

PCDD Formation from Chlorophenol on Fly Ash Surface Studied by Fourier Transform Infrared Spectroscopy

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Introduction

In 1987 Karasek and Dickson first demonstrated that PCDD formation from chlorophenol precursor is catalyzed by incinerator fly ash [1]. This catalytic reaction has later been confirmed in many flow reactor experiments, e.g. [2,3]. Recently Milligan and Altwicker suggested on the basis of model fitting to experimental data that this reaction is likely to occur through a Langmuir-Hinshelwood mechanism, rather than an Eley-Rideal mechanism [4]. We are interested in the mechanism of this catalytic reaction, in particular, the chlorophenol adsorbate structure and the surface elementary reaction steps. So we have studied this reaction using a surface technique based on the Fourier transform infrared spectroscopy (FT-IR).

Material and Methods

About 50 mg of incinerator baghouse ash was pressed into thin film (ca. 0.5 mm thick, 15 mm wide and 20 mm long) using a pressure of 6500 psi. The film was mounted inside a heatable IR transmission cell; IR spectra of the film were recorded using a Nicolt 730 FT-IR spectrometer in the wavenumber range from 400 to 4000 cm^{-1} at a resolution 4 cm^{-1} ; 512 scans were coadded for each spectrum. Pentachlorophenol (PCP) solution was prepared by mixing PCP powder with n-hexane and shaking. PCP is only slightly soluble in n-hexane; the concentration of the PCP solution prepared was estimated to be in the magnitude 10^{-3} M. To deposit the PCP solution onto fly ash surface, the fly ash film was taken out from the IR cell; PCP solution was added to the surface of the film on both sides until the surface was completely wetted. The film with adsorbed PCP was put back in the cell and IR spectra were taken. The film with adsorbed PCP was then heated up to 310°C at nominal heating rate 10°C/min under a flowing helium gas atmosphere. IR spectra were recorded at different temperatures while the film was heated up.

Results and Discussion

Spectrum (a) was taken on the original fly ash film. Spectrum (b) was taken after PCP adsorption; in this spectrum the strong peak around 1100 cm^{-1} is from C-O stretch of PCP, two strong peaks at 1380

and

1480 cm^{-1} are from aromatic C=C stretch, a strong peak at 2850 cm^{-1} and a medium peak at 2900 cm^{-1} are from C-H stretch of n-hexane, and a medium peak at 3000 cm^{-1} is from O-H stretch of PCP. Spectrum (c) was taken when the fly ash film with adsorbed PCP reached a temperature of 110°C; the peaks at 2850 and 2900 cm^{-1} have disappeared completely due to vaporization of the n-hexane. About one third of the aromatics remain on the fly ash surface, as suggested by a comparison of the height of the peaks around 1400 cm^{-1} in spectra (b) and (c). However, the peak at 3000 cm^{-1} from O-H stretch has disappeared completely, suggesting that the phenolic O-H bond has been broken. Two new, albeit weak peaks appeared at 1050 and 1200 cm^{-1} , which are likely from the symmetric and antisymmetric C-O-C stretch of O₈CDD, respectively [5]; these two new peaks indicate the formation of O₈CDD from PCP. Spectrum (d) was taken after the fly ash film was further heated to 150°C; the peaks at 1050 and 1200 cm^{-1} continued to grow slightly, indicating that more O₈CDD is formed. Other spectra recorded after heating the film up to 310°C are about the same as spectrum (d).

Previously Sommer et al. reported that for O₈CDD extracted from incinerator fly ash the wavenumbers of the symmetric and antisymmetric C-O-C stretch are 1110 and 1230 cm^{-1} , respectively (ref [5] and supporting information). In our spectra the wavenumbers of the symmetric and antisymmetric C-O-C stretch of O₈CDD are 1050 and 1200 cm^{-1} , respectively; our measurement results are in close agreement with those of Sommer et al. The present observation that O₈CDD formation from PCP starts at 110°C also agrees well with the flow reactor experiments of Sakurai et al. [6] where PCDD formation from chlorophenol was detected at a reaction temperature of 130°C. In our reaction system, only PCP adsorbed on fly ash surface is available as reactants; no gas-phase reactants are present (in the flowing helium gas atmosphere, the possibility that PCP desorbs from the fly ash surface to the gas phase, and then reacts with surface-bound PCP is very small). The O₈CDD formation in our experiments must be due to the coupling of surface PCP species, so it is demonstrated that O₈CDD formation from PCP occurs through a Langmuir-Hinshelwood mechanism under these experimental conditions. Nevertheless, the possibility that other reaction mechanisms are operating under other experimental conditions cannot be discounted at present.

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