

Mechanistic Studies of the Formation of PCDDs/PCDFs in the Petroleum Refining Industry

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Abstract

Coked catalyst of the catalytic reforming process in the petroleum refining industry (PRI) was studied with respect to its potential to form PCDDs and PCDFs. Laboratory experiments simulating the conditions during regeneration of the catalyst while adding a specific PCDD precursor (pentachlorophenol) indicate that the formation of PCDD/PCDF is not likely on the catalyst itself at temperatures above 300 °C - on the contrary, OCDD is effectively destroyed.

Introduction

PCDFs and PCDDs were recently encountered in the petroleum refining industry (1). Their concentrations in internal effluent streams generated by the regeneration of coked catalyst from the catalytic reforming process are similar to those found in municipal waste incineration. The goal of this project is to determine the mechanism of formation of PCDDs and PCDFs in this process. Once the mechanism is known, preventive measures to reduce emissions might be devised. The world's PRI has a reforming capacity of 1,000,000 m³/day corresponding to 400*10⁶ kg of catalyst (2) which indicates the scope, potential and importance of this source of PCDDs and PCDFs.

Experimental

A 16 g sample of coked catalyst (5.6 % wt. C, 0.9 % wt. H, 0.5 % wt. Cl) was extracted ultrasonically with

a total of 80 ml toluene at 67 °C in three successive 100 min steps. The extract was concentrated to 100 µl and analyzed for dioxins and dibenzofurans using an HP-5970 GC-MSD in selected ion monitoring mode as described previously (3). A GC-MS run in linear scan mode was carried out on an HP-5987 GC-MS to identify organic compounds in the extract by library search (probability based matching, library of 78,000 compounds).

A flow tube apparatus as delineated in (3, 4) was used to carry out catalytic activity tests with the coked (v.s.) catalyst regarding its potential to catalyze the formation of PCDD and PCDF from well known precursors. The flow tube was filled with 2.0 g of catalyst and 250 µg of ¹³C₆-labelled pentachlorophenol (PCP*) was added (in 50 µl methanol) in order to distinguish between PCDD/PCDF formed from this precursor and native PCDDs/PCDFs. The catalyst was dried at 110 °C under N₂ flow for 30 min. The reaction temperature varied from 150 °C to 500 °C for 1 hr reaction time. The gas flowing at a rate of 4 ml/min was N₂, air or a mixture of these containing 7 % O₂.

Results and Discussion

In the toluene extract from coked catalyst, a wide variety of aromatic hydrocarbons were identified ranging in molecular size from methyl and ethyl substituted benzenes and naphthalenes up to coronene (7 rings). A few oxygenated aromatic hydrocarbons were detected, however no known PCDD or PCDF precursors were found, as well as no chlorinated hydrocarbons.

OCDD Decomposition Products

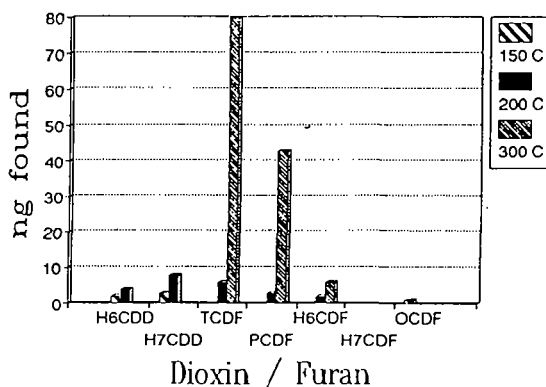


Figure 1: Products formed by decomposition of OCDD on coked reforming catalyst in air at different temperatures. 304 ng OCDD were added, reaction time was 1 hr.

Catalytic activity tests employing PCP* as a precursor: Two procedural blanks were carried out (i.e. no PCP* added to flow tube) at 300 °C in air and N₂; Neither ¹³C-labelled nor native dioxins or dibenzofurans were detected (d.l. 0.1 ng/2g catalyst). Table 1 shows the amounts of labelled PCDD formed from PCP* at different temperatures and O₂ contents of the reaction atmosphere. Only H₇CDD and OCDD were detected. Increasing the temperature leads to a sharp decrease in PCDD formation. Above 300 °C dioxins are not detected. The toluene extracts were also analyzed for unreacted PCP* (table 1). Although the recovery of PCP from coked catalyst by the applied extraction method was determined to be only 30 %, a comparison of the observed concentrations is feasible. A steep decline in unreacted PCP* with increasing temperature and oxygen content leads to the conclusion that PCP and PCDDs are destroyed on the catalyst at temperatures above 300 °C. To verify this hypothesis, unlabelled OCDD was added in three experiments using an air atmosphere (Table 2). Again the amounts observed decrease with increasing temperature. Among the decomposition products were less chlorinated PCDDs, but also PCDFs, in particular at 300 °C (Figure 1). This might correlate to the fact that dibenzofurans were found in much higher concentrations than dioxins in effluents from this process.

References

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Formation of PCDD* from PCP*					
	Temperature °C	ng H ₇ CDD	ng OCDD	ng sum	ng PCP*
7 % O ₂ , 93 % N ₂	150	2.1	9.0	11.1	10400.
	200	1.1	7.2	8.3	6000.
	300	n.d.	3.0	3.0	40.
	400	n.d.	n.d.	n.d.	n.a.
	500	n.d.	n.d.	n.d.	n.a.
21 % O ₂ , 79 % N ₂	150	0.1	1.0	1.1	1600.
	200	0.1	1.2	1.3	380.
	300	n.d.	n.d.	n.d.	100.

Table 1: Formation of ¹³C-labelled PCDDs from ¹³C-labelled PCP at different temperatures and oxygen contents in the gas stream. Also given are the amounts of PCP* found in the toluene extracts (250,000 ng were added to 2.0 g of catalyst). Detection limit = 0.1 ng (n.d.), n.a. = not analyzed. See text for details.

Decomposition of added OCDD			
Temp. °C	ng OCDD		% recovered
	added	found	
150	304	180	58
200	304	100	32
300	304	4	1

Table 2: Recovery of unlabelled OCDD from experiments for catalytic activity. Reaction were carried out in air (20 % O₂). See text for details.