



Development of palladium-resin composites for catalytic hydrodechlorination of 4-chlorophenol



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ABSTRACT

Polymeric resins have been widely used for the removal of halogenated compounds, however, the sustainability of resin adsorption is compromised by frequent resin regeneration and further treatment/disposal of concentrated brine. Palladium (Pd)-based catalytic hydrogenation is promising to treat various classes of contaminants, including halogenated compounds, and the development of Pd-polymeric resin composites is advantageous because the composites can convert halogenated compounds to less toxic chemicals *in situ* and mitigate challenges associated with resin regeneration. In this work, three neutral resins (MN200, MN100, and XAD4) and two anion exchange resins (IRA910 and IRA96) were used as Pd supports to evaluate 4-chlorophenol (4-CP) hydrodechlorination reactivity. Similar 4-CP adsorption and reduction kinetics were observed, i.e., adsorption and reduction were both faster at acidic pHs for the neutral resins but faster at basic pHs for the anionic resins. The developed Langmuir–Hinshelwood kinetic model based on surface reaction as the rate determining step also suggested an enhancing effect of adsorption on the catalytic reactivity. When adsorption was constant, the reactivity of the catalysts increased with increasing solution pH. This is because higher pH mitigates the adverse impacts of the dehalogenation products (i.e., H⁺ and Cl⁻) on the catalytic reaction. The inhibition effect of Cl⁻ was more pronounced on IRA910 than on MN200. IRA910 with anion exchange functional groups facilitates Cl⁻ adsorption and promotes the production of PdCl₃⁻ and PdCl₄²⁻ species, which are inactive for catalytic reduction. The accumulation of phenol, the dominant product in 4-CP reduction, on resin resulted in catalytic activity loss over eight cycles when 4-CP was repeatedly spiked into the same reactor; the catalytic activity was largely restored after resin regeneration.

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1. Introduction

Chlorophenols (CPs) are among priority contaminants in water and wastewater effluents due to their high toxicity on human health (e.g., carcinogenic), adverse environmental impacts (e.g., inactivation of functional bacteria for the removal of organics), and persistence in the environment [1,2]. They are commonly found in the waste effluents of pesticide, dye, and wood preservative industries [1–4]. World-wide production of CPs is estimated at ca. 100,000 tons per year [5]. Moreover, CPs are biodegradation byproducts of complex molecules such as pesticides in the environment [6]. Conventional water treatment technologies such as ion exchange and adsorption by activated carbon or clays [7–9]

are used for the removal of CPs, however, these processes produce large amounts of concentrated brine or secondary waste through the regeneration of the absorbents [10–13]. Pd-based catalytic hydrogenation has recently emerged as a promising technology for reductive destruction of a broad spectrum of contaminants, including halogenated compounds (e.g., CPs, trichloroethylene, diatrizoate), oxyanions (e.g., nitrate, nitrite, bromate, chlorate, perchlorate), and *N*-nitrosamines [14–17]. Catalytic hydrogenation is beneficial for CP degradation because hydrogen is used as a clean reductant, CPs are converted to less toxic chemicals, secondary waste or byproduct generation is reduced, and catalysts can be reused over multiple cycles in principle [18].

Reduction of CPs has been mostly demonstrated by Pd nanoparticles loaded on supports including alumina and activated carbon [19–22]. However, fouling and stability loss over multiple catalytic cycles are major barriers in a widespread application of Pd-based catalysis [11,22]. For conventional catalyst supports such as acti-

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vated carbon, both reactant and products (especially hydrophobic contaminants) may be strongly adsorbed to the support surface, which will inhibit the long-term performance of the catalyst. The non-selective adsorption of natural water constituents and foulants may compete with the contaminants for the reactive sites. In addition, catalyst selectivity for a target contaminant and production of desirable reaction products are additional important factors affecting the implementation of this technology [15]. Therefore, further efforts are required to develop alternative catalysts for cost-effective treatment of various classes of contaminants. Toward this end, the use of polymeric resins as catalyst supports is largely under-explored. On the other hand, polymeric resins have been extensively used to remove organic and ionic pollutants such as halogenated phenols from industrial wastewater effluents. Resins are advantageous because of their high surface area, enhanced porosity, and tunable pore size distribution and surface functional groups that can target the removal of specific contaminants [23–27]. These properties enable resins to be suitable support materials, especially when selectivity, long lifetime, ease of regeneration etc. are among important considerations. For example, resins with strong affinity to target contaminants may outperform conventional supports because catalytic reduction is a surface mediated reaction and the overall reactivity could be limited by contaminant adsorption on the catalyst [24,25,27]. This is especially beneficial for environmental applications in complex water matrices. Moreover, the immobilization of nanoparticles on resins can be enhanced by the presence of ionic functional groups and pores that promote electrostatic interactions and steric stabilization [28,29]. In addition, Pd enables the detoxification of CPs adsorbed on the resins and promotes *in situ* resin regeneration.

Several pioneer studies demonstrated the advantages of using resin supported Pd for catalytic hydrogenation of anions, but none examined the removal of halogenated compounds. In a study by Kim and Choi, a Pd-supported ion-exchange resin was developed for complete decomposition of perchlorate through adsorption onto a strong anion exchange resin followed by catalytic decomposition of the adsorbed ClO_4^- [30]. Nitrate reduction by bimetallic catalysts on cation and anion exchange resins was also investigated [12,31–34]. The results showed that the activity of the catalysts on the anion exchange resin was higher than that on the cation exchange resin. This is mainly due to the electrostatic attraction between NO_3^- and the functional groups of the anion exchange resin. In these studies, however, the adsorbed amounts of the target contaminants by the resins during the catalytic reactions were not tested. Therefore, it is difficult to attribute the decrease in soluble contaminant concentrations to either catalytic reduction or adsorption. In a few other studies, a combination of adsorption and catalytic reduction has been investigated to treat secondary waste streams of used resins [35,36]. Ion exchange onto anion exchange resins and catalytic reduction by bimetallic catalysts (Pd-Cu/ Al_2O_3 and Re-Pd/C) have been coupled to remove nitrate and perchlorate from contaminated water and to treat and reuse the regenerant brine [35–37]. The main advantage of this method is elimination of the secondary waste stream, but it still requires operation of ion exchange, resin regeneration, and catalytic reduction in different reactors.

Therefore, it is important to explore the possibility of simultaneous removal of contaminants and regeneration of Pd-loaded resins. One solution is to design Pd loaded resin catalysts with different adsorption affinity for the parent contaminant and the reduction product(s), i.e., to convert a target contaminant with high adsorption affinity to reduction product(s) with low adsorption affinity. The high adsorption affinity of the target contaminant enhances contaminant removal (i.e., adsorption and then catalytic reduction), and the reduction products with low adsorption affinity to the cata-

lyst support can be easily released to the aqueous phase to minimize the need for resin regeneration.

The main goal of this work was to develop novel Pd-based catalysts supported on polymeric resins, and to provide mechanistic insight into the catalytic reduction of CPs and the possibility of *in situ* regeneration of the resins. Two groups of resins including anion exchange resins and neutral resins with different structures and functional groups were selected to identify the key physical and chemical properties of the resins for impacting the catalytic activity, catalyst longevity, and the poisoning effect of Cl^- . The catalysts were characterized by transmission electron microscopy (TEM) to determine Pd nanoparticle size distribution, energy dispersive X-ray spectroscopy (EDX) to analyze the surface composition of the catalysts, and X-ray powder diffraction (XRD) to evaluate the crystallinity of the nanoparticles. Ion exchange capacity and Brunauer-Emmett-Teller (BET) surface area of the resins were measured before and after Pd loading. 4-Chlorophenol (4-CP) was selected as the target contaminant for removal. Effects of pH and Cl^- and 4-CP concentrations on the reactivity of the catalysts were examined to investigate the poisoning effect of Cl^- and to develop kinetic modeling. Longevity and the possibility of *in situ* regeneration of the catalysts over multiple cycles of 4-CP removal was also investigated, under extreme conditions where a high concentration of 4-CP (1 mmol L^{-1}) was repeatedly spiked into the same reactor.

2. Materials and methods

2.1. Materials and chemicals

Three nonionic polymeric resins, cross-linked Amberlite XAD-4 and hyper-cross-linked MN200 and MN100, were provided by Rohm and Hass (U.S.) and Purolite® (U.S.), respectively. MN200 and XAD-4 have similar polystyrene structures, but MN200 has a higher degree of cross-linkage which results in a larger surface area and additional micropores. The difference between MN200 and MN100 is that MN200 does not have any functional groups while MN100 has a small fraction of tertiary amine functional groups, with an ion exchange capacity of 0.1–0.3 meq/g (reported by the manufacture). Two polystyrene-based anion exchange resins (AXRs), Amberlite IRA910 and IRA96, were obtained from Dow® (U.S.). IRA910 is strongly basic with dimethyl-ethanolammonium functional groups. IRA96 is weakly basic with tertiary amine functional groups. Analytical grade 4-CP, NaPdCl_4 , and NaBH_4 were purchased from Fisher Scientific and Sigma-Aldrich and used without further purification. The 4-CP solution was prepared with ultrapure deionized water. Ultra high purity hydrogen gas (H_2 -99.999%) was supplied by Air Gas.

2.2. Catalyst preparation

Resin beads were soaked in a NaPdCl_4 solution, mixed gently overnight (300 rpm for at least 12 h), and collected after filtration. NaPdCl_4 was adsorbed onto the resin surface, and a nominal loading of 1% Pd (by weight) was achieved. Next, the NaPdCl_4 adsorbed resins were re-suspended in ultrapure water, and a NaBH_4 solution (pH 12) was added dropwise under violent stirring (600 rpm). The molar ratio of NaBH_4 to NaPdCl_4 was 20, in excess to the stoichiometric ratio to convert all Pd precursors into Pd^0 . The reaction lasted for 2 h, and the resins were collected by filtration and rinsed thoroughly with ultrapure water to remove free Pd particles from the resins. The actual Pd loading was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). In order to find the optimum cleaning procedure for the catalysts, the 1% Pd/resins were washed with ultrapure water for three additional times, and some resin beads were harvested for catalytic activity

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