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Chemosphere 59 (2005) 1399–1406

CHEMOSPHERE

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Formation of PCDD/Fs in the sintering process: role of the grid—Cr_2O_3 catalyst in the de novo synthesis

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Received 22 July 2004; received in revised form 24 November 2004; accepted 16 December 2004

Abstract

The sintering process is among the major sources of the very toxic polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in the environment. At the industrial scale, it has been shown that dust collected on the grid, which supports the feed, contains PCDD/Fs amounts between the values found in the bottom of the cake and the values found on dust collected during gas sampling in the wind boxes. This fact suggests that the grid, containing 25 wt.% of chromium, could have a catalytic activity in PCDD/Fs formation during the sintering process. This research tries to study this potential role. The de novo synthesis of PCDD/Fs is simulated at laboratory scale by thermal treatments of samples mixed with grid filings or Cr_2O_3.

The thermal experiments performed with E.S.P. dust (dust collected in the electrostatic precipitator of a sintering plant) or graphite mixed with grid filings do not allow to confirm a role of the grid in PCDD/Fs formation during the industrial process. On the other hand, it has been shown that Cr_2O_3 can be considered as a catalyst in the de novo synthesis of PCDD/Fs. This compound takes place in the two steps of the de novo synthesis: the degradation of the carbon matrix as well as the chlorination reactions.

Keywords: Polychlorodibenzo-*p*-dioxins (PCDDs); Polychlorodibenzofurans (PCDFs); De novo synthesis; Sinter plant; Grid; Chromium

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic compounds produced by some natural processes and different human activities, especially combustion processes. Reducing human risk towards PCDD/Fs implies a contamination monitoring of the food chain, but also the reduction of the emissions of these pollutants in the environment. Identification and control of the sources are thus essential.

Anthropogenic sources of PCDD/Fs include the incineration of waste and most combustion processes. Since the discovery of PCDD/Fs in the flue gas and fly ash of municipal waste incinerators (Olie et al., 1977), strict emission limits have been set at the European level for these facilities and improvements of the purification systems in these installations have strongly reduced PCDD/Fs emissions from incineration (Buekens and Huang, 1998). Metallurgical processes, and in particular the sintering process, are still significant sources of these

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doi:10.1016/j.chemosphere.2004.12.027

pollutants in the environment. In most European countries, the sintering process is now recognized as the major source of PCDD/Fs (Lahl, 1994; Quass and Fermann, 1997; Quass et al., 2000).

The sintering process is an essential step in an integrated iron and steel plant. In this process, the iron ore is converted to larger lumps able to be charged into the blast furnace. The sinter plant consists of a 50–100 m long, 3–5 m wide, horizontal grid, which supports the feed of hematite ores, coke breeze and lime, and moves slowly. Burners initiate the process by igniting the feed layer on top, and ambient air sucked through the layer moves the flame front downwards. The sinter is then cooled, broken and screened before being charged into the blast furnace. Separate chambers, called wind boxes and located below the strand, collect the off-gas prior to filtering in appropriate dust collectors (usually electrostatic precipitators).

The European Commission points out this metallurgical process as the most worrying in terms of PCDD/Fs emissions and underlines the necessity of corrective actions (COM, 2001). The huge amounts of fumes emitted (more than 10^6 N m^3/h) with high concentration of PCDD/Fs lead to a real need to reduce and control the discharges of these pollutants. This requires the understanding of the formation spots and formation mechanisms of these pollutants in the process as well as the knowledge of the factors influencing this formation.

The detailed mechanism(s) as well as the spots of PCDD/Fs formation in the sintering process remains unknown, although all the necessary ingredients are present: carbon from the coke, oxygen in the air sucked through the cake, chlorine and catalytic metals available in the ores.

These pollutants, emitted at the chimney, can be formed at different places of the process: in the cake, in the wind boxes or in the purification devices. In a previous study (Xhrouet et al., 2001a), dust collected in the electrostatic precipitator of a sinter plant has been shown to possess a great capacity to form PCDD/Fs by simple thermal treatment (de novo synthesis). It has been suggested that the electrostatic precipitator operates at a too low temperature for the dust collected in this device to contribute in a significant way to the PCDD/Fs formation emitted by the industrial process. Most of the PCDD/Fs released at the chimney are thus formed before this purification device: in the cake or in the wind boxes and fumes ducts.

At the industrial scale (Brouhon et al., 1999–2000), it has been shown that dust collected on the grid which supports the feed presented PCDD/Fs concentrations logarithmically intermediate between values found in the bottom of the cake and values found in dust collected during gas sampling in the wind boxes. This considerable PCDD/Fs formation can be explained by a simple de novo synthesis on the dust stuck on the grid. However, a catalytic activity of the grid perhaps takes place in the PCDD/Fs generation. Composition analysis of this grid was performed. This analysis reveals a content in chromium of about 25 wt.%. To our knowledge, no chromium catalytic activity concerning PCDD/Fs formation has been demonstrated. However, different studies show that this element catalyses many reactions, in particular hydrogenation and dehydrogenation reactions, with a possible formation of cyclic organic molecules, as well as oxidation reactions (Amiel et al., 1959). The formation of compounds with a similar structure as PCDD/Fs, catalyzed by oxidized chromium, has also been shown in the literature (Muzart, 1992).

The goal of this research is to point out critical elements that influence PCDD/Fs generation during the sintering process. In this study, particular interest is given to the grid, which supports the feed, and to its potential catalytic effect on the PCDD/Fs formation during the sintering process. Due to the high chromium content of this grid, the catalytic ability of Cr_2O_3 in the de novo synthesis of PCDD/Fs is also investigated because of the thermal surface oxidation that probably occurs in the industrial process. The homologue and isomer distributions are always considered to attain a better understanding of the formation mechanism of these toxic compounds. Preliminary results of our investigation have been published previously (Xhrouet et al., 2001b; Xhrouet, 2002; Xhrouet and De Pauw, 2002).

2. Experimental section

2.1. Materials

The following materials were used: solution of 2,3,7,8-Cl-substituted $^{13}C_{12}$-labeled PCDD/Fs (EPA 1613 LCS, Campro Scientific, Veenendaal, The Netherlands); toluene (p.a., Baker); hexane (p.a., Baker); dichloromethane (p.a., Vel); dodecane (Merck); sulfuric acid (95–97%, Baker); sodium chloride (p.a., Merck); potassium hydroxide (p.a., Merck); sodium sulfate anhydrous (Baker); aluminum oxide (activated, neutral, type 507c, Aldrich); glass wool (DMCS treated, Alltech Europe); technical dry air (Air Liquide, Belgium), Cr_2O_3 anhydrous (Merck).

2.2. Filings

Filings of the grid, which supports the feed, were collected by scratching a grid bar. These filings were used in the experiments as collected or pretreated in a flow of air at 400 °C for 3 h.

2.3. E.S.P. dust

Dust, described in Table 1, was collected in the electrostatic precipitator of a Belgian sintering plant. This