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Catalytic hydrodechlorination of dioxins over palladium nanoparticles in supercritical CO_2 swollen microcellular polymers

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HIGHLIGHTS

- Pd nanoparticles are embedded in microcellular high density polyethylene (Pd/m-HDPE).
- Pd/m-HDPE is used as heterogeneous catalysts in supercritical carbon dioxide (sc-CO_2).
- Dioxins are remedied via hydrodechlorination and hydrogenation over Pd/m-HDPE in sc-CO_2.
- The final products are dechlorinated and benzene-ring-saturated dioxins.
- Pd/m-HDPE can be recyclable and reusable without complicated cleaning procedures.

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ABSTRACT

In this study, palladium nanoparticles embedded in monolithic microcellular high density polyethylene supports are synthesized as heterogeneous catalysts for remediation of 1,6-dichlorodibenzo-*p*-dioxin and 2,8-dichlorodibenzofuran in 200 atm of supercritical carbon dioxide containing 10 atm of hydrogen gas and at 50–90 °C. Stepwise removal of chlorine atoms takes place first, followed by saturation of two benzene rings with slower reaction rates. The pseudo first order rate constant of initial hydrodechlorination for 2,8-dichlorodibenzofuran is 4.3 times greater than that for 1,6-dichlorodibenzo-*p*-dioxin at 78 °C. The catalysts are easily separated from products and can be recyclable and reusable without complicated recovery and cleaning procedures.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are a class of persistent organic pollutants (POPs) unintentionally generated from biochemical processes, combustion, and anthropogenic activities as the major source (e.g., incineration or industrial manufacturing) [1–3]. Their chemical structures are shown in Scheme 1. The number of chlorine atoms attached to the dibenzo-*p*-dioxin and dibenzofuran backbones is between 1 and 8 resulting in 75 PCDD and 135 PCDF congeners, respectively. PCDD/Fs can cause carcinogenic, neurological, and other adverse health effects in human beings, and the extent of their toxicity is graded relative to the most toxic congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. These toxic compounds enter the environment mainly through flue gas or fly ash, contaminate soil/sediment, and bio-accumulate in organisms. The high chemical and thermal stabilities of PCDD/Fs make their destruction difficult through natural processes (e.g., photodegradation). Consequently, development of a suitable remediation method for the destruction of PCDD/Fs is urgent and important.

Catalytic reductive dechlorination over noble metals has been exclusively studied in recent years for remediation of PCDD/Fs and seems to be a more promising method than oxidative, photolytic, biochemical, and other reductive methods because of its simplicity, high efficiency, mild operation conditions, and minimal possibility of generating new PCDD/Fs [1,2]. Current developed catalytic reductive dechlorination methods for remediation of PCDD/Fs over

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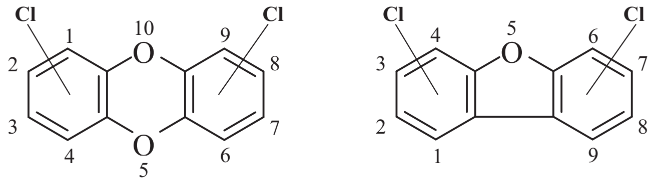

Scheme 1. Chemical structures of PCDDs and PCDFs.

noble metals can be classified into two major catalytic systems. One catalytic system uses H_2 as the hydrogen source [4–7] while the other catalytic system applies 2-propanol instead [8–14]. Both catalytic systems are carried out in aqueous/organic solvents over noble metals on powdered porous supports (e.g., Pt/C or Pd/Al_2O_3). The reason for using powdered forms of catalysts is to lessen the internal mass transfer resistance in the support structures. The usual products of both catalytic systems are partially and totally dechlorinated dibenzo-*p*-dioxin and dibenzofuran. The chlorine atoms are removed one by one following first-order kinetics. The residual PCDD/Fs and products are recovered by extraction with solvents, and the catalysts are separated by filtration, washed, sonicated, and dried for reuse. In some cases, a suitable amount of NaOH is used to neutralize generated HCl which may cause catalyst deactivation and metal leaching. Although current catalytic reductive dechlorination methods over noble metals for remediation of PCDD/Fs are efficient, several drawbacks are observed including slow external/internal mass transfer, generation of secondary liquid waste, and complicated recovery/cleaning of the powdered catalysts.

In the present work, supercritical carbon dioxide (sc-CO_2) and microcellular high density polyethylene stabilized palladium nanoparticles (Pd/m-HDPE) are used as the solvent medium and heterogeneous catalysts for H_2-based catalytic reductive dechlorination of PCDD/Fs (hydrodechlorination) to address the above-mentioned disadvantages. Mild critical conditions, non-toxicity, high diffusivity, low viscosity, and total H_2 miscibility are some advantages of sc-CO_2 over conventional solvents. PCDD/Fs are sc-CO_2-soluble and can be extracted from fish oil, soil, and sediments with high extraction efficiency [15,16]. By substituting aqueous/organic solvents with sc-CO_2 for catalytic hydrodechlorination of PCDD/Fs, remediation efficiency would be enhanced while generation of liquid waste would be minimized making the remediation method more environmentally friendly. Using Pd/m-HDPE as a new heterogeneous catalyst for hydrodechlorination of PCDD/Fs in sc-CO_2 is based on the following considerations: (1) Pd is good for H_2 dissociation and has high resistance to HCl attack; (2) high density polyethylene, containing only C, H, and single bonds, has no strong interaction with reactants and products, thus avoiding significant sorption problems which may retard reaction, product recovery, and catalyst cleaning; (3) polymers usually swell in sc-CO_2 and this phenomenon alleviates the internal mass transfer resistance in the polymer matrix; and (4) the microcellular structure of HDPE can further facilitate the diffusion of molecules inside the polymer. Since the internal mass transfer resistance is reduced by sc-CO_2-swollen microcellular HDPE, larger sizes of catalyst supports can be used instead of powdered form, which makes the handling and recovery of catalysts much easier.

The main objective of this paper is to determine the catalytic activity of Pd/m-HDPE for hydrodechlorination of PCDD/Fs in sc-CO_2. Two congeners, 1,6-dichlorodibenzo-*p*-dioxin and 2,8-dichlorodibenzofuran are used as examples for demonstration. The existence of external/internal mass transfer resistance, the time/procedure for product collection under different temperatures and concentrations, and the possible sorption of PCDD/Fs to Pd/m-HDPE are first tested and determined since these factors influence the calculated mass balance and the observed reaction rate. The process of catalytic hydrodechlorination of PCDDs in sc-CO_2 over Pd/m-HDPE is in situ monitored by UV/Vis spectroscopy, and the trap solution is analyzed by GC/MS to obtain product distribution information under different temperatures and reaction times. A reaction mechanism is proposed based on experimental results. The same procedure is then applied to catalytic hydrodechlorination of PCDFs over Pd/m-HDPE in sc-CO_2. In the final section, the rate constants of hydrodechlorination and hydrogenation of PCDD/Fs are compared with each other.

2. Experimental

2.1. Chemicals and reagents

Palladium hexafluoroacetylacetonate [Pd(hfa)$_2$] (97%), high density polyethylene beads (HDPE, diameter = 4 mm; height = 2 mm), hexane, 2-propanol, and *n*-dodecane as internal standard were obtained from Aldrich (Milwaukee, WI, USA). 1,6-Dichlorodibenzo-*p*-dioxin (1,6-DCDD), 1-monochlorodibenzo-*p*-dioxin (1-MCDD), dibenzo-*p*-dioxin (DD), 2,8-dichlorodibenzofuran (2,8-DCDF), 2-monochlorodibenzofuran (2-MCDF), and dibenzofuran (DF) were purchased from AccuStandard (New Haven, CT, USA). CO_2 and H_2 were provided by local suppliers in Taiwan.

2.2. Monolithic catalyst preparation

The experimental setups for Pd/m-HDPE synthesis and catalytic reactions of PCDD/Fs in sc-CO_2 as shown in Fig. 1 are similar to literature reports [17–19]. For preparing Pd/m-HDPE, three steps are involved: supercritical foaming, supercritical impregnation, and hydrogen reduction. A beaker filled with 2.5 g of white HDPE beads (T_m = 130 °C) was placed in a 20 mL high-pressure reactor maintained at 140 °C and pressurized with 200 atm of CO_2 for the supercritical foaming step. After 3 h, the reactor was depressurized in 10 s. A monolithic m-HDPE cylinder (height = 2.0 cm; diameter = 1.8 cm) was formed. Subsequently, 100 mg of Pd(hfa)$_2$ along with the m-HDPE cylinder were placed in the high-pressure reactor maintained at 90 °C and pressurized with 100 atm of CO_2 for the supercritical impregnation step. After 3 h, the reactor was depressurized. The Pd^{2+} in the precursor was reduced to a zero-valence state with 10 atm of H_2 under sc-CO_2 and the resulting Pd/m-HDPE catalyst was cleaned with sc-CO_2 to remove impurities.

2.3. Hydrodechlorination

The PCDD/F stock solution was prepared by dissolving 5–25 mg of PCDD/Fs in 50 mL of 2-propanol. For each PCDD/F hydrodechlorination experiment, 100–300 μL of the stock solution were added into a small beaker. After the solvent evaporated, the beaker was placed on top of the Pd/m-HDPE catalyst in a reactor (Cell 2) maintained at a temperature range of 50–90 °C. The reactor was then sealed and pressurized with 100 atm of CO_2 for pre-dissolution of PCDD/Fs. CO_2 (200 atm) containing 10 atm of H_2 in a storage cell (Cell 1) was introduced into the reactor. The CO_2 phase in the reactor was monitored by in situ UV/Vis spectrometer (Model 440, Spectral Instruments, Inc., Tucson, AZ, USA) [19]. After a variable reaction time, the outlet valve was opened and the system was flushed with 200 atm of CO_2 at a flow rate of 1 mL/min for 30 min for product collection and catalyst cleaning. The effluent was trapped in 10 mL of hexane. After depressurization, the end tubing was cleaned using 2 mL of hexane injected via a 0.5 mL syringe. The collection and cleaning hexane solutions were analyzed by UV/Vis spectroscopy (GENESYS 10S, Thermo Scientific) and GC/MS (Varian CP 3800 with Saturn 2000) with a VF-5ms column