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CATALYST ACTIVATION EFFECT FOR FORMATION OF PCDD/FS IN INCINERATION

S. Mosallanejad², M. Altarawneh¹, E. Kennedy², M. Stockenhuber², S. Jansson³, B. Dlugogorski¹

¹Murdoch University, Australia

²The University of Newcastle, Australia

³Umea University, Sweden

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) constitute an important group of persistent environmental pollutants¹. It is well documented that, formation rates of these compounds accelerate in the presence of transition metals especially copper and iron^{2, 3}, with mono and polychlorinated phenols (denoted in short as PCPhs for convenience) and mono and polychlorinated benzenes (PCBzs) playing a vital role in their formation^{4, 5, 6}. Several studies have reported surface-mediated appearance of PCDD/Fs from reactions of chlorinated phenols on neat silica or transition metals on silica support. For example, in our previous contributions, we studied the oxidation of 2-chlorophenol (2-CPh) on surfaces of neat silica⁷, silica-supported iron oxide⁸, comparing the activity of neat alumina with alumina-supported iron oxide⁹. Notwithstanding our recent investigation, there is general lack of information on the synthesis of PCDD/Fs on transition metals dispersed on alumina support. This is in spite of iron and aluminium oxides being the most abundant compounds in fly ash, and the fact that, in its own right, alumina represents a potent catalyst for formation of carbonaceous matrix in oxidation of phenolic species, the behaviour that is unlike that of silica.

For these reasons, in the present study, we investigate the catalytic decomposition of 2-CPh into toxic products including volatile organic compounds (VOCs, such as higher PCPhs and PCBzs), as well as PCDD/Fs on the surface of alumina-supported iron (III) oxide at a reaction temperature of 350 °C and the time on stream of 7 h. Selecting long time on stream has particular significance for the so-called memory and catalyst-activation effects in large-scale combustion systems, such as the incineration of municipal solid waste, where particles spend long time on walls or in air-cleaning devices. The memory effect is well known, but the catalyst-activation effect is not. As we will demonstrate below, short experiments, especially those that are less than four hours in duration, may not lead to realistic steady-state measurements of emission of PCDD/Fs. This is because, to be effective for generation of PCDD/Fs, the extremely reactive sites on alumina surfaces must first be covered by a layer of carbonaceous coating. Only then, the alumina particles become active for the formation of PCDD/Fs. As far as we can ascertain, the present investigation is the first that demonstrates unequivocally the importance of the catalyst-activation effect on rates of formation of PCDD/Fs.

Materials and Methods

We prepared 5 % iron (III) oxide catalysts on γ -alumina support by the method of incipient wetness¹⁰, as a model that contains both alumina and iron oxide for studying the low-temperature catalytic oxidation reactions of 2-CPh. The solution of Fe(NO₃)₃ was applied to wet the support, with subsequent drying of the samples at 110 °C and their calcination in air at 450 °C for 5 h. Catalyst particles of between 150 and 250 μ m in size were used for the experiment. We calcined the catalysts further for 1 h directly in the reactor immediately prior to the start of the reaction. To maintain the contact time between the gas and the catalyst of 40 ms, we consumed 89 mg (bulk density of 1.06 g/mL) of the alumina-supported iron oxides in each experiment. Catalyst was charged inside a 4 mm ID quartz tube and was kept immobilised in the tube by two skeins of quartz wool. 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 % O₂) over the surfaces of the catalyst. The duration (i.e., time on stream of catalyst) of the experiment corresponded to 7 h. The product gases (containing VOCs and PCDD/Fs) 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 VOCs and PCDD/Fs breakthrough from the first. We spiked the first XAD-2 adsorbent prior to the experiments with surrogate standards of 10 μ L of deuterated chlorobenzene (200 μ g/mL) and 2 μ L of 1,2,3-dichlorobenzofuran (50 μ g/mL). We extracted the resins with n-hexane for 2 h using a sonicator, at the end of each experiment. Finally, an Agilent 7200 quadruple time-of-flight GC/MS, operating in the splitless mode, served to identify VOCs and PCDD/Fs products. The GC oven housed an HP-5MS column (30 m \times 0.25 mm i.d. \times 0.25 μ m). The oven temperature was initially

held at 40 °C for 2 min, then increased to 270 °C at 6 °C/min and finally held for 3 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.

Results and Discussion

In the first three hours on stream, the entire amount of feed 2-CPh converts (see the conversion data in Table 1) to the carbonaceous matrix (coke) that covers the surface catalyst and to CO₂, CO and HCl, quantitated as the major products.¹¹ Only after the initial induction period, unreacted 2-CPh emerges from the reactor outlet, with the conversion of 2-CPh declining to 89.7 % in the final hour of the experiment. A demonstrable change in the catalyst colour, from orange to black, evidenced the coke deposition during the reaction in the first three hours of the experiment. Potter et al.¹² also reported high activity of γ -alumina for decomposition of 2-CPh that prevents condensation process of 2-CPh on the surface. We explain the high activity of γ -alumina by Al³⁺ Lewis acid sites present on catalytic surfaces, and by the surface hydroxyl groups that afford the condensation of VOCs species from the gas phase^{13, 14}.

As demonstrated in Tables 1-3, initially, we detected no PCPhs, but observed the generation of PCBzs, the appearance of PCDFs and a very small amount of PCDDs. Although the limits of detection and recoveries of PCPhs (1.5-3 ng/mL, 52-72 %) are inferior to those of PCBzs (1.0-2.5 ng/mL, 84-96 %), they cannot explain the paucity of PCPhs. Normally, the chlorodehydroxylation of PCPhs governs the production of PCBzs from PCPhs in combustion systems, explaining large amounts of 1,2-DCBz, 1,2,4-/1,2,3-TriCBzs and 1,2,3,5-TCBz forming from 2-CPh, as illustrated in Table 2 for longer induction time. Thus, initially, PCBzs arises from the coke deposited on catalyst surface rather than directly from 2-PCPh; i.e., by the de novo-like mechanism.

Once coke covers the catalyst surface, the most abundant congeners of chlorinated dibenzofurans, 4,6-DCDF and 4-MCDF (Figure 1), form via the Langmuir-Hinshelwood pathway by combining two adsorbed 2-chlorophenoxy (2-CPhx) keto-carbon-centred radicals on the surface¹⁵. Reaction mechanism operating in surface-catalysed formation of PCDD/Fs from PCPhs might be similar to analogous steps prevailing in the gas phase.¹⁶ Other PCDF congeners, 1,6-/2,6-/3,6-DCDFs, probably emerge from the condensation of 1,2,3-/1,2,4-TriCBz radicals with 2-CPhx on the surface. Likewise, DD, 1-MCDD, 1,6-/1,9-DCDD congeners (Figure 2) arise along the Eley-Rideal pathway as established by Lomnicki et al.¹⁵ The appearance of 1,9-DCDD indicates the Smiles rearrangement reaction. Generation of other PCDD/Fs takes place mainly by condensation of 2-CPh/2-CPhx with higher chlorinated PCPhs/PCPhxs. Production of other (usually minor) congeners of PCDD/Fs involves electrophilic chlorination reactions.^{13,17} These reactions also account for the formation of some higher chlorinated PCBzs. Finally, trivial amounts of DF and relatively small selectivity of 2-CPh to Ph (Tables 3 and 1, respectively) signify limited importance of dechlorination pathways in our system. This observation also follows from examining the fingerprint of PCBzs, defined by chlorodehydroxylation of PCPhs present in our system. Hydrodehydroxylation of PCPhs or chlorination and dechlorination of PCBzs seem less important in explaining the PCBz fingerprint.

Evidently, the low ratios of PCDDs to PCDFs (Table 3) indicate that, the de novo pathway operates at short induction times in our system (as also noted above for the formation of PCBzs). This is because all 2-CPh converts to coke and permanent gases, blocking the precursor synthesis of PCDD/Fs. As coke covers the surface, the precursor pathway unblocks with the catalytic sites promoting the generation of PCDD/Fs. This process is reflected by an increasing ratio of PCDDs to PCDFs, and, hence, rapidly declining importance of the de novo mechanism. We conclude that, the alumina particles require a long induction time to become active for the formation of PCDD/Fs in partial oxidation of PCPhs. Previous studies, including large-scale measurements of emission of PCDD/Fs in incineration processes, overlooked this important catalyst activation effect.

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Table 1. Yields (mol %) of Ph and M-TCPs as function of time on stream during the initial 7 h at 350 °C, X_{2-CPh} stands for conversion of 2-CPh. *Does not include phenol.

Products	Time on stream (h)						
	1 th h	2 nd h	3 th h	4 th h	5 th h	6 th h	7 th h
X_{2-CPh}	100	100	100	99.0	97.7	93.1	89.7
Phenol	0.0043	0.0051	0.0056	0.0044	0.0051	0.0092	0.011
2,4-DCPh	0	0	0	0.013	1.2	3.0	4.9
2,6-DCPh	0	0	0	0.019	2.1	3.7	5.1
2,4,6-TriCPh	0	0	0	0.054	1.7	2.2	2.2
2,3,4,6-TCPH	0	0	0	0	0.029	0.042	0.040
Σ PCPhs*	0	0	0	0.086	5.03	8.94	12.2

Table 2. Yields (mol %) of Bz and CBzs as function of time on stream during the initial 7 h at 350 °C. *Does not include benzene.

VOC Products	Time on stream (h)						
	1 th h	2 nd h	3 th h	4 th h	5 th h	6 th h	7 th h
Benzene	0.00052	0.0011	0.0013	0.0018	0.0022	0.0023	0.0022
CBz	0.0020	0.012	0.015	0.021	0.027	0.026	0.026
1,3-DCBz	0.00042	0.0035	0.0038	0.0053	0.0078	0.0077	0.0072
1,4-DCBz	0.00004	0.00083	0.00082	0.00098	0.0012	0.0012	0.0012
1,2-DCBz	0.0021	0.029	0.028	0.033	0.047	0.051	0.053
1,3,5-TriCBz	0.00002	0.00024	0.00030	0.00046	0.00072	0.00079	0.00078
1,2,4-TriCBz	0.00024	0.0026	0.0035	0.0050	0.0076	0.0079	0.0075
1,2,3-TriCBz	0.00018	0.0020	0.0019	0.0023	0.0046	0.0024	0.0020
1,2,3,5-TCBz	0.00009	0.00093	0.0010	0.0013	0.0019	0.0013	0.00093
1,2,3,4-TCBz	0.00001	0.00008	0.00009	0.00013	0.00020	0.00015	0.00013
PCBz	0	0.00004	0.00004	0.00005	0.00006	0.00005	0.00004
HCBz	0	4.8×10^{-6}	3.5×10^{-6}	3.9×10^{-6}	6.6×10^{-6}	5.0×10^{-6}	3.5×10^{-6}
Σ PCBzs*	0.0051	0.0512	0.0545	0.0695	0.0981	0.0985	0.0988
PCPhs/PCBzs	0	0	0	1.24	51.3	90.8	124

Table 3. Yields (mol %) of DD/DF and M-TriCDD/Fs as function of time on stream during the initial 7 h at 350 °C. *Includes MCDD/Fs.

PCDD/Fs Congeners	Time on stream (h)						
	1 th h	2 nd h	3 th h	4 th h	5 th h	6 th h	7 th h
DF	0	0	0	0.00074	0.0010	0.0011	0.0012
DD	0	0	0	0.010	0.16	0.25	0.33
1-MCDF	0	0	0.0047	0.0052	0.0067	0.0073	0.0069
2-MCDF	0	0	0	0	0.0051	0.0052	0.0053
3-MCDF	0	0	0	0.0046	0.0050	0.0051	0.0051
4-MCDF	0	0.0047	0.0064	0.012	0.024	0.024	0.025
2-MCDD	0	0	0.0048	0.042	0.58	0.85	1.0
1-MCDD	0	0	0.0069	0.27	2.2	2.5	2.5
1,6-DCDF	0	0.0082	0.015	0.025	0.038	0.038	0.038
3,6-DCDF	0	0.0040	0.0050	0.0078	0.013	0.014	0.015
2,6-DCDF	0	0.0044	0.0061	0.0099	0.020	0.023	0.025
4,6-DCDF	0	0.013	0.031	0.067	0.14	0.16	0.16
1,3-DCDD	0	0	0.0080	0.083	0.49	0.71	0.84
1,7-/1,4-DCDD	0	0	0.0055	0.015	0.063	0.074	0.082
2,7/2,8-DCDD	0	0	0.0056	0.016	0.076	0.10	0.12
1,6-DCDD	0	0.0050	0.015	0.19	0.92	1.1	1.3
1,9-DCDD	0	0	0.0074	0.047	0.35	0.44	0.50
1,2/2,3-DCDD	0	0	0.0052	0.012	0.062	0.084	0.10
1,3,6-TriCDF	0	0.00096	0.0015	0.0030	0.0067	0.0077	0.0083
1,4,6-TriCDF	0	0.0014	0.0017	0.0028	0.0050	0.0051	0.0055

2,4,6-TriCDF	0	0.0032	0.0060	0.0097	0.022	0.022	0.022
1,2,6-TriCDF	0	0.00058	0.00077	0.0017	0.0047	0.0060	0.0062
2,3,6/3,4,7-TriCDF	0	0	0.00068	0.0018	0.0067	0.0088	0.0095
3,4,6-TriCDF	0	0.00059	0.00092	0.0026	0.0079	0.011	0.012
1,3,6-TriCDD	0	0.0054	0.016	0.058	0.23	0.29	0.31
1,3,9-TriCDD	0	0.0049	0.0085	0.030	0.13	0.17	0.18
Σ M-TriCDDs	-	0.02	0.08	0.76	5.08	6.32	6.95
Σ M-TriCDFs	-	0.04	0.08	0.15	0.30	0.34	0.35
PCDDs/PCDFs*	-	0.37	1.04	4.98	16.7	18.8	20.0

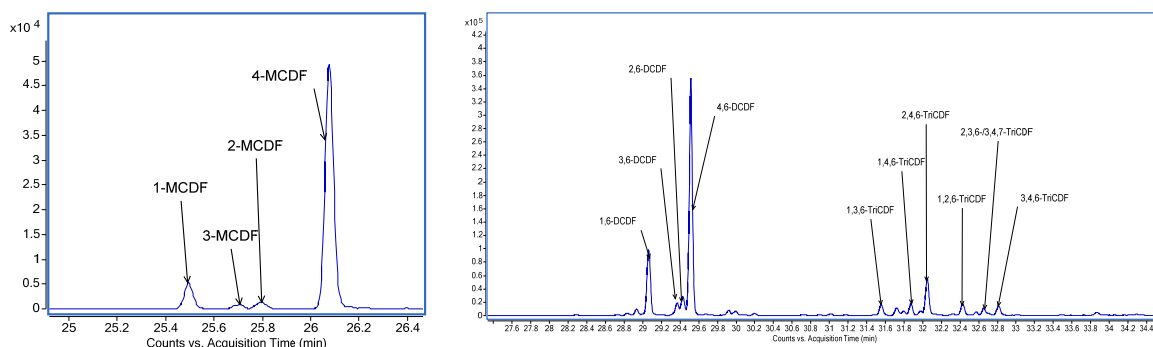


Figure 1. Extracted ion chromatogram and elution orders of M-TriCDF.

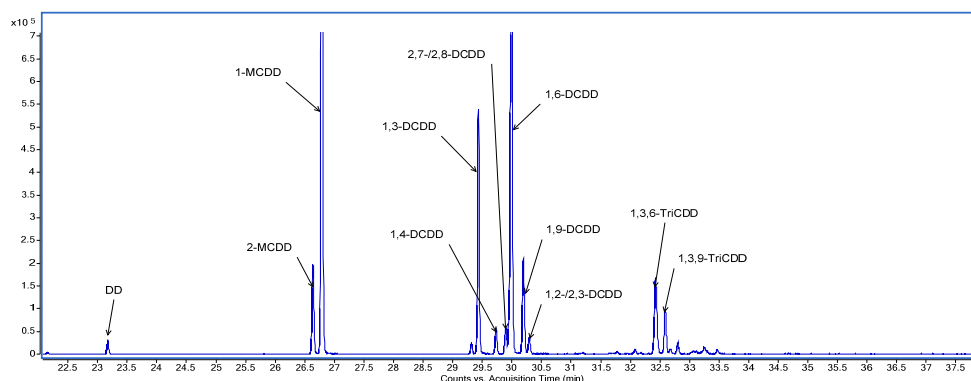


Figure 2. Extracted ion chromatogram and elution orders of DD and M-TriCDD.