

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

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Introduction

The general pathways for formation of polychlorodibenzo-*p*-dioxin and polychlorinated dibenzofurans (PCDD/F, aka dioxins) comprise non-catalytic^{1, 2} and catalytic^{3, 4} reactions. The catalytic reactions include precursor and de novo syntheses that occur in the temperature range of between 250 and 400 °C^{4, 5, 6, 7}. Non-catalytic precursor reactions that arise between 550 and 700 °C appear less important in practical systems and fall outside the scope of the present contribution. The catalytic reactions constitute the main corridor for formation of PCDD/F in incinerators, fires, and other combustion processes, where the rates of precursor-based reactions that form PCDD/F exceed the rates of the de novo reactions⁸. The catalytic precursor pathway entails synthesis of PCDD/F from molecules of chlorinated phenols, chlorobenzenes or chlorinated biphenyls, whereas the de novo synthesis involves aryl moieties that arise in oxidation of complex polycyclic soot matrices. Typically, in the catalytic precursor synthesis, the initiation reactions involve adsorption of chlorinated phenol onto the terminal hydroxyl groups of active sites forming chlorophenolate anion, followed by electron transfer from chlorophenolate to the active site⁹. Finally, physisorbed chlorophenoxy and chlorohydroxyphenoxy radicals¹⁰ generate PCDD or PCDF either via Eley-Rideal (a reaction comprising an adsorbed radical and a gas-phase molecule) or Langmuir-Hinshelwood (a reaction involving two adsorbed radicals) mechanism. Presence of metal oxide such as copper, nickel, iron, and zinc is essential in the formation of PCDD/F in the catalytic reaction⁵.

Oxides of iron, alumina and silica occur in abundance in fly ash and can 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) oxide¹¹ and on the surfaces of neat alumina and alumina-supported iron oxide particles¹². In the current contribution, we aim to compare 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 alumina- and silica-supported iron oxide at a reaction temperature of 350 °C. In particular, this study concentrates on gaining an understanding of the effects of alumina and silica supports for iron oxide and other transition metals for catalysing low-temperature oxidation reactions in combustion systems.

Materials and Methods

We prepared 5 % iron (III) oxide catalysts on γ -alumina and silica supports by the method of incipient wetness³, as models of the iron rich material for studying the low-temperature catalytic oxidation reactions of 2-CPh. The solution of Fe(NO₃)₃ was applied to wet the supports, with subsequent drying of the samples at 110 °C and their calcination in air at 450 °C for 5 h. The experiments involved catalyst particles of between 150 and 250 μ m in size. 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 0.04 s, we consumed 89 mg (bulk density=1.06 g/mL) and 50 mg (bulk density=0.59 g/mL) of the alumina- and silica-supported iron oxides, respectively, in each experiment. We charged the catalysts inside a 4 mm ID quartz tube and kept them 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 and 75 ppm in a dilute stream of oxygen in nitrogen (10 % O₂) over the surfaces of alumina and silica respectively. The duration of the Fe(III)/Al₂O₃ experiments corresponded to 4 h and those involving Fe(III)/SiO₂ to 1 h. The product gases (containing VOC and PCDD/F) 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. 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 ¹²C₁₃-2,3-dichlorobenzofuran (50 μ g/mL). The resins were extracted with *n*-hexane for 2 h using a sonicator, at the conclusion of each experiment. 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 an 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 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

The oxidative degradation of 2-CPh on the surface of silica- and alumina-supported iron oxide shows significant differences. In spite of 10 times higher concentration of 2-CP in Fe(III)/Al₂O₃ than in Fe(III)/SiO₂ experiments, we detected no breakthrough of 2-CPh and no formation of polychlorinated phenols in first 3 h of the experiments. In this period, 2-CPh decomposed completely to CO₂, naphthalene, carbonaceous compounds on the surface, and minor non-chlorinated species, tentatively identified as ethylethenylbenzene and methylindene. After 3 h, it appeared that, soot covered all active sites allowing unconverted 2-CPh to emerge from the catalyst bed. However, in experiments involving silica-supported iron oxide, we identified unreacted 2-CPh and other chlorinated phenols within 1 h of commencing the reaction. Figure 1 presents the EI (extracted ion) chromatogram of the extracted resin in each hour for 2-CPh decomposition on the surface of alumina-supported iron oxide.

Figure 2 compares the integrated yield of chlorinated phenols emerging from the catalyst bed of alumina-supported iron oxide with that from the bed of silica-supported iron oxide catalyst. The collection of chlorophenols lasted 4 h in the Fe(III)/Al₂O₃ experiments and 1 h in the Fe(III)/SiO₂ experiments. Although the concentration of 2-CPh in the incoming gas stream in Fe(III)/Al₂O₃ experiments exceeded that in Fe(III)/SiO₂ trials by 10 times (750 ppm vs 75 ppm), the results indicate significantly lower formation of chlorinated phenols.

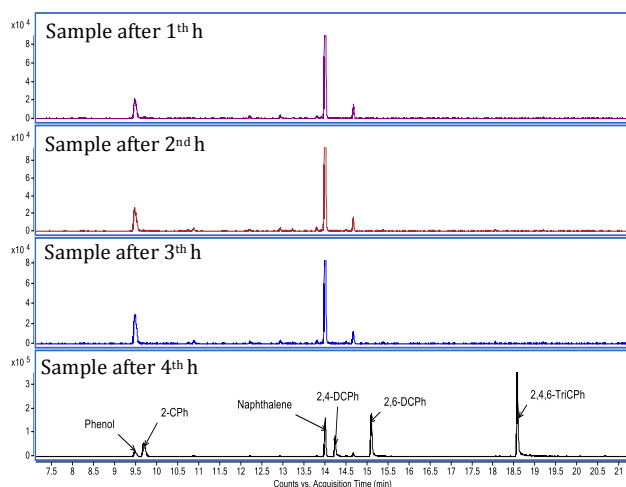


Figure 1. EI (extracted ion) chromatogram of phenolic species adsorbed on the XAD resin during consecutive hours after the onset of 2-CPh decomposition on the surface of alumina-supported iron oxide at 350 °C; $m/z = 94.0398, 128.0008, 161.9614$ and 195.9210 .

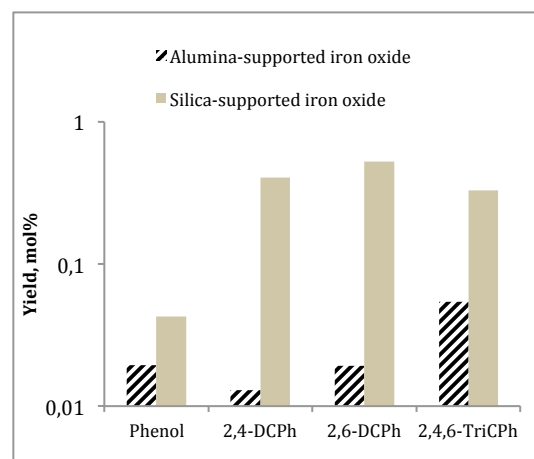


Figure 2. Comparison of the produced phenol and chlorinated phenols on the surface of alumina- and silica-supported iron oxide at 350 °C. The collection of chlorophenols lasted 4 h in the Fe(III)/Al₂O₃ experiments and 1 h in the Fe(III)/SiO₂ experiments.

The fresh alumina-supported iron oxide catalyst chlorodehydroxylates the chlorinated phenols to form polychlorinated benzenes (PCBz), especially 1,2-DCBz, 1,2,4-TriCBz, 1,2,3-TriCBz and 1,2,3,5-TeCBz. This observation accords with that of Ryu et al.⁶, who identified 1,2-DCBz as the major product of chlorodehydroxylation of 2-CPh. Ryu et al. also reported 1,2,4-TriCBz, 1,2,3-TriCBz and 1,2,3,5-TriCBz as the dominant congeners of PCBz appearing in catalytic chlorodehydroxylation of 2,4-DCPh, 2,6-DCPh and 2,4,6-TriCPh, respectively. Further chlorination of 1,2-DCBz appears to produce several higher chlorinated congeners of PCBz. Figure 3 presents the EI chromatogram of the extracted resin for the first 4 h of the reaction on the

Fe(III)/Al₂O₃ catalyst and Figure 4 compares the accumulated yields of chlorinated benzenes during the 4 h long Fe(III)/Al₂O₃ experiments, with those from 1 h collection during the and Fe(III)/SiO₂ experiments.

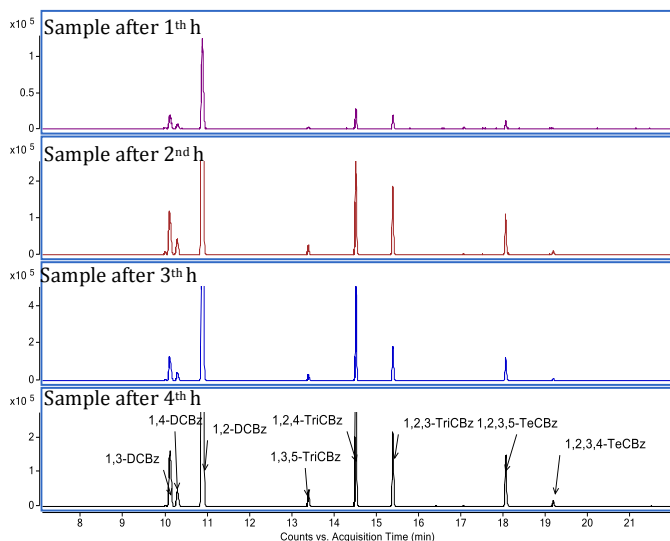


Figure 3. EI chromatogram of extracted resin in each hour after 2-CPh decomposition on the surface of alumina-supported iron oxide at 350 °C; $m/z = 145.9676, 179.9277$ and 215.8858 .

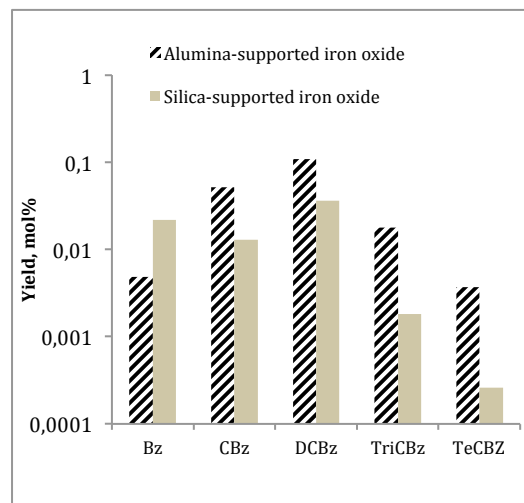


Figure 4. Comparison of the produced benzene and chlorinated benzenes on the surface of alumina- and silica-supported iron oxide at 350 °C.

Mono-TriCDD/F constitute the dominant congeners of PCDD/F during the decomposition of 2-CPh on the surface of the catalysts. The formation of Mono-TriCDD/F commenced after 1 h on the surface of alumina-supported iron oxide catalyst. Figures 5 and 6 compare the integral yields of Mono-TriCDD/F. The experiments lasted 4 h and 1 h for Fe(III)/Al₂O₃ and Fe(III)/SiO₂ catalysts, respectively.

The ratio of PCDF:PCDD is higher in the experiment comprising alumina-supported iron oxide catalyst (0.31) than in the experiment involving the silica-supported iron oxide catalyst (0.21). This is because Fe(III)/Al₂O₃ produces more CBz that tend to synthesise with CPh to form PCDF rather than PCDD.¹³ A large amount of carbon formed on the surface of alumina-supported iron oxide. In a study of Hell et al.¹⁴, carbon in fly ash is reported as the main source of PCDF (more than 90 %). Hell et al. considered the condensation of intermediate monoaromatic rings as the main source PCDDs (more than 50 %). The main congeners of Mono-TriCDDs arising on both catalysts comprise 1-MCDD, 2-MCDD, 1,6-DCDD, 1,9-DCDD, 1,3,6-TriCDD and 1,3,9-TriCDD, and those of Mono-TriCDF include 4-MCDF, 4,6-DCDF, 1,6-DCDF, 2,6-DCDF, 3,6-DCDF, 2,4,6-TriCDF, 3,4,6-TriCDF and 2,3,6-/3,4,7-TriCDF. Finally, we report being unable to identify dibenzofuran (DF) during the first 3 h in the experiment involving alumina-supported iron oxide experiment, a minute amount of DF appeared in the 4th hour, probably resulting from the decomposition of the soot on the surface of the catalyst.

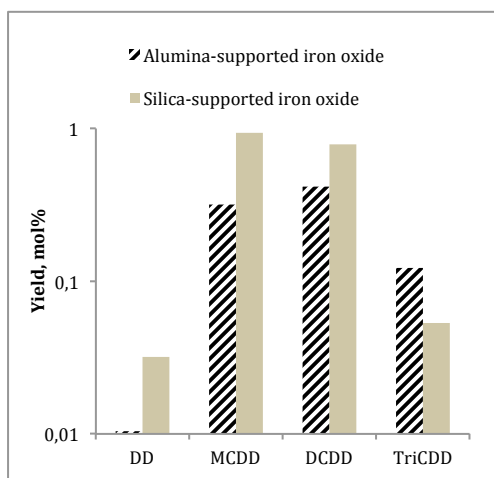


Figure 5. Comparison of the DD and Mono-TriCDD formed on the surface of alumina- and silica-supported iron oxide catalyst at 350 °C. The collection of PCDD lasted 4 h in the Fe(III)/Al₂O₃ experiments and 1 h in the Fe(III)/SiO₂ experiments.

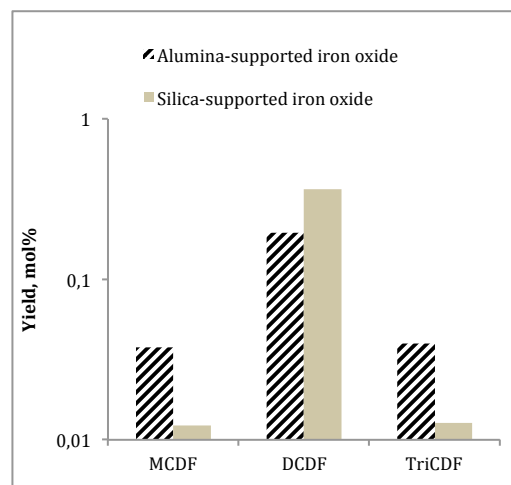


Figure 6. Comparison of the Mono-TriCDF formed on the surface of alumina- and silica-supported iron oxide catalyst at 350 °C. The collection of PCDF lasted 4 h in the Fe(III)/Al₂O₃ experiments and 1 h in the Fe(III)/SiO₂ experiments.

Acknowledgements

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