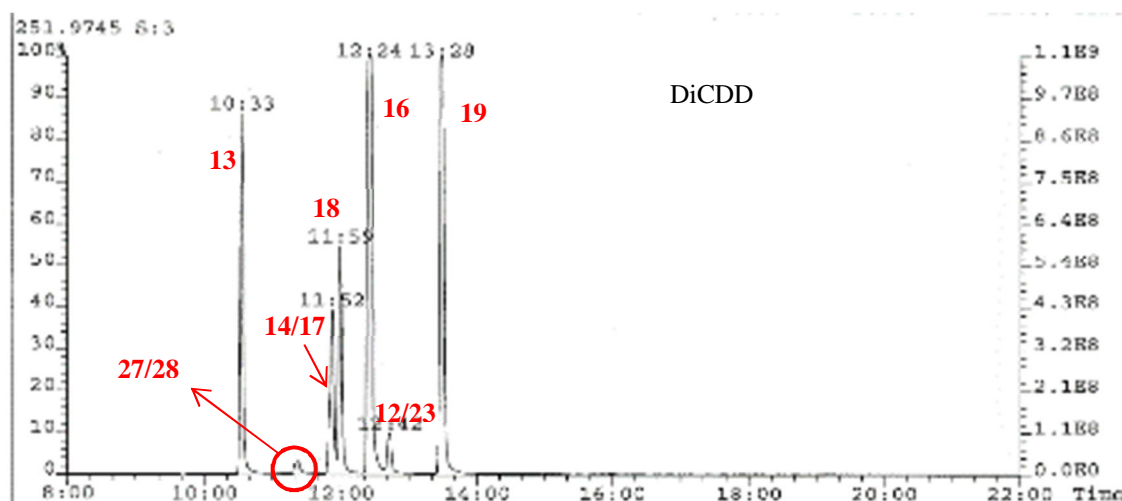


Figure 2. Selected ion monitoring of the sample collected in experiment conducted at 350 °C at DiCDD segment with SP-2331 column.

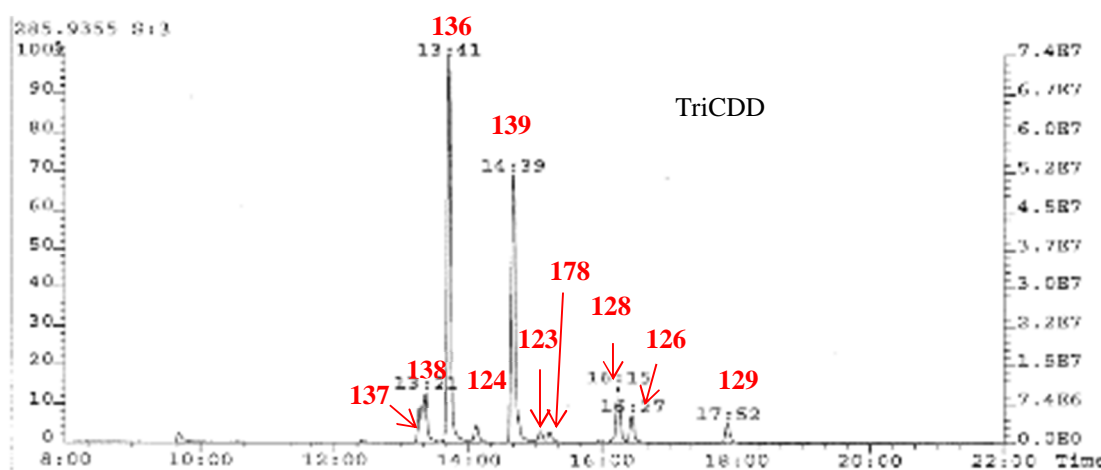


Figure 3. Selected ion monitoring of the sample collected in experiment conducted at 350 °C at TriCDD segment with SP-2331 column.

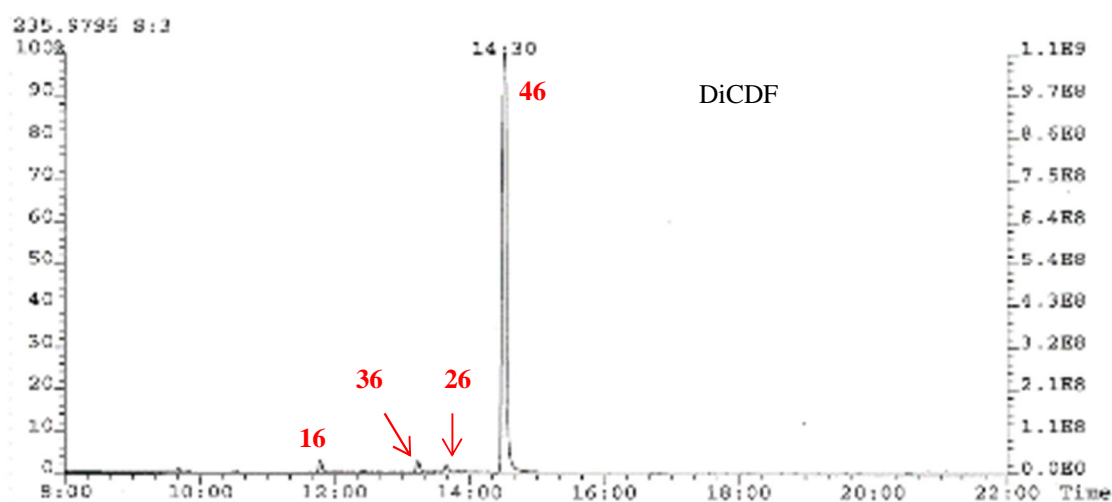


Figure 4. Selected ion monitoring of the sample collected in experiment conducted at 350 °C at DiCDF segment with SP-2331 column.

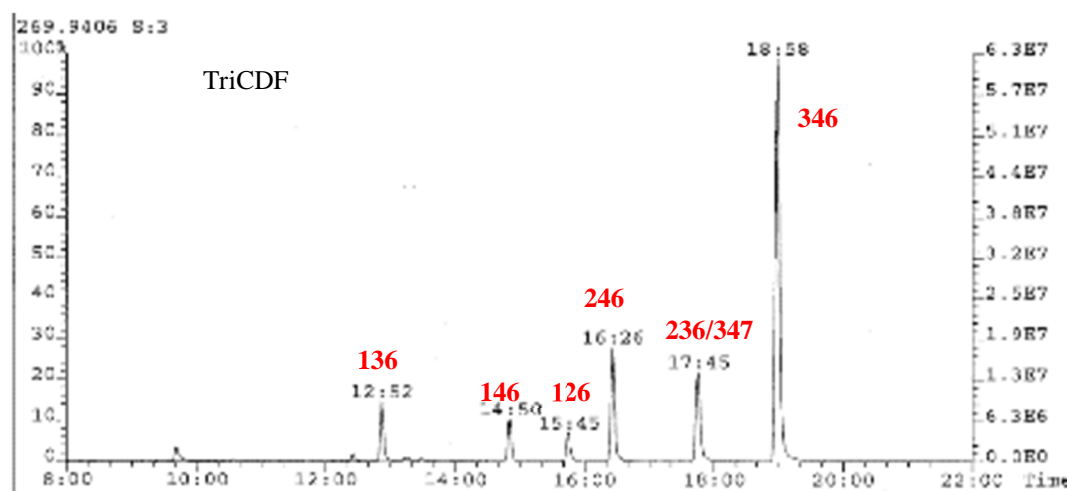


Figure 5. Selected ion monitoring of the sample collected in experiment conducted at 350 °C at TriCDF segment with SP-2331 column.

Conclusions

We have demonstrated that, products from the oxidative decomposition of 2-CPh on the surface of iron oxide supported on silica resemble those of the analogous reactions involving surfaces of fly ash, CuCl₂ and CuO with PCDD:PCDF ratio greater than one, however with less affinity for chlorination/dechlorination reactions. Additional products compared to previous studies (2,7-/2,8-, 1,2-/2,3-DiCDD, 1,6-, 2,6-, 3,6-DiCDF, 1,3,7-, 1,3,8-, 1,3,9-, 1,2,4-, 1,2,3-, 1,7,8-, 1,2,8-, 1,2,6-, 1,2,9-TriCDD and 1,3,6-, 1,4,6-, 1,2,6-, 2,4 6-, 2,3,6-/3,4,7-, 3,4,6-TriCDF) were identified and most of them quantitated here. The condensation of VOC precursors, as well as electrophilic chlorination and dechlorination reactions govern the distribution of the congeners of PCDD/F.

Acknowledgements

This study has been funded by a grant from the Australian Research Council (ARC). SM acknowledges The University of Newcastle for a postgraduate scholarship. We highly appreciate Masanobu Yokota from Miura Co. Ltd., Matsuyama in Japan for helping in analytical analyses.

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