



# Degradation of lindane and hexachlorobenzene in supercritical carbon dioxide using palladium nanoparticles stabilized in microcellular high-density polyethylene



Bei-Zen Wu<sup>a</sup>, GuanYu Chen<sup>a</sup>, HwaKwang Yak<sup>b</sup>, Weisheng Liao<sup>a, \*\*</sup>, KongHwa Chiu<sup>a, \*</sup>, Shie-Ming Peng<sup>c</sup>

<sup>a</sup> Department of Chemistry, National Dong-Hua University, Hualien, 97401, Taiwan, ROC

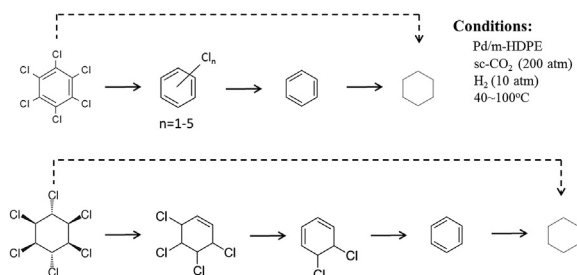
<sup>b</sup> Department of Chemistry, Chung Yuan Christian University, Chung Li, Taoyuan, 32023, Taiwan, ROC

<sup>c</sup> Department of Chemistry, National Taiwan University, Taipei, 10617, Taiwan, ROC

## HIGHLIGHTS

- HPDE with melt index of 2.2 g/10 min is chosen as Pd nanoparticle support due to its physical and chemical stability in scCO<sub>2</sub>.
- Hydrodechlorination of lindane and hexachlorobenzene over Pd/m-HDPE in scCO<sub>2</sub> below 100 °C generates cyclohexane.
- The dechlorination process of lindane involves dechloroelimination while one chlorine atom substitution is suggested for HCB.
- Most chlorinated products are not detected due to their direct transformation to cyclohexane on metal surface.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Palladium nanoparticles stabilized in microcellular high-density polyethylene prepared through supercritical foaming, supercritical impregnation, and H<sub>2</sub> reduction are used for the hydrodechlorination of lindane and hexachlorobenzene in supercritical carbon dioxide below 100 °C. Both lindane and hexachlorobenzene can be almost 100% transformed to cyclohexane in 1 h. Reaction intermediates, such as lower chlorinated products or benzene, are not observed or exist in trace amount indicating that most of them may undergo reactions without leaving the metal surface.

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\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [liao1427@alumni.uidaho.edu](mailto:liao1427@alumni.uidaho.edu) (W. Liao), [ckh@mail.ndhu.edu.tw](mailto:ckh@mail.ndhu.edu.tw) (K. Chiu).

## 1. Introduction

$\gamma$ -Hexachlorocyclohexane ( $\gamma$ -HCH or lindane) and hexachlorobenzene (HCB) are classified as persistent organic pollutants (POPs) in the Stockholm Convention because of their high toxicity, persistency, semivolatility, and bioaccumulation (Tong and Yuan, 2012; Usman et al., 2014). POPs are a group of chemicals that have been intentionally or inadvertently produced and introduced into the environment. Because of their stability and transport properties, POPs are now widely distributed worldwide and are even found in places where they have never been used. Lindane, a neurotoxin, affects the nervous system, liver, and kidneys and may act as an endocrine disruptor and may be carcinogenic to humans. Lindane is an essential organochlorine pesticide used extensively for agricultural and public health purposes in India and other developing countries. Because HCB persists in the environment, it has been banned globally under the Stockholm Convention. Once released in the environment, POPs break down slowly in the air, water, soil, and living organisms. Consequently, POPs are subjected to long transboundary air pollution transport where they are carried over long distances through atmospheric transport and human activities.

The chemical structures of lindane and HCB are shown in Scheme 1, in which six chlorine atoms are attached to cyclohexane and benzene, respectively. Both chemicals can cause severe damage to human health. Consequently, developing remediation methods for both these environmental pollutants is essential.

Among remediation methods such as biodegradation or photodegradation, catalytic hydrodechlorination (HDC) is considered effective. Therefore, it has recently become a popular *ex situ* method for degrading polychlorinated biphenyls in aqueous solvents, organic solvents, or supercritical carbon dioxide (scCO<sub>2</sub>) (Wu et al., 2012a). Replacing conventional solvents with scCO<sub>2</sub> greatly reduces liquid waste generation and facilitates high reaction rates because of high mass transfer properties and H<sub>2</sub> miscibility in scCO<sub>2</sub> (Seki et al., 2008; Munshi and Bhaduri, 2009; Han and Poliakoff, 2012). Activated carbon- or alumina-supported metal particles such as Pd/C or Pd/Al<sub>2</sub>O<sub>3</sub> are commonly used heterogeneous catalysts for the HDC of environmental pollutants. These nanosized channel-containing catalysts are typically in powder form to reduce internal mass transfer resistance; consequently, their handling, recovery, and dispersion in a reaction system are difficult. High-density polyethylene-stabilized palladium nanoparticle catalysts (Pd/HDPE) have been developed as heterogeneous catalysts for chemical reactions in scCO<sub>2</sub>. The principle of using Pd/HDPE in

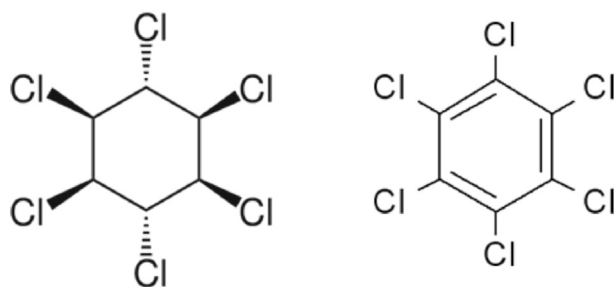
scCO<sub>2</sub> is based on the swelling phenomenon of solid polymers in scCO<sub>2</sub> so that reactants can diffuse into the polymer structure in contact with the embedded palladium nanoparticle catalysts for reactions (Ohde et al., 2004; Liao et al., 2007; Yuan and Marshall, 2007; Wang and Chiu, 2009; Liao et al., 2011; Chen et al., 2012). The degree of swelling depends on factors such as CO<sub>2</sub> pressure, temperature, or addition of modifiers. Subsequently, Pd/HDPE are made microcellular (Pd/m-HDPE) through supercritical foaming to allow greater molecular diffusion of reactants inside the HDPE structure (Liao et al., 2012; Wu et al., 2012b). Molecular diffusion in porous materials depends on pore sizes. The diffusion coefficient of a gas-phase molecule in pores >100 nm is more than 10<sup>-2</sup> cm<sup>2</sup>·s<sup>-1</sup>, whereas in pores <10 nm is less than 10<sup>-4</sup> cm<sup>2</sup>·s<sup>-1</sup>. The height and diameter of Pd/m-HDPE are 2.0 and 1.8 cm, respectively, and can be varied easily. Polychlorinated biphenyls, dibenzo-*p*-dioxins, and dibenzofurans are efficiently converted to bicyclohexyl, dodecahydro-dibenzo-*p*-dioxin, and dodecahydro-dibenzofuran, respectively, in scCO<sub>2</sub> at temperatures less than 100 °C over these monolithic catalysts.

In this study, common polyolefins including polyethylene and polypropylene with different melt index (MI) are tested to determine which polyolefin possesses a suitable microcellular structure through supercritical foaming and chemical/physical stability in scCO<sub>2</sub>. The polyolefin chosen based on our experimental results is used as a palladium nanoparticle support for HDC of lindane and hexachlorobenzene in scCO<sub>2</sub>. Reaction mechanisms for both catalytic reactions are proposed and compared with literature reports.

## 2. Experimental section

All chemicals, including low-density polyethylene (LDPE, MI = 25 g/10 min), high-density polyethylene (HDPE, MI = 12 and 2.2 g/10 min), syndiotactic polypropylene (PP, MI = 2.2 g/10 min), Pd(hfa)<sub>2</sub> (hfa = hexafluoroacetylacetonate), Pt(acac)<sub>2</sub> (acac = acetylacetonate), Rh(acac)<sub>3</sub>, Co(acac)<sub>2</sub>, Ni(acac)<sub>2</sub>, hexachlorobenzene, benzene, cyclohexane, pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, 3,4,5,6-tetrachlorocyclohex-1-ene, toluene, hexane,  $\gamma$ -hexachlorocyclohexane, and acetone, were purchased from Aldrich (St. Louis, Missouri United States). CO<sub>2</sub> and H<sub>2</sub> were obtained from local suppliers in Taiwan.

The experimental setups for Pd/m-HDPE synthesis and catalytic reactions in scCO<sub>2</sub> is similar to those mentioned previously (Liao et al., 2012; Wu et al., 2012b). For preparing Pd/m-HDPEs, three steps are involved, namely supercritical foaming, supercritical impregnation, and metal ion reduction (Scheme 2) (Liao et al., 2012; Wu et al., 2012b). In supercritical foaming, 2.5 g of commercial HDPE beads ( $T_m = 130$  °C) are placed in a 20-mL high-pressure stainless steel reactor maintained at 140 °C (Scheme 2-1a). After pressurized to 200 atm and maintained for 3 h, CO<sub>2</sub> diffuses into molten HDPE (Scheme 2-1b). During fast depressurization, CO<sub>2</sub> is released from HDPE when the temperature drops below  $T_m$  of HDPE and a microcellular structure is formed (Scheme 2-1c). In supercritical impregnation, the monolithic m-HDPE cylinders (height = 2.0 cm; diameter = 1.8 cm) is placed in a reactor with 100 mg of Pd(hfa)<sub>2</sub> at 90 °C and 100 atm CO<sub>2</sub> for 3 h. With scCO<sub>2</sub> at a temperature below  $T_m$  of HDPE, m-HDPEs swells and allows Pd(hfa)<sub>2</sub> to diffuse into their structure while the microcellular structure of HDPE is maintained (Scheme 2-2a, 2-2b). After rapid depressurization, Pd(hfa)<sub>2</sub> are well-dispersed in the HDPE structure



Scheme 1. Chemical structures of lindane (left) and HCB (right).

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