

A mechanism of the formation of polychlorinated organic compounds in the process of 1,2-dichlorobenzene catalytic oxidation

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Abstract: The possibility of polychlorinated organic compounds formation in the catalytic oxidation process of chlorinated volatile organic compounds, which has limited the widespread application of catalytic oxidation technology in industry. In this study, catalytic oxidation of 1,2-dichlorobenzene on commonly commercial catalysts and was investigated to elucidate the mechanism of the polychlorinated organic compounds formation in the catalytic oxidation of 1,2-DCB. During the oxidation processes, substantial amounts of polychlorinated organic by-products are formed over all catalysts. Based on the byproducts formation, a formation mechanism of polychlorinated organic compounds was developed.

Keywords: Catalytic oxidation, 1,2-dichlorobenzene, Reaction Mechanism, Polychlorinated organic compounds.

1. Introduction (11-point boldface)

Chlorinated volatile organic compounds (CVOCs) are considered potent environmental pollutants due to their acute toxicity, strong bioaccumulation potential. Catalytic oxidation is able to decompose the CVOCs into CO₂, HCl, and H₂O at low operating temperatures (< 500 °C). Supported noble metals are considered as promising active components for CVOCs catalytic oxidation. However, the main drawbacks are the formation of polychlorinated organic compounds, which are more toxic and stubbornness than the starting material. In this paper, 1,2-dichlorobenzene (1,2-DCB) were selected as model of chlorinated aromatic compounds to elucidate the mechanism of the polychlorinated organic compounds formation over commonly commercial catalysts (Pd/γ-Al₂O₃, Pd/ZSM-5, and Pd/SiO₂).

2. Experimental (or Theoretical)

Palladium-loaded catalysts were prepared using an impregnation (IMP) method. Catalytic oxidation of 1,2-dichlorobenzene (1,2-DCB) was tested in a fixed-bed reactor at atmospheric pressure. The reactants and chlorinated by-products were analyzed by an on-line FID gas chromatograph (Agilent 6890). The concentration of CO₂, CO and HCl production were analyzed on-line by using FTIR Spectrometer (MultiGas™ 2030).

3. Results and discussion

The catalytic activities of 1,2-DCB oxidation over all catalysts are shown in Fig. 1. Obviously, the overall activity of different supports was Pd/ZSM-5(25) > Pd/γ-Al₂O₃ > Pd/ZSM-5(200) > Pd/SiO₂. Fig. 2 shows the organic byproducts distribution in the process of 1,2-DCB catalytic oxidation. In all cases, tetrachloroethylene (C₂Cl₄), chlorobenzene (CB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4,5-Tetrachlorobenzene (1,2,4,5-TeCB) and 1,2,3,4-Tetrachlorobenzene (1,2,3,4-TeCB) were observed as organic byproducts. In addition, trace pentachlorobenzene (PCB) was detected over Pd/ZSM-5(200) and Pd/SiO₂ catalysts at high reaction temperature.

The process of chemisorption for 1,2-DCB consisted of two pathways: (i) elimination of a molecule HCl and (ii) elimination of two molecules HCl. Once 1,2-DCB was chemisorbed to surface, 1,2-DCB transfers an electron onto Pd(II), which reduced to Pd(I), forming surface-associated free radicals such as

chlorophenoxy radicals, which existed three different tautomerizations, and semiquinone-type radicals. These free radicals of oxygen-centered or carbon-centered mesomers could be stable, just as the radicals are in upper path. When chemisorption occurs on the surface of the catalyst, the adsorbed species could pass through multiple transformations, such as oxidation and chlorination reaction through Mars van Krevelen mechanism. The formation of polychlorinated organic compounds was attributed the presence of oxo-chloride species at the surface and the interaction of residual chlorine with metallic sites. Oxygen molecule was chemisorbed to Pd(I)Cl species surface, an electron transfer process occurred from Pd(I)Cl species to O₂ via electrophilic substitution, which form oxo-chloride species. The formation of surface oxo-chloride species could explain the different concentration of polychlorinated organic compounds over different catalysts.

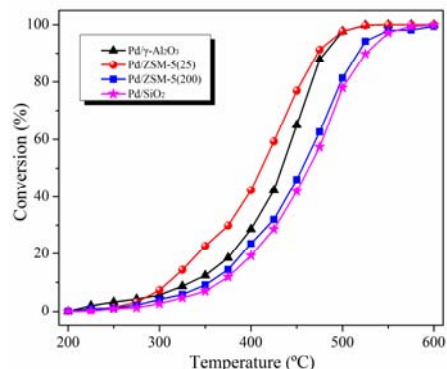


Figure 1. Conversion curves of palladium (0.5wt.%) catalysts supported on various material. Conditions: 1,2-DCB, 450 ppm, Air, total flow: 250 ml min⁻¹.

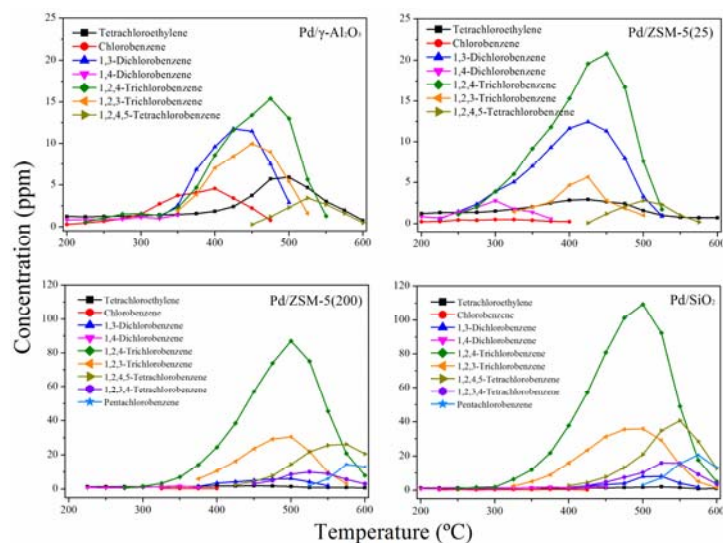


Figure 2. Polychlorinated organic compounds from catalytic oxidation of 1,2-DCB.

4. Conclusions

Complete conversion of 1,2-DCB is reached at ca. 500 °C over all catalysts (Pd/γ-Al₂O₃, Pd/ZSM-5, and Pd/SiO₂), in which Pd/ZSM-5(25) catalyst exhibited the best activity for 1,2-DCB catalytic oxidation. During the oxidation processes, substantial amounts of polychlorinated organic by-products are formed over all catalysts. Palladium oxo-chloride species were possibly responsible for the formation of polychlorinated organic by-products.

References

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