



PCDD/F catalysis by metal chlorides and oxides



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HIGHLIGHTS

- A sequence for de novo activity of metal chlorides and oxides.
- CuCl₂ is the most active PCDF catalyst, CrCl₃ is its PCDD antagonist.
- Oxygen affects the output of PCDD/F and the PCDF/PCDD-ratio.
- Congener signatures refute the thermodynamic control hypothesis.

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ABSTRACT

Model fly ash (MFA) samples were composed of silica, sodium chloride, and activated carbon, and doped with metal (0.1 wt% Cu, Cr, Ni, Zn and Cd) chloride or oxide. Each sample was de novo tested at 350 °C for 1 h, in a flow of gas (N₂, N₂ + 10% O₂, +21% O₂ or +10% H₂) to investigate the effect of metal catalyst and gas composition on PCDD/F formation. Total PCDD/F yield rises rapidly with oxygen content, while the addition of hydrogen inhibits the formation and chlorination of PCDD/F. The amount of PCDD on average rises linearly with the oxygen concentration, while that of PCDF follows a reaction order of about 1/2; thus the PCDF to PCDD ratio drops when more oxygen becomes available. Some samples do not follow this trend. Chlorides are much more active than oxides, yet there are marked differences between individual metals. Principal component analysis (PCA) was applied to study the signatures from all samples, showing their unique specificity and diversity. Each catalyst shows a different signature within its individual homologue groups, demonstrating that these signatures are not thermodynamically controlled. Average congener patterns do not vary considerably with oxygen content changing from oxidising (air) to reducing (nitrogen, hydrogen).

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1. Introduction

Ever since the discovery of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in the effluents from Municipal Solid Waste Incineration (MSWI) (Olie et al., 1977) numerous endeavours were launched to identify their major pathways of formation. Some consensus was reached on potential pathways capable of forming PCDD/F during waste incineration (Addink et al., 1995; Huang and Buekens, 1995; Addink and Olie, 1995a; Fiedler, 1998, 2003; Stanmore, 2004). The homogeneous pyrogenic route takes place in the gas phase between 500 °C and 800 °C, supplying PCDD/F as

well as its precursors. Low temperature catalytic routes proceed mainly between 200 °C and 400 °C by heterogeneous gas/solid reactions subdivided into (a) de novo synthesis, starting from macro-molecular carbon or from polycyclic aromatic hydrocarbons (PAHs) structures, and (b) precursor pathways starting from organic molecules similar to PCDD/F, including e.g. chlorophenols (CP), chlorobenzenes (CBz) and polychlorinated biphenyls (PCB). Both routes proceed at the surface of solid carbon (e.g., soot, charred materials) on fly ash particles, catalysed by certain metal ions (Addink and Olie, 1995a). PCDF are released directly by catalytic oxidation of suitable structures in the carbon matrix, while PCDD form by both routes, i.e. the condensation of precursor compounds and direct release from the carbon matrix (de novo formation) (Hell et al., 1997, 2001).

Residual carbon, precursor compounds, chlorine atoms and

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metal ions in fly ash (FA) from MSWI are the basic ingredients for heterogeneous formation reactions. Separate studies discuss de novo synthesis theory and testing. Catalysis by various metals and its suppression, the chemical compound classes formed and the effect of operating variables, such as temperature, time, oxygen, HCl, and Cl₂ deserve special attention. In order to scrutinise their effect, tests at laboratory scale use either real fly ash or artificially composed model fly ash (MFA), typically composed of inorganic matrix material, a source of chloride and carbon, and catalyst (Kuzuhara et al., 2003; Fujimori et al., 2009; Yang et al., 2015a). Real fly ash is much more reactive (Addink and Olie, 1995a; Stieglitz, 1998), yet the precise source of this activity remains elusive. Before its use in tests, it is either Soxhlet extracted, to remove precursors, or thermally treated with air to oxidise native carbon, without altering the mineral matrix or catalytic compounds.

Numerous chlorides or oxides (Ca, Cd, Fe, Hg, Mg, Mn, Ni, Pb, Sn, Zn, K, Cr and Cu) were tested as catalyst, to form PCDD/F and other chlorinated aromatic compounds (Kuzuhara et al., 2003; Ryan and Altwicker, 2004; Takaoka et al., 2005a; Öberg et al., 2007a, b, 2008; Fujimori et al., 2009, 2011; Chin et al., 2012; Yang et al., 2015a; Liao et al., 2016). Copper has been identified as strongest catalyst (Olie et al., 1998; Takaoka et al., 2005a); both CuCl and CuCl₂ act as catalyst and as chlorine source simultaneously (Addink and Olie, 1995a; Mul et al., 1997; Taylor et al., 2000; Takaoka et al., 2005b). Also the precursor route is enhanced in the presence of Cu (II), up to three orders of magnitude (Gullett et al., 1992); the chlorination and condensation of acetylene and dichloroacetylene to form PCDD/F occur only in the presence of CuCl₂/CuCl (Taylor et al., 2000).

In de novo tests, CuCl₂ plays an important role not only in the chlorination of carbon, but also during the oxidative breakdown of carbonaceous material (Stieglitz et al., 1993; Stieglitz, 1998). It is also the preferred catalyst to generate chlorine from hydrogen chloride by the Deacon reaction. Takaoka et al. (2005a) evaluated the chemical speciation of copper in real MSWI fly ash samples and their formation of chlorinated aromatics: the amount of CuCl₂·3Cu(OH)₂ correlated well with the formation of chlorinated aromatics in real fly ash. An oxychlorination cycle described by Takaoka et al. (2005b) shows the dynamic changes of copper speciation in fly ash during de novo synthesis of PCDD/F.

Other metals represented in fly ash, like Zn, Pb, Cr, Cd and Ni, possibly possess substantial catalytic activity (Ferreira et al., 2003), either as such, or combined with matrix materials and/or carbon. Gullett et al. (1992) and Oehme et al. (1989) suggested that nickel compounds could catalyse the formation of PCDD/F. Öberg et al. (2007b) correlated the elemental composition of fly ash and chlorinated aromatics, suggesting that Cr and Ni could contribute to de novo formation. Conversely, their tests showed that addition of CrCl₃ and Cr₂O₃ decreased the formation of CBz and PCDD/F and that NiCl₂ did not show significant effects (Öberg et al., 2007a, b).

Chin et al. (2012) examined both de novo and precursor reactions in MSWI fly ash, doped with metal chlorides and chlorinated aromatic precursors. When adding 10 wt% of FeCl₂, ZnCl₂ and CuCl₂ onto the fly ash test medium, the resulting PCDD/F concentration is 8.8, 25.5 and 369.5 ng/g (2,3,7,8-PCDD/F), respectively. Thus, the catalytic activity of ZnCl₂ accounted for 5–10% of that for CuCl₂. Fujimori et al. (2009) tested eleven different samples and ranked their catalytic capacity of forming different chlorinated aromatic compounds as follows:

CuCl₂·2H₂O > Cu₂(OH)₃Cl > FeCl₃·6H₂O > FeCl₂·4H₂O > CuO > Fe₂O₃ > PbCl₂ > Blank > ZnCl₂ > PbO > ZnO

The role of zinc depends on its speciation and the presence of other metals as catalyst. With only zinc present, the formation of

chlorinated aromatic compounds was promoted by its chloride, yet blocked by its oxide (Fujimori et al., 2011).

Pekárek et al. (2001) tested the effect of the matrix used methodically, with CuCl₂ as common catalyst. The numerous samples used showed a wide range of activities with, however, a common signature, characterised by high chlorination and a PCDF/PCDD-ratio larger than one.

Oxygen is essential for PCDD/F formation through the de novo route. Several authors noted a parallelism between carbon oxidation and creation of organochlorines. Two routes suggested were (1) the metal ligand mechanism, requiring oxygen for reactivating reduced transition metals (Stieglitz, 1998) and (2) the production of Cl₂ through the Deacon reaction (Olie et al., 1998) and direct chlorination of aromatic rings through substitution reactions. During de novo tests on MSWI fly ash samples, the oxygen concentration was varied from 0 to 10% (Addink and Olie, 1995b). At 10% O₂, eleven times more PCDD and three times more PCDF were created than with 1% O₂ in N₂. Precursor route formation (via condensation of two CP entities) may proceed without any oxygen (Addink et al., 1995). Contradictory reports exist on the effect of oxygen on condensation reactions: both enlarged and diminished PCDD formation were found from CP as precursor (Ross et al., 1989; Dickson et al., 1992; Tuppurainen et al., 2000).

A reducing atmosphere (in the presence of H₂) causes a decline in PCDD/F formation, both through de novo route and precursor pathways, as well as a shift towards lower chlorinated congeners (Evans and Dellinger, 2003, 2005; Altarawneh et al., 2007; Yang et al., 2015b).

Still, these numerous studies differ in their purpose, test conditions, and in nature, speciation and concentration of metal compounds present, resulting in significant variances in both formation rate and fingerprints of PCDD/F. Their output depends on numerous factors and it is impossible changing all of these within a single study. To investigate their major pathways and mechanisms in a particular case, it is essential to analyse the homologue profiles and congener patterns within each homologue group (Hatanaka et al., 2002, 2004; Aurell, 2008; Aurell et al., 2009). Fujimori et al. (2009) adopted a hierarchical cluster analysis to compare and classify eleven catalytic compounds, based on their resulting homologue distribution for PCDD/F, PCB and CBz at 300 °C for 30 min under a flow of 10% O₂/90% N₂. Hatanaka et al. (2002, 2004) illustrated the catalytic effect of copper chloride on PCDD/F formation and correlated changes in isomer distribution patterns of PCDD/F with copper content, analysing congener profiles within each homologue group.

In addition, the catalysis and congener pattern obtained from phenol precursors was surveyed in several studies (Addink et al., 1995; Sidhu et al., 1995; Weber and Hagenmaier, 1999; Hell et al., 2000; Ryu et al., 2005a, b), providing a diagnostic utensil for formation mechanisms of PCDD/F. In the reported studies, however, only copper was tested and evaluated for its impact on isomer distribution patterns. A systematic comparison of the influence of different metal compounds on each isomer is required, in order to draw a consolidated conclusion.

In this study, the influence of five metal chlorides and oxides on the formation of PCDD/F (P: poly-, P = 4–8) is investigated at constant conditions (350 °C, 1 h reaction time). Model fly ash samples were tested at small, laboratory-scale, under reaction conditions involving a full range of oxidising and reducing atmospheric conditions, ranging from air (21 vol % of oxygen) to nitrogen and nitrogen +10 vol % of hydrogen. In principle, de novo reactions require carbon, catalyst, and oxygen. Air flow was used in some PCDD/F catalytic formation tests (Stieglitz et al., 1997; Lee et al., 1998; Chin et al., 2012), while 10% O₂ mimics MSWI flue gas cooling conditions (Pekárek et al., 2001; Grabic et al., 2002; Takaoka

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