

Effects of temperature, atmosphere and metal catalysts on the formation of PCDD/Fs and EPFRs from 1,2,3-trichlorobenzene

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Introduction

Chlorobenzenes are proved to be important precursors for formation of PCDD/Fs^[1-3], with several differences and lack of studies compared with chlorophenols. Furthermore, environmental persistent free radicals (EPFRs) could be found on the surfaces of metal catalysts from oxidation or pyrolysis of precursors^[4-7]. Characteristics of PCDD/Fs and EPFRs generated from 1,2,3-trichlorobenzene were studied under the effects of different temperature, atmosphere and metal compositions.

Materials and methods

The reactions of 1,2,3-TrCBz over a CuO/silica surface were performed in a quartz glass reactor located in a tubular furnace. The detailed designs of experiments are shown in Table 1 and Fig.1. The method of incipient wetness was used to prepare the catalytic materials. The products from the reaction collected in XAD-II resins, toluene and catalysts were Soxhlet extracted together and then analyzed for tetra- to octa-PCDD/Fs by HRGC/HRMS. EPFRs on catalysts after reactions were also detected by Bruker EMX Plus EPR spectrometer.

Table 1. Experiments on temperature, atmosphere and metal catalysts in detail

reactant	metal catalysts	atmosphere	temperature
1,2,3-TrCBz	5%wt CuO/SiO ₂	80%N ₂ , 20%O ₂	250 □
			350 □
			400 □
			450 □
			500 □
			550 □
1,2,3-TrCBz	5%wt CuO/SiO ₂	N ₂	350 □
		N ₂ : O ₂ =9:1	
		N ₂ : O ₂ =8:2	
1,2,3-TrCBz	5%wt CuO/SiO ₂	80%N ₂ , 20%O ₂	350 □
	2.5% wt Fe ₂ O ₃ /SiO ₂ +2.5%wt CuO/SiO ₂		
	5%wt Fe ₂ O ₃ /SiO ₂		

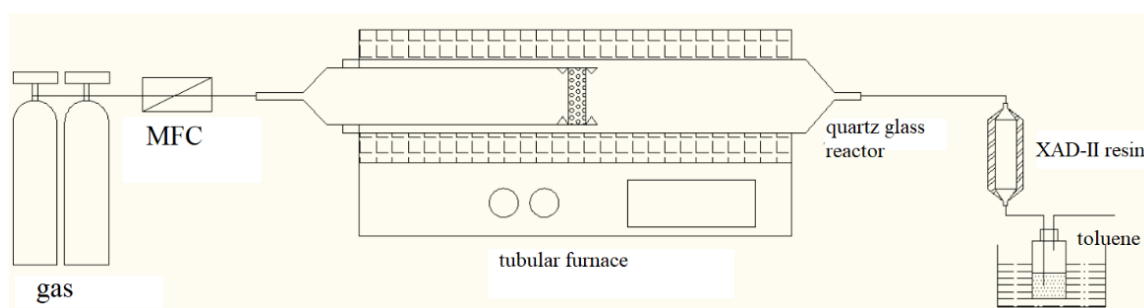


Fig.1 diagram of the experiment

Results and discussion:

Effects of temperature

The productions of PCDD/Fs increased exponentially from 250 °C to 550 °C, which could be described by a fitting formula, $\ln(\text{PCDD/Fs}) = 1.036 \times \text{temperature} + 0.008$, $R^2 = 0.94$. At 400 °C the productions of PCDD/Fs were 3380.92 ng/g. At 450 °C the productions increased by 17.4 times. PCDD/Fs had the maximum growth in the range of 400-450 °C. All the ratios of PCDDs and PCDFs were below 0.12. PCDFs were mainly generated from chlorobenzenes. PeCDF dominated among the congeners. With the rise of temperature, formations of PeCDF and HxCDF were promoted. Chlorination were enhanced. The production of dibenzofuran (DF) is shown in Fig.3. The effect of temperature on DF was much different from that on PCDD/Fs. There are two obvious "peaks" in the results of DF. The yield of DF reached the first peak value of 19.5 µg/g at 400 °C and then reached the second peak value of 40.3 µg/g at 500 °C. Below 400 °C the amount of DF was higher than that of PCDD/Fs, and over 400 °C it became opposite.

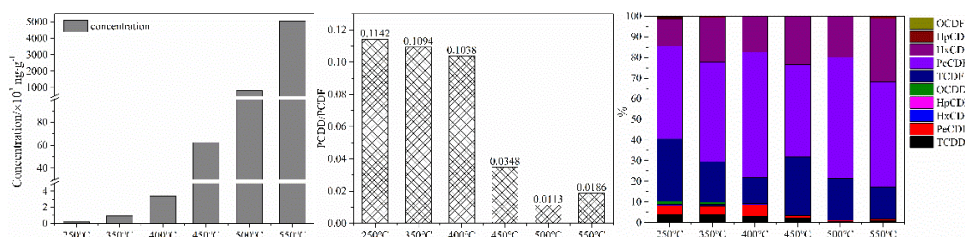


Fig.2 The formation results of PCDD/Fs at different temperatures

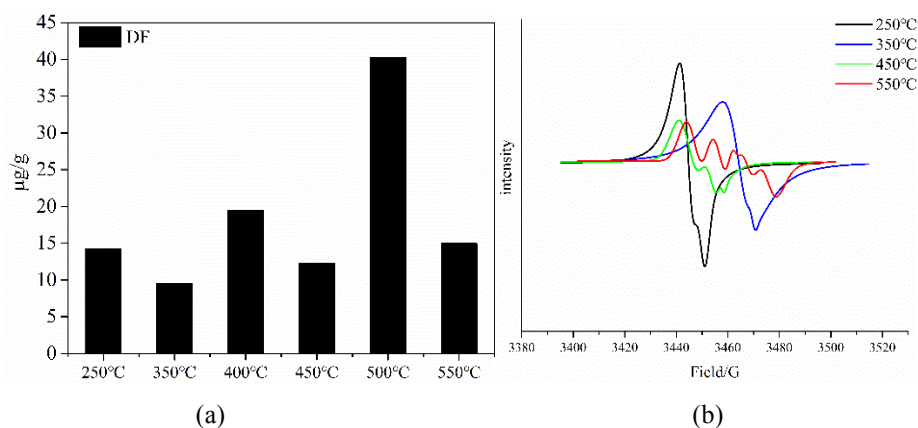


Fig.3 The productions of DF (a) and fitting signals of EPR (b) at different temperatures

Table 2 The concentrations and *g* values of EPR signals at different temperatures

temperature/ °C	<i>g</i> ₁	line width/G	spins/g	<i>g</i> ₂	line width/G	spins/g	<i>g</i> ₃	line width/G	spins/g
250	2.0046	6.71	3.82×10^{14}	2.0017	3.78	1.30×10^{13}			
350	2.0044	12.56	1.86×10^{15}	2.0014	2.40	1.81×10^{12}			
450	2.0053	8.61	1.09×10^{14}	2.0047	6.78	1.90×10^{14}	1.9979	2.00	9.21×10^{11}
550	2.0075	7.58	8.98×10^{13}	2.0021	8.14	1.25×10^{14}	1.9983	4.64	4.27×10^{12}

EPR signal results at 250 °C, 350 °C, 450 °C and 550 °C are shown in Fig.3b and Table 2. At lower temperatures, the oxygen-center radicals, chlorinated phenoxy, which have high *g* values of 2.0044-2.0047, were found. The spin concentrations of carbon-center radicals (*g* value = 2.002-2.003) and F-center signals (*g* value < 2.002) were much lower than that of chlorinated phenoxy. At higher temperature another new oxygen-center radical, chlorinated o-semiquinone was found, which was from the high-temperature pathway to PCDD/Fs from chlorobenzenes. Enhanced signals with low *g* values resulted in the dramatic increase of PCDD/Fs.

Effects of atmosphere

PCDD/Fs and DF could be both generated on CuO/silica from 1,2,3-TrCBz under nitrogen atmosphere (100%N₂). With the increase of oxygen content, the productions of PCDD/Fs rose up first and then went down. There is an optimal concentration of oxygen for PCDD/Fs formation. The lower oxygen content (10%) promoted PCDD, especially TCDD. The higher oxygen content (20%) promoted PCDF especially TCDF. But DF still became less as the oxygen content increased. The oxygen content also promoted oxygen-center radicals, with higher spin concentrations.

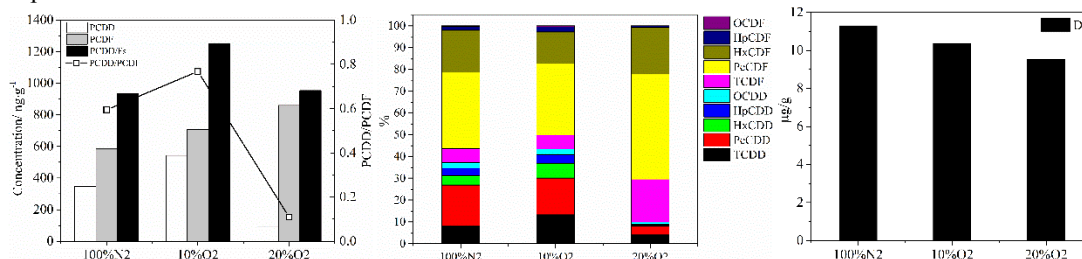


Fig.4 The formation results of PCDD/Fs and DF in different atmospheres

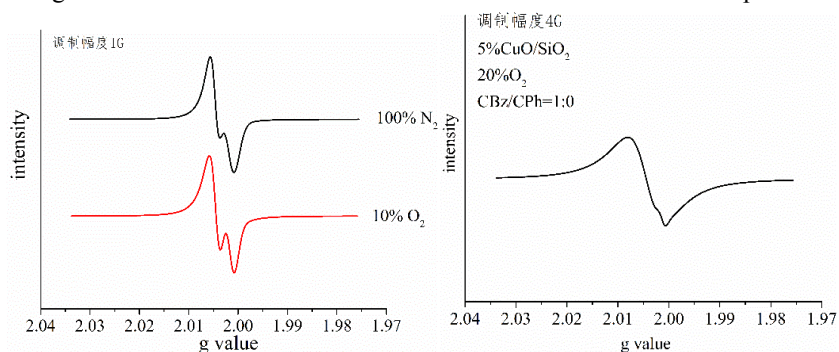


Fig.5 The fitting signals of EPR in different atmospheres

Table 3 The concentrations and g values of EPR signals in different atmospheres

atmosphere	g ₁	spins/g	g ₂	spins/g
100%N ₂	2.0047	2.58×10 ¹⁴	2.0021	9.41×10 ¹³
10%O ₂	2.0046	4.12×10 ¹⁴	2.0017	4.90×10 ¹³
20%O ₂	2.0044	1.86×10 ¹⁵	2.0014	1.81×10 ¹²

Effects of metal catalysts

Effects of 5% wt CuO/silica, mixture of 2.5%wt Fe₂O₃/silica and 2.5% wt CuO/silica and 5%wt Fe₂O₃/silica were compared as the metal catalysts. Iron oxide promoted the formation of PCDD/Fs, especially PCDFs. The productions of PCDFs with 5% of iron oxides were 23 times higher than that with 5% of copper oxides. Furthermore, iron oxides enhanced dichlorination, which resulted in much more DF and low chlorinated PCDD/Fs, such as TCDF.

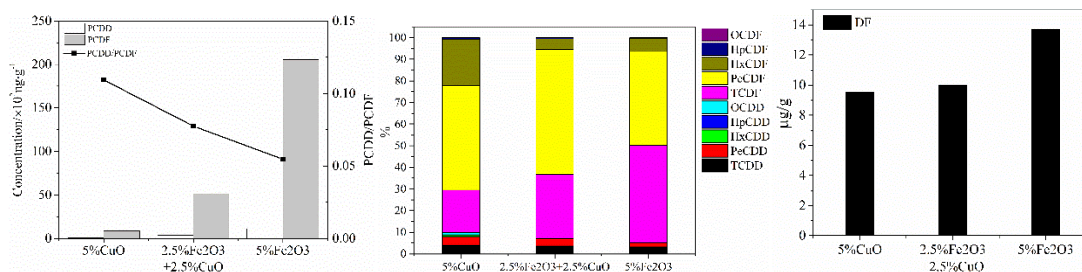


Fig.6 The formation results of PCDD/Fs and DF with different metal catalysts

When only copper oxides used, the concentrations of chlorinated phenoxy radicals with a g value of 2.0044 dominated. When iron oxides added, the concentrations of oxygen-center radicals went down but signals with low g values were raised up. Finally, with only iron oxides, the g value of oxygen-center radicals decreased to 2.0040 and the concentrations became nearly 10% of the concentrations with only copper oxides. Signals with lower g values came up.

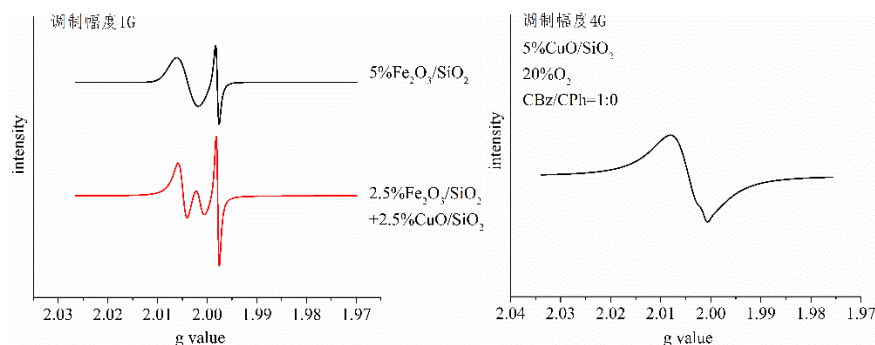


Fig.7 The fitting signals of EPR with different metal catalysts

Table 4 Concentrations and g values of EPR signals with different metal catalysts

metal catalysts	g_1	spins/g	g_2	spins/g	g_3	spins/g
5%Fe ₂ O ₃ /SiO ₂	2.0040	2.70×10^{14}	1.9980	4.30×10^{13}		
2.5%Fe ₂ O ₃ /SiO ₂ +2.5%CuO/SiO ₂	2.0049	2.59×10^{14}	2.0015	1.70×10^{14}	1.9979	6.33×10^{13}
5%CuO/SiO ₂	2.0044	1.86×10^{15}	2.0014	1.81×10^{12}		

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