



Water-promoted catalytic hydrodechlorination of transformer oil-contained PCBs in liquid system under mild conditions



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ABSTRACT

The influences of solvent system on the hydrodechlorination (HDC) of transformer oil-contained PCBs with H₂ over Pd/C catalyst were studied. The addition of water in solvent system significantly accelerated the HDC reaction, which suggested its critical role for enabling Pd/C catalyst to keep high activity and stability. The mechanism of this phenomenon was studied through catalyst characterization (TEM, XRD and XPS), and the change of surface composition of Pd/C catalyst in different solvent in the HDC reaction was revealed. Above results indicated that water in isopropanol–water prevented NaCl accumulating on the surface of catalyst, which avoided the decline in activity and stability of the catalyst. On the basis of these studies, isopropanol–water (60/40, v/v) solvent system was developed to dispose high concentration transformer oil-contained PCBs, where the chloride atom removal ratio of transformer oil-contained PCBs at 2% (w/w) and 5% (w/w) concentration could reach 95.2% and 88.0% for 10 h under mild conditions respectively, and the Pd/C could be recovered and reused at least 10 times without any loss of catalytic activity.

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1. Introduction

Polychlorinated biphenyls (PCBs), which are a family of 209 chemical compounds with different numbers and positions of chlorine atoms on a biphenyl skeleton, have been widely used as an additive in electrical equipment. Commercial production of PCBs has been banned since the mid-1970s due to their toxicity of carcinogenicity, teratogenicity and mutagenicity, persistence in the environment, bioaccumulation and biomagnifications in the food chains [1,2]. Therefore, it is an urgent task to develop a proper decontamination of PCBs, which should be disposed by 2028 based on Stockholm Convention on Persistent Organic Pollutants (POPs) [3]. Currently, PCBs are mainly being destroyed by incineration [2], which consumes a large amount of fuel and probably produces highly toxic substances, including polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzo-furans (known as dioxins) [4,5]. In order to avoid the production of noxious chemicals, various destruction methods have been developed to detoxify PCBs including bioremediation [6,7], super/subcritical degradation [8,9], irradiation [10,11], photochemical degradation [12,13], oxidative degradation [14,15], reductive dechlorination [16–21], and so on. Unfortunately, most of these methods require harsh reaction conditions with special facilities, and many of them are

frequently incomplete. Among these methods mentioned above, reductive dechlorination that involves hydrogen cleavage of one or more C–Cl bonds, lowering the toxicity of chlorinated organic compounds (COCs) and preventing the formation of the hazardous by-products [20,21], was considered to be an environmental friendly method to detoxify.

For the reductive dechlorination, there are two different approaches: metal-mediated reductive dechlorination [16–19] and catalytic hydrodechlorination (HDC) [20,21]. Reductive dechlorination using modified zero-valent metal (zinc, iron, magnesium, ZVM), has been proposed for PCBs and other POPs dechlorination, but slow reaction rate and incomplete dechlorination have hindered the use of this approach in the field [22,23]. Recently, the ZVM system has been further advanced in previous research in the degradation of PCBs through deposition of a noble metal (such as Pd, Ni) on the substrate metal surface [22]. Yang et al. [17,24] propose that the enhanced reactivity of bimetal might be due to their reaction with highly reductive atomic hydrogen [H] adsorbed on a noble metal, which is generated by ZVM corrosion. However, the formation of metal (hydr)oxides on particle surface, which is produced by ZVM corrosion, is regarded as a key factor which affects the effectiveness of the bimetallic system [20,24,25]. Generally, the metal-mediated reductive dechlorination with either ZVM or bimetal is used to treat low concentrations and/or low chlorinated COCs with large amount of metal corrosion [20,26,27]. Compared with the metal-mediated reductive dechlorination, catalytic HDC is a more promising technology for its potential economic and

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environmental advantages and wide application for POPs dechlorination under relatively mild conditions [28]. Liquid-phase catalytic HDC reaction system satisfies not only sustainable chemistry but also economical requirements for advanced chemical processes development since the process occurs at ordinary temperature and the products can be recovered to use [29]. In the past decades, the research on discovery of catalysts has received broad attention in the liquid-phase HDC and a series of supported Pd, Rh, Ni, Pt catalyst have been developed [20,21,30–32]. Among these catalysts used in the liquid-phase HDC, supported Pd catalyst has been the most active one [21,29,33]. Additionally, active carbon is always used as catalyst support due to its large surface area and high stability [33].

Besides catalysts, solvent systems are considerably important factors to influence the liquid-phase HDC reaction [21,33–35]. However, little attention has been paid to solvent system in liquid-phase catalytic HDC. In the literatures reported, alcohols (mainly methanol and ethanol) are the most usual choice as solvent for liquid-phase HDC [33]. In our previous work, the Pd/C catalyst exhibited higher activity in alcohols than in alkanes, arenes and heterocycles in the HDC of COCs, and the HDC rate could be improved by adding water to the reaction solvents [36,37]. And some literature reported the similar results [34,35,38]. However, there is no agreement on the effect of added water. Gómez-Quero et al. [34,35] have linked the HDC activity dependency on dielectric constant (ϵ) to the capacity of the solvent to stabilize the arenium intermediate. Xia et al. [36,37] have suggested that higher HDC rate was achieved because of better removal of absorbed reaction products from the catalyst surface by added water.

In this study, our primary objective was to investigate the mechanism that the solvent system influences the activity and stability of catalysts in the HDC reaction of transformer oil-contained PCBs. The catalytic HDC of transformer oil-contained PCBs was performed in different solvents using 5% Pd/C(0) catalyst. In order to investigate the influence of solvent system on the catalyst, samples of the catalyst were analyzed by characterization (TEM, XRD and XPS). On the basis of these researches, a highly effective and environmental catalytic HDC solvent system was developed and applied to the disposal of transformer oil-contained PCBs at high concentration in liquid system under mild conditions.

2. Experimental

2.1. Chemicals

5% Pd/C(0) catalyst used in this study was prepared by impregnation from HCl solution of PdCl₂. 5% Pd/C (Pd/C(1)) and 5% Pd/C (Cat.: 205680) (Pd/C(2)) were purchased from C&P Chemical Co., China and Sigma–Aldrich, USA, respectively. The three kinds of catalysts were not pre-treated before all experiments and only kept in a hermetical desiccator. Transformer oil-contained PCBs were obtained in viscous liquid form from an incineration plant, China. The other reagents, such as solvents and bases, were analytical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in the reaction. The purities of hydrogen used in the experiments were more than 99.99%.

2.2. Transformer oil HDC studies

Each HDC run was carried out in a stirred three-necked flask with magnetic stirring at 300 rpm. The reaction vessel (50 ml) was placed in a temperature-controlled heating water bath with a precision of ± 1 °C. Transformer oil-contained PCBs or 4-chlorobiphenyl was treated with hydrogen gas over 5% Pd/C in different solutions (methanol, ethanol, isopropanol, and isopropanol–water) under mild conditions. NaOH (about 1.1 amounts of chlorine atoms of transformer oil-contained PCBs) was added to prevent catalyst

deactivation caused by HCl formed in the HDC reaction. The intermediate products and the composition of the reaction system in the HDC of transformer oil-contained PCBs were both determined by GC/MS.

2.3. Analytical methods

For the determination of transformer oil-contained PCBs, Gas chromatography/mass spectrometry (GC/MS) analysis was conducted using Thermo TRACE gas chromatograph coupled to ITQ 900 mass spectrometer operated in EI mode at 70 eV. The temperatures of the injection port, the MS transfer line and the ion source were all 280 °C. Samples were injected in the splitless mode onto a 30 m TR-5MS capillary column (0.25 mm I.D., 0.25 μ m film thickness) using the following temperature program: the initial temperature of the column was 60 °C, held for 4.0 min, and the rate of the temperature increase was 25 °C/min up to 200 °C, and held for 2.0 min. Then, the increase rate was changed to 3 °C/min up to 280 °C, with a final hold time of 3 min. The carrier gas was He with a purity of 99.999%. The detection limit was 1 pg mL⁻¹.

Measurements of transformer oil-contained PCBs detected before and after the HDC reaction were divided into 11 groups on the basis of numbers of chlorine atoms on a biphenyl nucleus. The average chlorine atom number (ACN) is obtained as follows [39]:

$$ACN = \sum_{i=1}^j iC_{PCB_i}$$

C_{PCB_i} is the percentage of PCB with i chlorine atom(s); i is the number of chlorine atom(s) on a biphenyl nucleus.

There are overlaps between the retention times of PCBs with different numbers and positions of chlorine atoms, so the calculated ACNs which are used for evaluating PCB congeners mixtures and the HDC reaction, are only approximate but sufficient for following comparison.

2.4. Characterizations

The catalysts after the reaction in the liquid-phase system were separated from the solution, washed with the 95% ethanol, isopropanol and *n*-hexane to remove absorbed organic compounds, and dried in a N₂ flow at 200 °C prior to characterization analysis. The morphology of the fresh and used catalyst was characterized using transmission electron microscopy (TEM, a JEOL Model JEM-2011EM, Japan) at an accelerating voltage of 120 kV. The crushed catalysts are prepared first by dispersing in ethanol, and then two drops of the dispersed samples depositing on a copper mesh grid. X-ray diffractograms (XRD) of the catalysts were recorded with XRD-6100 of Shimadzu with a Cu K α radiation at 40 kV and 30 mA. The samples were scanned at a rate of 0.1°/s over the $5^\circ \leq 2\theta \leq 80^\circ$ range with a scan time of 5 s step⁻¹. The surface composition of fresh and used catalysts was analyzed by X-ray photoelectron spectroscopy (Thermo Escalab 250Xi XPS) with Al K α radiation as the excitation source. Al K α radiation was operated at 15 kV and 14.9 mA. Binding-energy values were referred to the C (1s) peak at 285.0 eV.

3. Results and discussion

3.1. HDC pathway of transformer oil-contained PCBs in liquid-phase system

The catalytic HDC of transformer oil-contained PCBs was performed in a solution of NaOH over 5% Pd/C(0) catalyst under mild conditions [5]. Compared with four kinds of commercial

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