Catalytic Hydrodechlorination of trichloroethylene by Anion Exchange Resin Supported Palladium Catalysts

by

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ABSTRACT

A new class of supported palladium catalyst with high metal content was developed and used for catalytic hydrodechlorination of trichloroethylene in water. The palladium catalyst was prepared successfully by a simple and straightforward way using two commercial strong base anion (SBA) exchange resins (Amberlite IRA-900 and Amberlite IRA-958) as catalyst carrier. Batch kinetic experiments demonstrated that at an catalyst dose of 1 g/L with palladium content of 17 wt% , the trichloroethylene in the system was degraded within 2 hours at ambient temperature.

For the IRA-900 supported Pd catalysts, the apparent kinetic constant (k_{app}) increased from 0.0400 min^{-1} to 0.2651 min^{-1} as Pd loading increased from 13.6 to 39.0 wt%. For the IRA-958 supported Pd, the rate constant increased from 0.0470 min^{-1} to 0.2344 min^{-1} as Pd loading increased from 11.0 to 33.0 wt%. At the end of the reaction, the catalysts remain active and can be repeatedly used in multiple cycles of treatment without reactivity loss. IRA-900 supported Pd catalysts offered better catalytic activity with DOM concentration of 3 mg/L and 10 mg/L. This kind of SBA resin supported Pd catalysts may serve as a class of effective catalysts in water treatment.

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TCE   Trichloroethylene

SBA   Strong base anion

VOC   Volatile organic compounds

DOM   Dissolved organic matter

TOC   Total organic carbon

PTFE   Polytetrafluoroethylene

DNAPL   Dense non aqueous phase liquid

MCL   Maximum contamination level

CHAPTER 1 INTRODUCTION

Trichloroethylene (TCE) is a volatile organic chemical (VOC) used primarily as an industrial solvent (US EPA, 2007). Studies have shown that it is reasonably anticipated to be a human carcinogen (ATSDR, 2011). The presence of TCE in environment can cause additional problem when it transformed into more toxic compounds as vinyl chloride through natural processes (Nutt et al. 2005).

Catalytic Hydrodechlorination is a promising technology currently used for destroying hazardous chlorinated organic wastes as the reaction occurs at a low temperature, and chlorinated organic compounds are transformed into harmless non-chlorinated organic compounds (Martino et al., 1999). The excellent chemisorptions of hydrogen, highly selectivity towards reactants and resistance to oxidation make palladium one of the most effective catalysts for hydrodechlorination (Hubicki et al. 2006).

Palladium catalysts loaded on various inorganic supports such as alumina, active carbon have been studied for TCE hydrodechlorination. While these palladium catalysts have been proved to be effective for TCE hydrodechlorination, deactivation of the catalyst due to palladium leaching during the reaction makes this carbon/alumina supported Pd catalysts hard to be reused and hence increases the total cost. Recently, fabrication of palladium nanoclusters over ion exchange resins has been addressed in several industrial processes. Various resins such as cation exchange resins (Yun et al. 2005), weakly basic anion resins (Neyertz et al. 2010) and designed

functional resins (Centomo et al. 2009) have been studied. Unlike deoxygenation and hydrogenation catalysts which require high thermal stability and specific selectivity of the resin support, TCE hydrodechlorination in water, which occurs in a relatively mild environment, may employ strong basic anion (SBA) exchange resins supported palladium as an effective catalyst.

In general, the reaction rate generally increases with the amount of catalysts in heterogeneous catalysis (Spiro et al., 1973). It can be expected that higher rate of catalysis rate can be maintained using a resin-supported Pd catalyst with higher metal loading. However, most studied Pd catalysts are of metal content in the range from 0.5 to 5 wt.%.

The overall purpose of this project was to develop and to evaluate the reactive properties of a new class of simple and straightforward palladium catalysts supported on macroporous strong base anionic exchange resins for hydrodechlorination of TCE with high metal content.

The specific objectives of this study are listed as follows:

- Study of palladium (II) complexes and palladium sorption equilibrium.
- Test the feasibility of using these SBA supported Pd catalysts for TCE hydrodechlorination in water. The catalytic reaction rate, stability of these resin supported palladium catalysts will be investigated.
- Evaluate the effect of palladium content on the catalyst reactivity.
- Examine the effect of dissolved organic matter (DOM) on the catalytic activity.
- Study the effect of the physical properties (especially hydrophobicity) of the resin supports on the TCE hydrodechlorination.

CHAPTER 2 LITERATURE REVIEW

2.1 Background

2.1.1 Trichloroethylene Occurrence

Trichloroethylene occurs naturally in some species of marine algae and microalgae (Abrahamsson et.al, 1995). Manmade trichloroethylene has been produced by chlorination of ethylene or acetylene since the 1920s (IARC, 1995). It is manufactured to be used mainly in degreasing metal parts and textiles. Other applications include industrial dry cleaning, printing and extraction processes (WHO, 2000). Trichloroethylene is also a major ingredient for many consumer products such as adhesives, paint removers, strippers and other cleaning fluids (U.S. EPA, 2007).

Hundred thousands of pounds of trichloroethylene are manufactured and released each year (Heneghan, 2000). It was produced by 22 manufacturers worldwide in 2009, including two U.S manufacturers: DOW Chemical in Texas and PPG Industries in Louisiana (NTP, 2011). The combined annual production capacity of these two manufacturers was reported to be 330 million pounds in 2005 (CMR 2005). Total Toxics Release Inventory (TRI) reported U.S environmental disposals and releases of TCE were over 5.6 million pounds in 2005 and 3.6 million pounds in 2008 (U.S. EPA, 2007; NTP, 2011). According to the U.S. EPA's Toxic Substances Control Act Inventory, U.S imports of trichloroethylene were 60 million pounds in 2007, while exports were 55 million pounds (NTP, 2011).

As a result of use, most trichloroethylene (99%) is released to the environment (WHO, 2000). It has been found in ambient air, surface water, and ground water (U.S. EPA, 2007). Trichloroethylene is one of the most frequently organic compounds found at the National Priorities List sites in the United State. In fact, it has been found in 301 of the NPL sites (ATSDR, 2011). TCE has also been detected in human food items. By the U.S Food and Drug Administration's Total Diet Study in 2006, the presence of trichloroethylene has been identified in a wide range of foodstuffs including coffee, fruits, meat, vegetables, beverages and other oil/fat products (FDA, 2006; NTP, 2011).

2.1.2 Physicochemical Properties of Trichloroethylene

At room temperature, trichloroethylene is a non-flammable, volatile, colorless liquid with a sweet ethereal odor. The summary of its relevant physic-chemical properties at 25°C is listed in the following Table 2-1.

Table 2-1. Physical and chemical properties of trichloroethylene *.

Property	Information
Chemical formula	C_2HCl_3
Molar mass	131.40 g/mol
Density	1.4 g/mL
Boiling point	86.7°C
Water solubility	1.366g/L
Vapor pressure	74mmHg
Log K_{ow}	2.42
Henry's law constant	0.011 atm-m^3/mol

*Source: WHO 2000, NTP 2011, Pavel 2002.

Once released into the atmosphere, trichloroethylene may react with photo-chemically produced hydro radicals with an estimated half-life of 7days (WHO, 2000; U.S. EPA, 2007). It can be easily removed from surface water by volatilization, however, once introduced into

groundwater aquifers, trichloroethylene does not readily evaporate and can form a dense non-aqueous phase liquid (DNAPL) at high concentration, which makes it very recalcitrant and mobile in groundwater (U.S. EPA, 2007). Due to its high solubility and persistence, trichloroethylene is very difficult to remove from groundwater effectively and it may exist in the environment for several years (Pavel, 2002).

2.1.3 Trichloroethylene Toxicity and Regulations

Trichloroethylene is rapidly adsorbed in the human lung and gastrointestinal tract when inhaled. About 27-64% of the inhaled TCE was taken up in the human lungs and 40-75% of the retained dose of inhaled TCE is metabolized (ATSDR, 1993; WHO, 2000). It has been reported that exposure to trichloroethylene affects the central nervous system, immune system and endocrine system and other organs as liver and kidney in adults (U.S. EPA, 2007). For example, adverse effects as headache, confusion and blurred vision on the human central nervous system were found on long-term occupational TCE exposure (WHO, 2000). Worse more, TCE exposure during pregnancy has been associated with low birth weight and other birth defects (U.S. EPA, 2007). Concern also remains regarding the association between TCE exposure and increased risk of human cancer (U.S. EPA, 2007).

Due to its toxicity, the U.S. EPA has set a maximum contaminant level (MCL) of 5 µg/L and a maximum contaminant level goal (MCLG) of 0 mg/L for TCE in drinking water (EPA 2011).

2.1.4 Remediation Technologies

There are many technologies which can remove trichloroethylene from water including thermal incineration, bioremediation, photo catalytic degradation and catalytic hydrodechlorination.

Thermal incineration has been widely used for abatement of various organochlorinated compounds. However, the especially high temperature needed (1000°C) for this process may bring several disadvantages, for example, the presence of oxygen in this environment may result in formation of harmful partial oxidation products such as phosgene and dibenzodioxins (Martino et al. 1999). Photo-catalytic degradation is usually limited in their application to wastewater treatment as the need of transparency of pretreated wastewater (Herrmann et al. 1993).

Catalytic hydrodechlorination using supported palladium as the catalyst hydrogen as the electron donor has attracted increasing interest in recent years (Lowry et al. 1999; McNab et al. 1998, Lowry et al. 2000; Sriwatanapongse et al 2006; Ordonez et al. 2010). Compared to other treatment technologies such as biological and thermal oxidation, the catalytic process offers the following advantages (Lowry et al. 1999; McNab et al. 1998): 1) it can rapidly and completely degrade TCE into innocuous products such as chloride and ethane, which are inoffensive in comparison to thermal incineration products; 2) the supported catalyst can be reused in multiple cycles of applications without activity loss (Zhang et al. 2013); 3) it can be readily applied to water treatment processes in either batch or fixed bed reactors, and 4) the reductive dechlorination takes place at ambient temperature, and thus, offers economic advantage as opposed to incineration (Salvador et al. 2000).

2.2 Catalytic Hydrodechlorination for Trichloroethylene Remediation

2.2.1 Principles

Catalytic hydrodechlorination of chlorinated organic compounds is more energy efficient than oxidation as the reaction can occur at ambient temperature (25-50°C) (Pirkanniemi et al. 2002). The overall reaction can be expressed as follows (Kovenklioglu et al. 1992):

$$C_xH_yCl_z + zH_2 \xrightarrow{\quad catalyst \quad} C_xH_{y+z} + zHCl$$
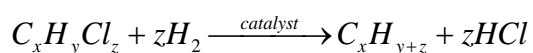
When noble metal catalyst employed in this reaction, high conversion could be achieved at ambient temperature and pressure (Kovenkioglu et al. 1992).

2.2.2 Supported Palladium Catalysts for Trichloroethylene Removal

A number of supported Pd catalysts have demonstrated to be promising for hydrodechlorination of TCE contaminated water (McNab et al. 2000; Lowry et al. 2000). Among the most cited supporting materials are porous media such as alumina and activated carbon (Xia et al. 2004; Roy et al. 2004; Yuan et al. 2004). For example, Xia et al. (2004) demonstrated that a commercial Pd/C catalyst was able to catalyze hydrodechlorination of aromatic halides in water. Roy et al. (2004) studied alumina-supported Pd for chlorophenols dechlorination and observed that the alumina-supported Pd catalyst along with hydrogen gas was sufficient to quantitatively hydrodechlorinate 4-chlorophenol and 2,6-dichlorophenol in 1 h. Zhang et al. (2013) developed a new type of alumina supported Pd catalysts by immobilizing polysaccharide stabilized Pd nanoparticles on an alumina support, and they observed that the new catalyst was 7 times more reactive than its commercial counterpart when applied for TCE hydrodechlorination.

Conventionally, Pd particles are prepared in the slurry form and then loaded on a support via the incipient wetness impregnation method. However, due to the lack of specific interactions between Pd and the supporting materials, the loaded Pd catalysts are prone to leaching when applied in water treatment, leading to loss in the catalytic activity and preventing the rather expensive catalyst from being reused in multiple cycles of operations. For instance, Forni et al. (1997) used a catalyst consisting of 0.5 wt.% Pd on activated carbon (Pd/C) for degradation of polychlorinated biphenyls and observed a 20% Pd leaching after 20 h. Yuan and Keane (2004) reported up to 40% leaching of Pd from a 1 wt.% Pd/C catalyst when tested for hydrodechlorination of chlorophenols.

To enhance particle immobilization and reduce leaching, it has been commonly practiced that the pre-loaded Pd particles are subjected to calcination followed by hydrogen reduction at elevated temperatures (400-500 ^{o}C for alumina and ~300 ^{o}C for carbon supports) (Zhang et al. 2013). However, such high temperature treatments not only consume large amounts of thermal energy, but often result in substantial activity drop due to surface contamination by the supports and irreversible oxidation of the catalyst.

2.3 Palladium Nanoparticles Supported on Ion Exchange Resins

Recently, fabrication of palladium nanoclusters over functional organic polymers has received enormous attentions due to their potential applications in industrial process. The palladium is incorporated on the polymers by reaction of the functionalized support with suitable palladium precursors, i.e., ion exchange or co-ordination. In particular, palladium supported on ion exchange resins has been addressed in several publications which mainly focused on

hydrogenations, nitrates reductions, and deoxygenation of water (Caporusso et al. 2005; Yun et al. 2005; Neyertz et al. 2010; Centomo et al. 2009; Corain et al. 2003).

To this end, various resins such as cation exchange resins (Yun et al. 2005), weakly basic anion resins (Neyertz et al. 2010) and designed functional resins (Centomo et al. 2009) have been studied. Weakly basic anion resins as well as strong cation exchange resins have been successfully employed in nitrates reductions and deoxygenation. Yun et al. (2005) prepared a polymer-supported Pd catalyst over cation exchange resin by ion-exchange and subsequent reduction. They observed that the 3.5 wt.% Pd catalyst was effective for dissolved oxygen removal at ambient temperature with a contact time of ~2.9 minutes. Neyertz et al. (2010) successfully prepared bimetallic Pd catalysts (Pd-Cu and Pd-In) over weakly basic anion resin (WA30) for catalytic reduction of nitrate in water. Corain and cowork (Centomo et al. 2009; Corain et al. 2003; Caporusso et al. 2005) used designed functionalized polymers (usually built up with a co-monomer as structure and another one as functional group) as supports for palladium nanoclusters. Despite the fact that the cation exchange resin supported palladium tend to release palladium more easily than the strong basic anion exchanger catalysts, strong basic anion (SBA) exchange resins are limited in these application with respect to their thermal, mechanical and osmotic stability (Oeckl et al. 1989).

Compared to conventional supports such as alumina and activated carbon, functional polymers may offer the some advantages when used for preparing supported catalysts. First, the functional groups allow a metal catalyst to be loaded in a different fashion from the incipient wetness impregnation approach. For example, a metal catalyst may be first loaded onto a resin in its precursor ionic form through ion pairing, and then be reduced to its elemental oxidation state.

This method may eliminate the need for the thermal treatments and sustain the high catalytic activity of the metal catalyst. Second, there have been diverse types of ion exchange (IX) resins available on the market with a wide range of physical-chemical characteristics (functionality, pore size, porosity, matrix hydrophobicity, and surface area). Because the characteristics of a support can greatly affect the catalytic behavior of the supported catalyst, the choice of the supporting polymeric matrix can facilitate fabrication and optimization of the supported catalyst. And third, because the catalyst loading is started by adsorption of ionic species, the metal precursors are expected to be much more evenly loaded on the resin's surface, compared to particles, such more even distribution of the metal precursors enables more Pd to be loaded on the resin without clogging the micropores. Unlike deoxygenation and hydrogenation catalysts which require high thermal stability and specific selectivity of the resin support, TCE hydrodechlorination in water usually occurs in a relatively mild environment. Therefore, strong basic anion exchange resins supported palladium catalysts may serve as an effective catalyst for catalytic hydrodechlorination in water treatment.

It has been known that the reaction rate generally increases with the amount of catalysts in heterogeneous catalysis (Spiro et al., 1973). Kralik et al. (1995) studied the hydrogenation of p-nitrotoluene and cyclohexene over a cation exchange resin supported Pd catalysts, and observed that the hydrogenation rate was proportional to the metal content with 1.0 and 0.5 wt.% Pd catalysts, i.e., the ratio was 7.44 $mol \cdot L^{-1} \cdot s^{-1} \cdot M^{-1}$ and 5.61 $mol \cdot L^{-1} \cdot s^{-1} \cdot M^{-1}$, correspondingly. Based on our literature review, the Pd content for supported Pd catalysts falls in the range from 0.5 to 5 wt.% (Yun et al. 2005; , Forni et al. 1997; Yuan et al. 2004; Lowry et al. 1999; Lowry et al. 2000; McNab et al. 1998; McNab et al. 2000). For the conventional incipient wetness

impregnation, the maximum loading is limited by the concentration of the precursor (solutes or particles). As the aqueous solubility/dispersibility of particles is often very limited, the maximum Pd loading to a support is also confined. The use of functional polymeric supports may overcome this constraint and likely to greatly increase the Pd loading. This is because: 1) the broad choices of IX resins of various porosity, functionality and specific surface area allow for optimal loading conditions for a given precursor, and 2) compared to the direct particle impregnation, the adsorption-reduction of ionic precursors is much more uniform, and makes better use of the surface capacity of the supports, and moreover, it can be repeated multiple times to achieve higher Pd loading.

CHAPTER 3 MATERIALS AND METHODS

3.1 Materials

The following chemicals were used as received: trichloroethylene (TCE) (>99%, spectrophotometric grade, Aldrich Chemicals, Milwaukee, WI); sodium tetrachloropalladate (Ⅱ) trihydrate ($Na_2PdCl_4 \cdot 3H_2O$, 99%, Strem Chemicals, Newburyport, MA); sodium borohydride ($NaBH_4$, ICN Biomedicals, Aurora, OH); sodium chloride (NaCl, >99.5%, Fluka Chemie GmbH); hydrochloric acid (HCl, 34-37%, ARISTAR PLUS, West Chester, PA); hexane (pesticide grade, Fisher Scientific, Fairlawn, NJ) and methanol (ACS grade, Fisher, Fairlawn, NJ); hydrogen gas (UHP grade, Airgas South, Opelika, AL). Lab-produced deionized water (DI water) was used in preparing all solutions.

Two anion exchange resins, Amberlite IRA-900 (Cl⁻ form) and IRA-958 (Cl⁻ form) (Rohm & Haas, Philadelphia, PA) were purchased from Sigma Aldrich. Table 3-1 presents salient properties of the two anion exchange resins used in this study. Before use, the resins were conditioned following a procedure of cyclic exhaustion with 1N sodium hydroxide, rinsing successively with DI water, 1N hydrochloric acid, 1N NaCl, and then air-dried (Xiong et al. 2007).

Table 3-1. Salient properties of anion exchange resins used in this study *.

Sorbent	IRA 900	IRA 958
Description	SBA resin	SBA resin
Functional Group	$CH_3-N^+-CH_3$ with R and CH_3	$CH_3-N^+-CH_3$ with R' and CH_3
Matrix	-CH$_2$-CH-CH$_2$- (benzene ring) Polystyrene, macroporous	-CH$_2$-CH-CH$_2$-, C=O, HN-CH$_2$-CH$_2$ Polyacrylic, macroporous
Size (mm)	0.65-0.82	0.63-0.85
Capacity (meq/g)	3.6[a]	3.4[a]
Water Content (%)	58-64	66-72
Average pore diameter (nm)	37.2[e]	6.46[d]
BET Surface Area (m^2/g)	22[d]	2.03[b]
Operating temperature (°C)	< 60	< 80

* All data obtained from Rohm and Haas Technical Bulletins unless specified otherwise; [a]From Henry et al. (2004). [b]From Kolodynska et al. (2010). [c]From Delgado et al (2007). [d]From Greluk et al. (2010). [e]From Schouten et al. (2007).

To study the effect of dissolved soil organic matters (DOM) on TCE degradation of the catalysts, a potting soil (HYPONEX@, OH, USA) purchased from a local Wal-Mart Store (Auburn, AL, USA) was used. The soil was fist washed following the method by Zhang et al. (2012). First, the soil was sieved through a U.S standard sieve of 2 mm openings, and then washed with tap water to remove fine colloids and other soluble compositions. After air-dried, 100g of the washed soil were mixed with 0.5 L DI water for 2 weeks. Afterwards, the slurry was

centrifuged at 400 g-force for 20 min and filtered through a 0.45 µm membrane. The supernatant was then quantified by measuring TOC with a Shimadzu TOC-VCPN analyzer (Columbia, MD, USA).

3.2 Methods and Procedures

3.2.1 Equilibrium sorption tests

In order to achieve the optimum operating conditions, sorption isotherms were constructed for the two ion-exchangers through a series of sacrificial batch equilibrium. The Pd salt (Na_2PdCl_4 •$3H_2O$) was dissolved in a chloride medium. To study the pH effect, batch equilibrium tests were carried on at a final solution pH of 2 and 4. First, known masses of ion exchange resin (0.01-0.80 g) were added into a set of 43 mL glass vials, then the glass vials were filled with a solution containing a solution containing $[PdCl_4]^{2-}$, obtained by dissolution of Na_2PdCl_4•$3H_2O$ in 0.05M NaCl with different pH of 2 and 4. The pH value was adjusted by addition of HCl. Afterwards the bottles were capped with an open-top screw cap and PTFE-lined septa, leaving no head-space in the vials. The glass vials were then attached to a rotary actuator and allowed to reach equilibrium for one week at 30 rpm. At equilibrium, Pd ions in the solution were analyzed and the uptake was determined by calculations based on mass balance.

3.2.2 Preparation of supported palladium catalyst

Pd catalysts supported/dispersed on ion exchange resin beads were prepared by a two-step process (incipient wetness method). At first, the palladium was fixed on the resins by addition of a solution containing $[PdCl_4]^{2-}$, obtained by dissolution of $Na_2PdCl_4 \cdot 3H_2O$ in 0.05 M NaCl. The palladium complex was allowed to exchange with the chlorine ions of the resins at ambient

temperature for 72h with rotary stirring (30 rpm) to maintain uniformity. In a typical preparation, 0.1 g of the specific anionic exchange resins (IRA 958/IRA 900) were added into 100mL of palladium solution in 127mL amber bottles capped with open-top cap and PTFE-lined septa. Afterwards, the Pd^{2+} impregnated in the ion exchange resin was reduced to Pd^0 by adding an aqueous $NaBH_4$ solution. When gas (hydrogen) evolution ceased, the as-prepared shining black-palladium-coated resin beads $[R(Pd)^0]^+Cl^-$, were washed with 100 mL DI water and directly employed as solid phase catalysts for hydrodechlorination of TCE. Pd loss was negligible (< 0.02%) during the washing.

Palladium nanoparticles were reduced and deposited on the resin through the following redox reaction and the mechanism of the synthesis procedure is presented in **Figure3-1**:

$$[PdCl_4]^{2-} + NaBH_4 \rightarrow Pd^0 + BH_3 + 4Cl^- + Na^+ + H^+$$
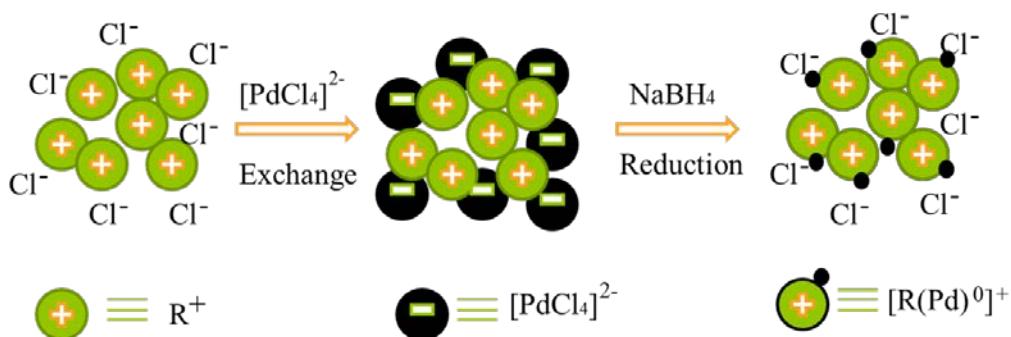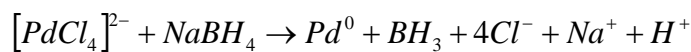
Figure 3-1. Mechanism of synthesis of the palladium nanoshell-coated resin beads.

The reduction of palladium complexes can be monitored by a resin color change from yellowish-brown to black as shown in Figure 3-2.

(a)   (b)   (c)
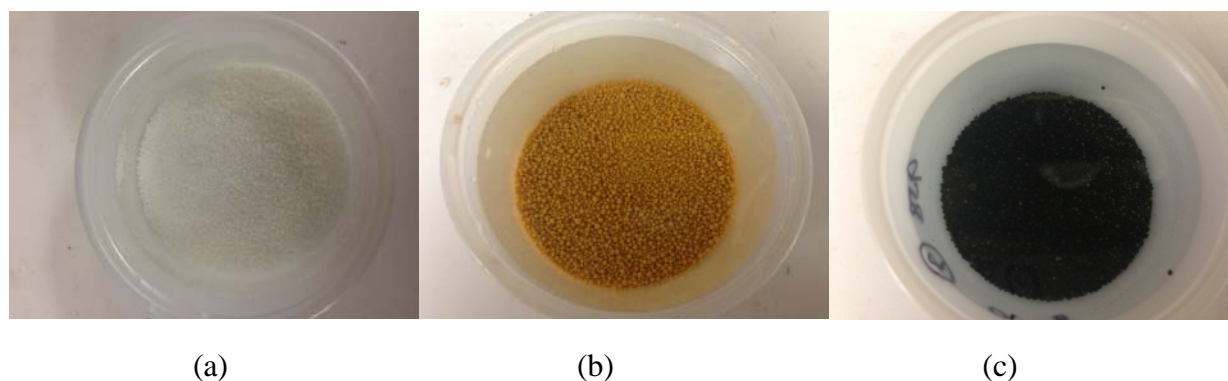
Figure 3-2. Color change of the ion exchange resin during the preparation: (a) bare resin beads ($[R]^+Cl^-$), (b) resin loaded with $PdCl_4^{2-}$ ($[R]^+[PdCl_4]^{2-}$) and (c) resin loaded with Pd^0 ($[R(Pd)^0]^+Cl^-$).

For the multiply loading catalysts, the loading procedure was repeated up to 4 times.

In all cases, the palladium loadings were determined by Inductively Coupled Plasma – Optical Emission Spectrometer (Varian 710-ES, Varian, Walnut Creek, CA, USA) of the initial and final concentrations of the preparation solution.

3.2.3 Physical Characterization

The elemental compositions and topography of the resin-supported Pd catalysts were investigated by scanning electron microscopy (SEM JSM-7000F, JEOL, USA) equipped with Energy-dispersive X-ray spectroscopy (EDS). For the SEM and EDS analysis, the supported Pd catalysts were first washed by DI water and vacuum-dried at room temperature. To explore the internal distribution and morphology of Pd, the Pd-laden beads were bisected in selected cases.

All specimens were plated with a thin layer of gold to improve conductivity and prevent accumulation of surface charges during the electron scanning.

3.2.4 Hydrodechlorination of TCE

Batch experiments were conducted in 127 mL serum bottles containing 100mL DI water and 0.1g supported palladium to evaluate the catalytic activity. In brief, after the preparation of the supported palladium, 100mL of DI water were added each bottle to wash out the excess NaBH$_4$. The DI water after washing was also collected to calculate the exact amount of palladium in the system. Then another 100mL DI water were added in the bottles. Afterwards the system was purged with hydrogen gas for 20 min to saturate the aqueous phase and fill up the headspace, the bottles were then capped with an open-top screw cap and PTFE-lined septa. The TCE hydrodechlorination was then initiated by injecting 25uL of TCE stock solution, which resulted in an initial TCE concentration of 50mg/L, to the solution with the palladium catalysts. The reactors were then mixed on a rotary shaker (30 rpm) at room temperature. At selected time intervals, 0.1 mL of the aqueous sample was transferred into a 2 mL GC vial containing 1 mL of hexane using a 100uL gas-tight syringe for extraction of TCE and other potential byproducts. After phase separation, the extract was analyzed for TCE with an HP 6890 Gas Chromatograph (Hewlett Packard, Palo Alto, CA, USA) equipped with an electron capture detector (ECD) following the method by He et al. Control experiments were also conducted under the same condition without palladium to determine if significant amount of TCE was adsorbed to the resin. All experimental points were duplicated.

3.2.5 Catalyst Lifetime

The lifetime and reusability of the resin-supported catalyst evaluated by an 8 consecutive cycles of TCE hydrodechlorination tests and the same catalyst was repeatedly used without any treatment. Each cycle of the test was carried out in the same manner as mentioned in previous study (Zhang et al. 2012). TCE degradation kinetics was monitored until no TCE can be detected in the aqueous phase. Aqueous samples were also acidified and analyzed for Pd bleeding during the experiment.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Species of palladium (II) complexes and equilibrium sorption isotherms.

The palladium precursor used in this study ($Na_2PdCl_4 \cdot 3H_2O$) is relatively insoluble in pure water at room temperature. As the palladium (II) speciation diagram showed in Figure 4-1, neutral [$Pd(OH)_2(H_2O)_2$], which is insoluble (solubility of 4.1×10^{-9} g/L) at 20°C, is the dominant species for pH 4-12 (Hermans et.al, 2010). Similar results of Pd (II) speciation diagram were obtained by MINTEQ and presented in Figure 4-2.
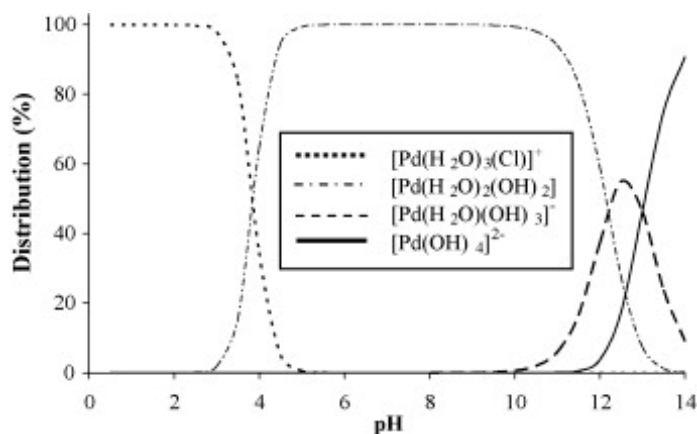
Figure 4-1. Distribution of Pd (II) species at a function of pH: H_2O, Cl^- and OH^- as ligands, $pCl = 2.77$.

(Hermans et. al, 2010).
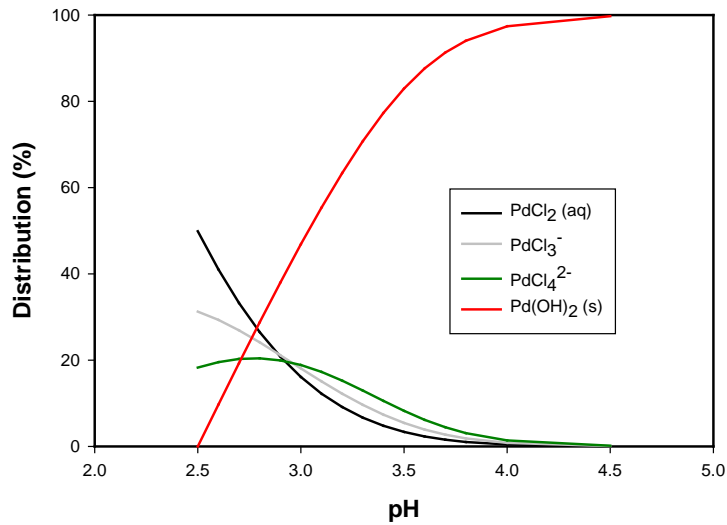
Figure 4-2. MINTEQ result for distribution of Pd (II) species in DI water: Cl⁻ and OH⁻ as ligands (total Pd concentration = 200 mg/L).

Improved solubility of palladium salt was actualized by providing the necessary chloride ions for palladium complexation with a chloride medium. Elz et al. (1997) studied the recovery of palladium using ion exchange resin (IRA-900). In their study, the palladium salt (K_2PdCl_4) was dissolved in an HCl medium. They also studied the effect of Cl^- concentration on Pd (II) uptake and found that the uptake decreased dramatically at Cl^- concentration higher than 0.25M. As they revealed, the addition of chloride ions would result in two opposing effects: on one hand, adding chloride ions can improve the palladium salt solubility and therefore promote the palladium uptake; on the other hand, chloride ions can also compete with the negative charged palladium complexes. Wolowicz et al. (2010) also studied the species of palladium (II) complexes in the chloride solutions. Hydrolysis as well as complexation has been taken into

consideration. Palladium can form chloride complexes ($[PdCl]^+$, $[PdCl_2]$, $[PdCl_3]^-$, $[PdCl_4]^{2-}$) in solution with abundant chloride ions. The complexation reactions are listed as follows:

$$Pd^{2+} + Cl^- \rightarrow [PdCl]^+, \qquad \log K_1 = 6.1;$$

$$Pd^{2+} + 2Cl^- \rightarrow [PdCl_2], \qquad \log K_2 = 10.7;$$

$$Pd^{2+} + 3Cl^- \rightarrow [PdCl_3]^-, \qquad \log K_3 = 13;$$

$$Pd^{2+} + 4Cl^- \rightarrow [PdCl_4]^{2-}, \qquad \log K_4 = 16.$$

It was suggested that $[PdCl_4]^{2-}$ will be the predominant species ($> 90\%$) in an acidic solution with chloride concentration greater than 0.03M. On this basis, a solution containing 0.05M NaCl ($\log (Cl^-) = -1.3$) was chose in this study. Based on the MINTEQ predication (Figure 4-3), more than 98 % of the palladium ions exist as negative palladium complexes with a total palladium concentration of 200 mg/L in the 0.05M NaCl solution when pH < 4.5.

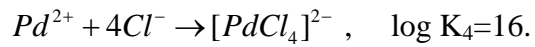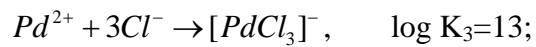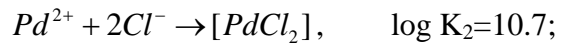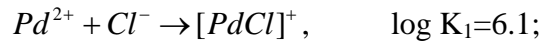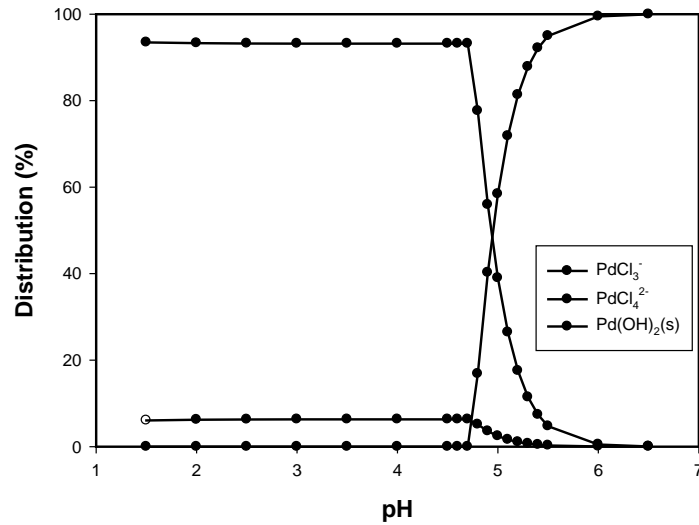Figure 4-3. MINTEQ result for Distribution of Pd (II) species in 0.05M NaCl solution: Cl⁻ and OH⁻ as

ligands. (total Pd concentration = 200 mg/L).

Figure 4-4 presents the experimental isotherms for the two ion exchangers under pH=2 and

pH=4. The equilibrium data could be fitted best with the linearized Langmuir model (Wang et al.

2006). Table 4-1 lists the fitted Q and b values.

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}$$

where q_e is the sorption capacity, mg/g; C_e is the equilibrium concentration of palladium ions,

mg/L; Q is the maximum sorption capacity, mg/g; b is the Langmuir constant, L/g.
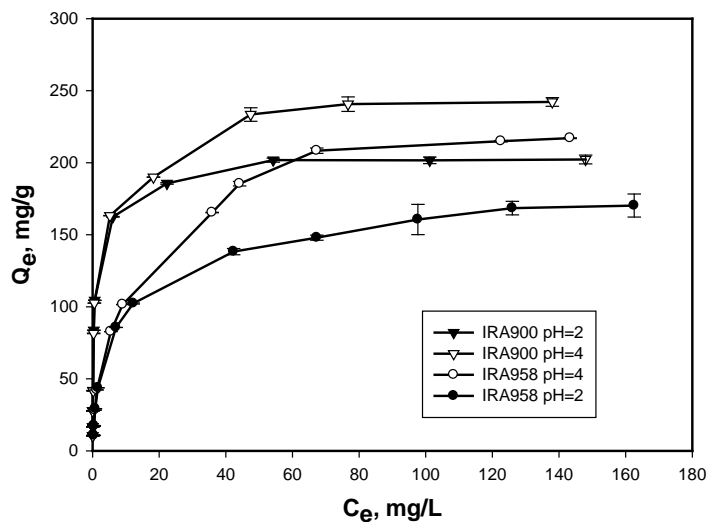
Figure 4-4. Palladium sorption isotherms for strong base polystyrene resin IRA-900 and strong base polyacrylic resin IRA-958 at pH =2 and pH =4. Initial Pd^{2+} = 200 mg/L, Na^+ = 0.05 M, Cl^- = 0.05M. Data plotted as mean of duplicates, and errors refer to standard deviation.

Table 4-1. Langmuir model parameters for the equilibrium sorption isotherm.

Resin support	pH=2			pH=4		
	Q, mg/g	b, L/g	R^2	Q, mg/g	b, L/g	R^2
IRA-900	204.1	1.1136	0.99	243.9	0.6613	0.99
IRA-958	175.4	0.1545	0.99	227.3	0.1236	0.99

As it shown in Table 4-1, the palladium sorption on the resins are favored in higher pH value (pH =4). Both IRA-900 resin and IRA-958 resin can get higher palladium uptake in pH=4. To get the high loading of the palladium, pH= 4 was chose for the preparation procedure.

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Therefore, the preparation of the resin supported Pd catalysts was carried out in a 0.05 M NaCl solution with initial pH =4.

It also can be found that the IRA-900 resin get higher palladium uptake than the IRA-958 resin in the same condition, which is in agreement of the manufacture's information.

4.2 Catalyst Characterization.

Figure 4-5 and Figure 4-6 show the SEM images of the Pd nanoshell-coated resin beads as well as the bare resins.

While the so-called "egg-shell" (Gross et al. 2010) morphology was observed in all resin supported Pd catalysts, it has been furthermore been found that this morphology is favored by higher palladium content on the resin support. Similar observation was reported by Gross et al. (2010) who studied weak-basic-anion resin supported Pd catalysts for catalytic deoxygenation of water. The unusual morphology can be interpreted as the heterogeneous distribution of palladium together with the contribution from reduction of resin matrices (Biffis et al. 2000; Kralik et al. 2001). On the one hand, an enrichment of Pd particles on the outer shell can be formed by increased mass transfer resistance for sodium borohydride to reach the "Pd^{2+}" ions inside resin pores. While the palladiation of the resin occurs readily at the outer shell and some inside resin pores during the catalyst preparation, the reduction rate with $NaBH_4$ varies at the macroporous surface and the internal pores: i.e., a relatively fast rate at the surface, whereas a slower rate was expected inside the deeper pores. Accordingly, there would be a difference between the concentration of "$PdCl_4^{2-}$" complexes at the resin surface and the internal resin pores; this difference will form a concentration gradient of "$PdCl_4^{2-}$" complexes and drive the Pd complexes

to migrate from the interior of the nodules towards the resin shell (Biffis et al. 2000). On the other hand, the palladium particles on the resin may heat up hence "burn" the polymer chains of the resin matrices under certain conditions, i.e., under oxidative or reductive environment. Kralik et al. (2001) prepared a resin supported Pd-Cu catalyst following similar adsorption-reduction procedure and using a SPSDVB (sulphonated poly-styrene-co-divinylbenzene) resin. They also observed a similar "egg-yolk" shape for the polymer supported Pd catalyst with Pd loading of 8 wt%; however, when Pd loading was lower (less than 2 wt%), no such a peculiar behavior was observed. They attributed this phenomenon to partial hydrogenolysis and degradation of the polymer backbone catalyzed by the supported metals. At elevated Pd loadings, both direct burning and reductive degradation of the polymeric matrices are increased. As a result, formation of thicker egg-shells is favored as evidenced by the SEM results. Moreover, the egg-shell morphology appears to be more evident for IRA-900 supported Pd than IRA-958 supported Pd at the same Pd content, which agrees with the temperature tolerance data (Table 3-1) that IRA-958 is more heat-resistant than IRA-900.

EDS results also show the presence of metallic palladium in both exterior and interior of the as-synthesized resin particles (Figure 4-7 and Figure 4-8). Higher palladium peak was observed at the shallow surface of the resins when compared with the interior EDS spectrum, which is in agreement with SEM results where an enrichment of palladium was found at the outer shell. Furthermore, chlorides were found in all EDS results, indicating that the functional group on the SBA resins are still active after Pd loading, which allows the possibility of multiply loading on the resin supports.
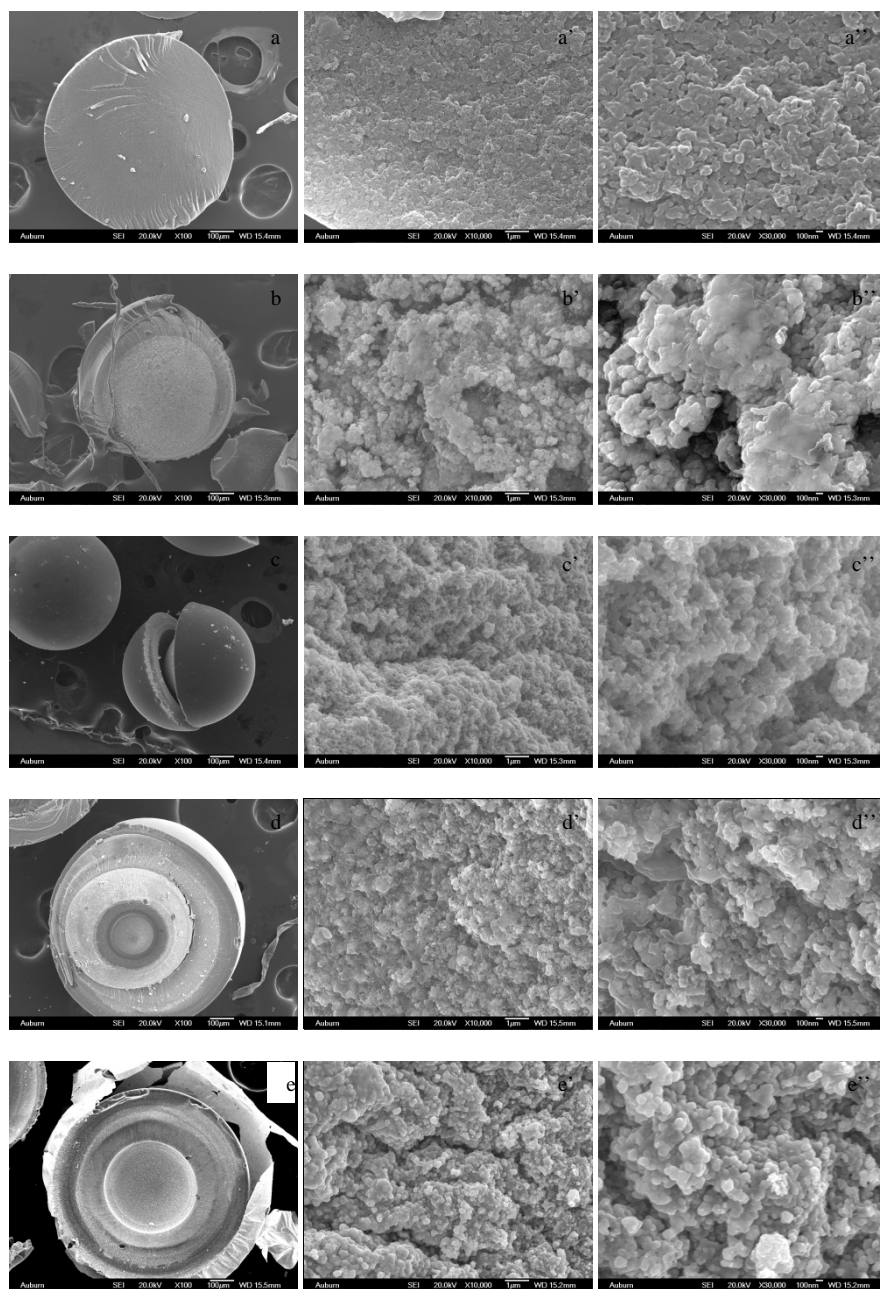
Figure 4-5. SEM micrographs of IRA 900 resin beads with various Pd loadings: (a) 0 Pd (bare IRA 900), (b) 13.6 wt% Pd, (c) 26.8 wt% Pd, (d) 39.0 wt% Pd, and (e) 52.0 wt% Pd. Micrographs in Column 1 (a-e), Column 2 (a'- e') and Column 3 (a''- e'') correspond to images of the bead with magnifications:×100; ×10,000 and ×30,000, respectively.
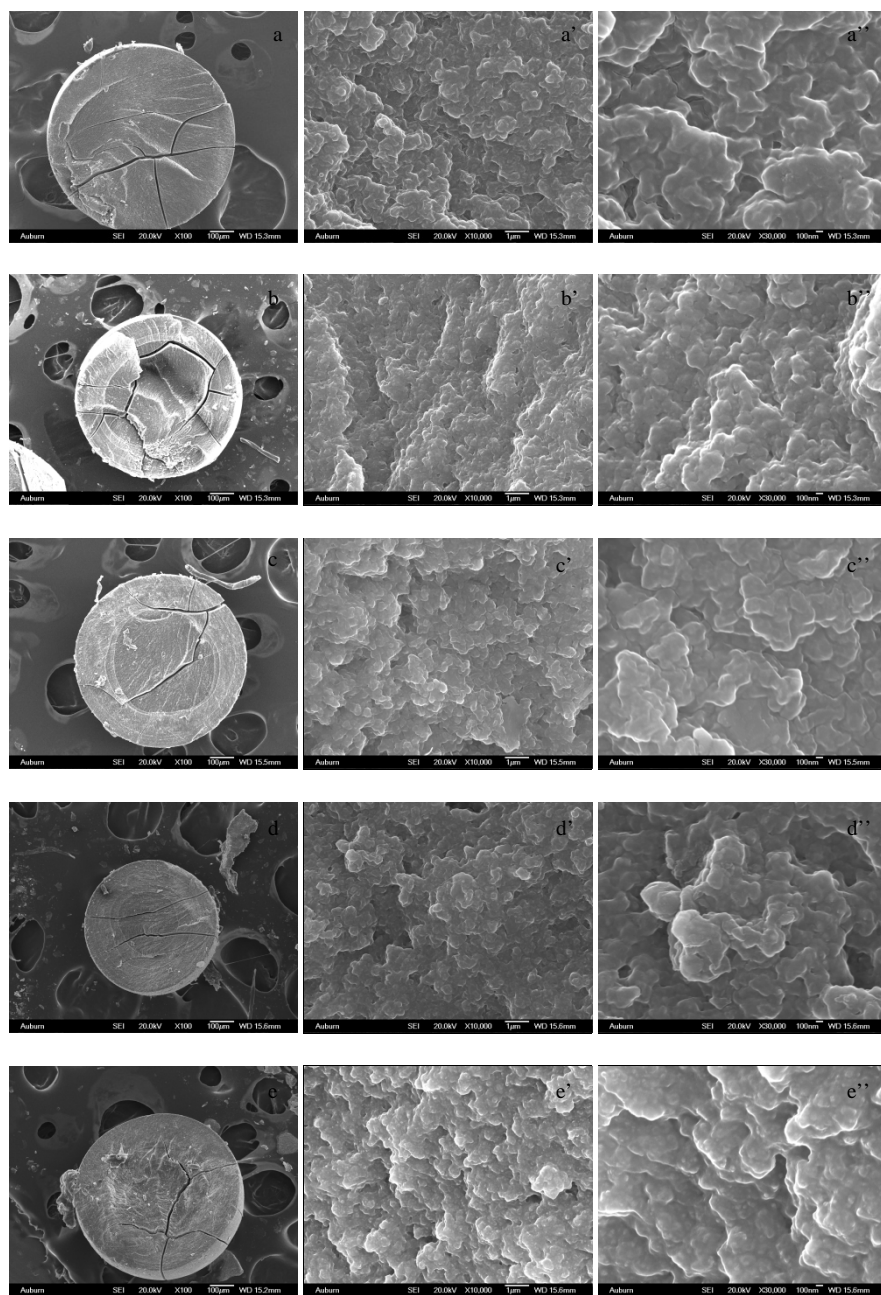
Figure 4-6. SEM micrographs of IRA 958 resin beads with various Pd loadings: (a) 0 Pd (bare IRA 958), (b) 11.0 wt% Pd, (c) 22.0 wt% Pd, (d) 33.0 wt% Pd and (e) 44.0 wt% Pd. Micrographs in column 1 (a-e), column 2 (a'- e') and column 3 (a''- e'') correspond to images of the bead with magnifications:×100; ×10,000 and ×30,000, respectively.
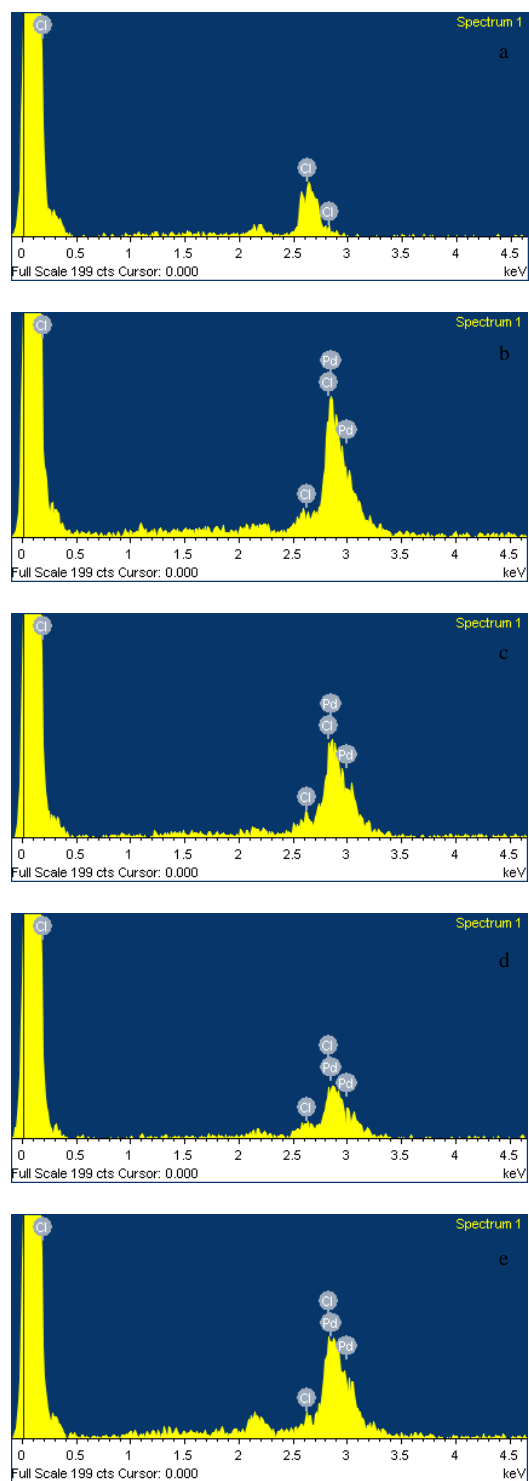
Figure 4-7. Energy dispersive X-ray spectrometer spectrum of the IRA 900 resin beads with Pd mass loading: 0 wt% Pd loading (plain IRA 900) (a), 13.6 wt% Pd loading (b), 26.8 wt% Pd loading (c), 39.0 wt% Pd loading (d) and 52.0 wt% Pd loading (e).
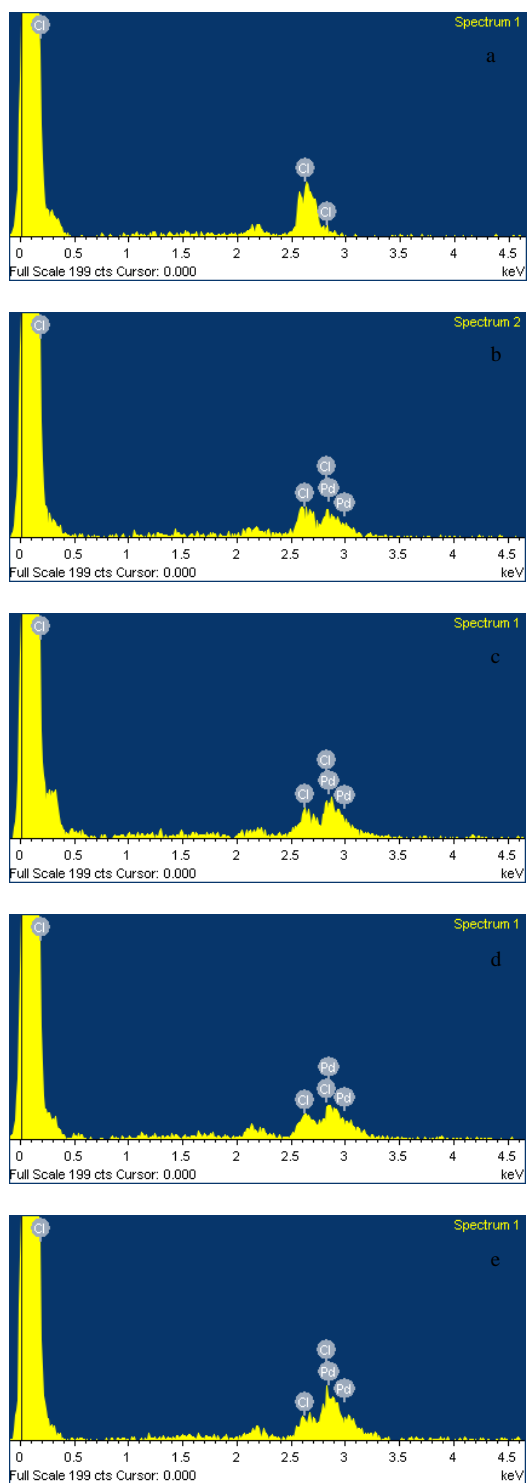
Figure 4-8. Energy dispersive X-ray spectrometer spectrum of the IRA 958 resin beads with Pd mass loading: 0 wt% Pd loading (plain IRA 958) (a), 11.0 wt% Pd loading (b), 22.0 wt% Pd loading (c), 33.0 wt% Pd loading (d) and 44.0 wt% Pd loading (e).

4.3 Catalytic activity.

The catalytic hydrodechlorination of trichloroethylene with hydrogen was studied using resin-bound palladium nanocomposites as catalyst in water. Figure 4-9 compares the catalytic activity of IRA-900 and IRA-958 supported Pd catalysts. Each data point reported in all figures represents the means of duplicates. Control tests indicated that the resin template and H2 did not degrade TCE without palladium and that the TCE adsorption on the resin was negligible ($< 2\%$) with the resin dosage (1g/L).

Hydrogen supply was ~10 times the stoichiometric demand and remained nearly constant throughout the test in all cases (Zhang et al. 2013). Furthermore, due to the sufficiently low activation energy needed for H2 chemisoprtion on palladium (almost zero), the rate of H2 adsorption onto the catalyst sites are very high and can be presumed to occur simultaneously (Pintar et al. 1996; Lowry et al. 1999). Hydrogen mass transfer was also ~10 times greater than mass transfer of TCE, i.e., $[C_{H2} \times D_{H2}]/[C_{TCE} \times D_{TCE}]$ = $[0.8\text{mM} \times 4.5 \times 10^{-5}$ $\text{cm}^2/\text{s}]/$ $[0.38\text{mM} \times 9.1 \times 10^{-6}$ $\text{cm}^2/\text{s}]$ =10.4 (where C_{H2} is the solubility of H_2, C_{TCE} is the initial concentration of TCE in the system, and D_{H2} and D_{TCE} are diffusion coefficients of H_2 and TCE in water, respectively) (Zhang et al. 2013).
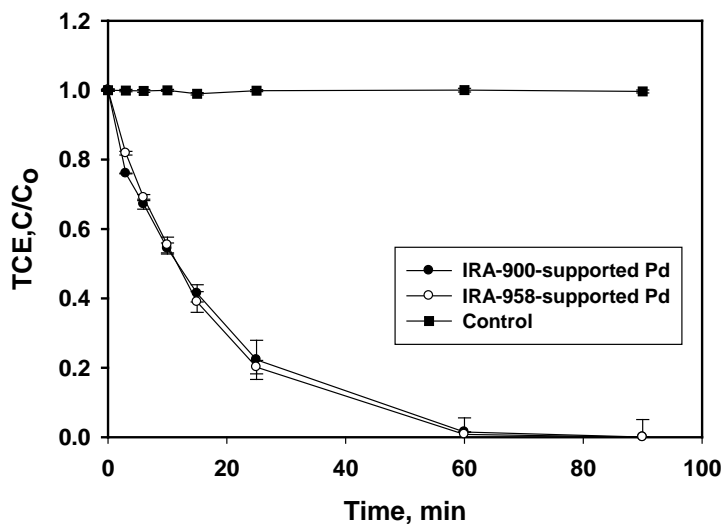
Figure 4-9. Hydrodechlorination of TCE using resin-bound Pd nanocomposites (Initial TCE=50 mg/L, resin=1g/L, Pd=17.0 wt% resin). Data plotted as mean of duplicates, error bars indicate deviation from the mean.

On an equal mass basis, both IRA-900 supported Pd catalyst and IRA-958 supported Pd catalyst were able facilitate rapid TCE hydrodechlorination. No significant difference was observed for the two different resins supported Pd catalysts (*P*=0.981).

TCE transformation data were fitted using a simple pseudo first order model as reported by Lowry and co-workers (1999) and plotted in Figure 4-10:

$$-\frac{dC_{TCE}}{dt} = k_{app}C_{TCE}$$

with $k_{app} = k_{obs}C_{cat}$, where:

k_{obs} is the observed rate constant;

C_{cat} is the concentration of Pd employed in the reaction;

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C_{TCE} is the TCE aqueous-phase concentration.
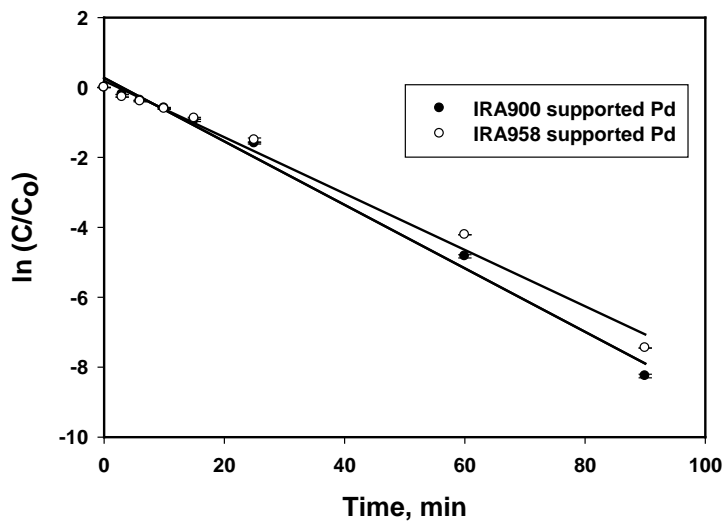
Figure 4-10. Linearized plot of the TCE hydrodechlorination kinetic data of Figure 4-9.

The apparent reaction rate constant was estimated to be 0.0807 ± 0.0033 min^{-1} for the IRA-900 supported Pd catalyst and 0.0696 ± 0.0024 min^{-1} for the IRA-958 supported Pd catalyst with a Pd loading of 17 wt%.

4.4 Catalyst Lifetime.

Evaluation of the lifetime of the catalyst was tested in recycling TCE hydrodechlorination tests. Eight consecutive runs were carried out and no loss in activity was found during the test. Figure 4-11 shows kinetic profiles of TCE hydrodechlorination in Runs 1, 2, 3, 6, and 8 (data for Runs 4, 5 and 7 are not shown for brevity). It can be seen that the TCE can be effectively degraded in all cases with the repeat use of the same resin catalysts. Moreover, no negligible Pd bleeding ($< 0.1\%$) was detected during the reaction. The Pd nanoshell-coated resin is stable and the catalyst activity remains unaltered over three months.
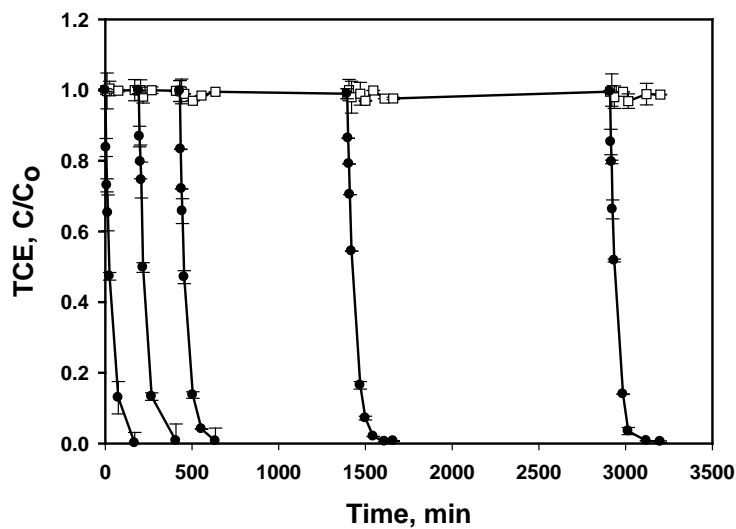
(a)
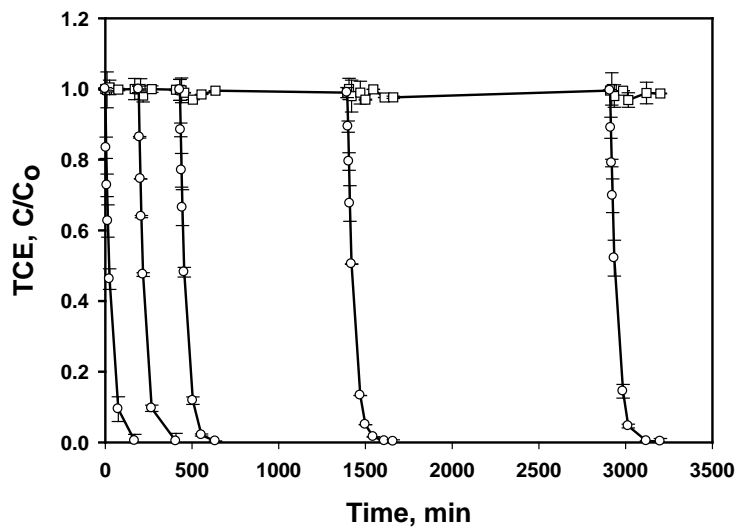
(b)

Figure 4-11. Kinetic profiles of TCE hydrodechlorination in eight consecutive batch experiments

repeatedly using the same catalyst: (a) IRA-900 supported Pd catalyst; (b) IRA-958 supported Pd catalyst.

(Initial TCE = 50 mg/L, resin = 1g/L, Pd = 17.0 wt% of resin). Data plotted as mean of duplicates, error

bars indicate deviation from the mean.

4.5 Effect of Amount of Palladium.

In case of heterogeneous catalysis, the reaction rate generally increases linearly with the amount of the catalyst (Jana et al., 2006; Spiro et al., 1973). To investigate the effect of Pd coverage on the reaction rate, the amount of palladium was varied while keeping other parameters constant in this study. Figure 4-12 shows kinetics of TCE hydrodechlorination using the Pd catalysts with various Pd mass loading.

Calculations indicate that the IRA-900 supported Pd catalysts contain 13.6, 26.8, 39.0, 52.0 wt % Pd and IRA-958 supported Pd catalysts contain 11.0, 22.0, 33.0, 44.0 wt % Pd, respectively.
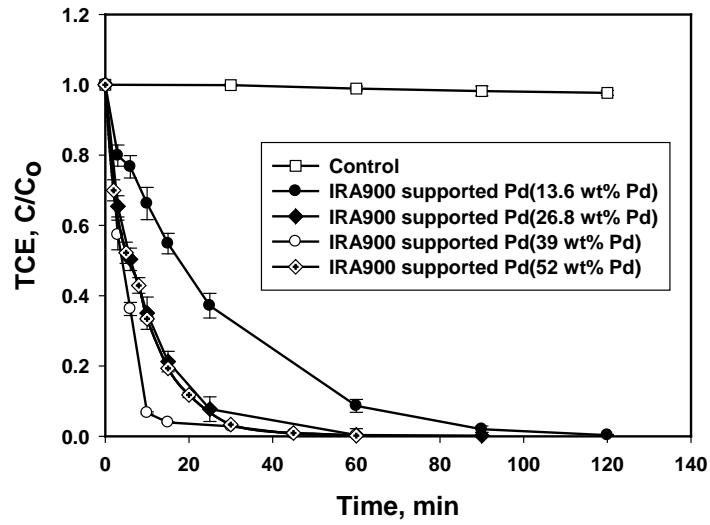
(a)
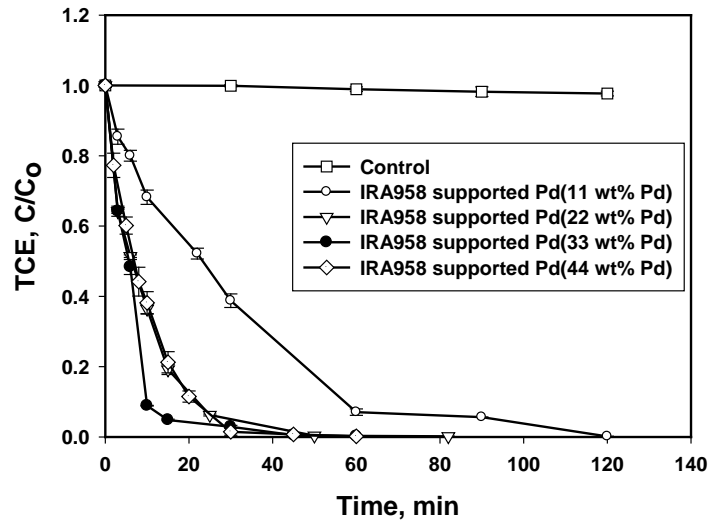
(b)

Figure 4-12. Hydrodechlorination of TCE using resin-bound Pd particles with different metal contents on different resin: (a) IRA-900 resin; (b) IRA-958 resin. (Initial TCE=50 mg/L, resin=1g/L). Data plotted as mean of duplicates, error bars indicate deviation from the mean.

The detailed rate values on varied content of Pd are listed in Table 4-2.For the IRA-900 supported Pd catalysts, with Pd coverage increasing from 13.6% to 39.0%, the observed kinetic constant (k_{obs}) also increased from 0.0400 min^{-1} to 0.2651 min^{-1}. For the IRA-958 supported Pd, the rate constant increased from 0.0470 min^{-1} to 0.2344 min^{-1} as Pd loading increased from 11.0 to 33.0 wt%.

Table 4-2. Rate Constants of Supported Pd catalysts for TCE Hydrodechlorination.

Support Type	Pd content (wt.%)	k_{app} (min^{-1})	R^2
Pd/IRA-900	13.6	0.0400±0.0009	0.9977
	26.8	0.0999±0.0023	0.9979
	39.0	0.2651±0.0476	0.9394
	52.0	0.1035±0.0035	0.9944
Pd/IRA-958	11.0	0.0470±0.0049	0.9301
	22.0	0.1089±0.0035	0.9958
	33.0	0.2344±0.0564	0.8962
	44.0	0.1056±0.0031	0.9956

Figure 4-13 shows kinetic data fitted using the pseudo first order model for the resin supported catalysts with various Pd contents.
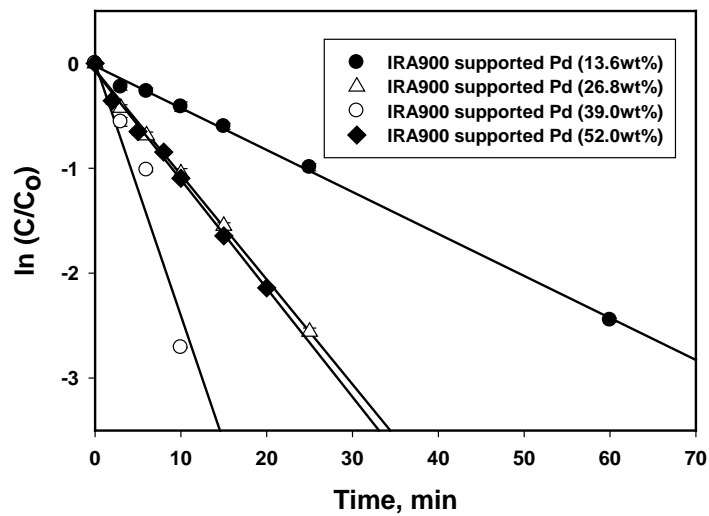
(a)
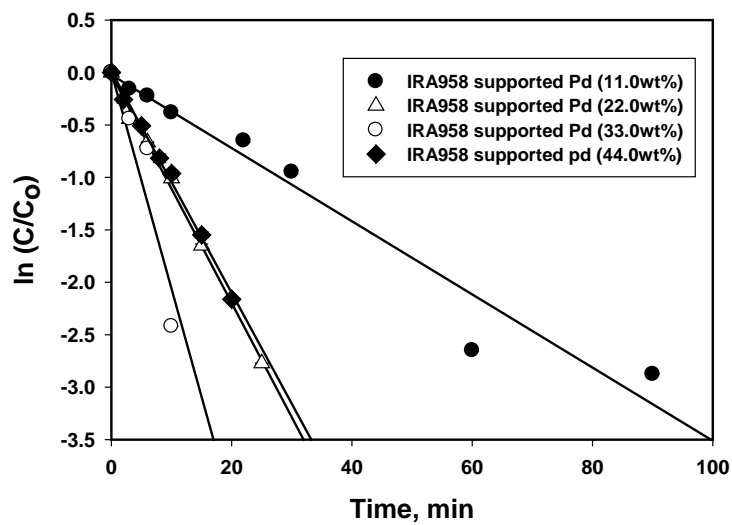
(b)

Figure 4-13. Linearized plot of the TCE hydrodechlorination kinetic data of Figure 4-12.

Evidently, increasing Pd loading enhances the degradation rates, especially during the initial induction periods. The observation suggests that the higher Pd loadings, the greater the active Pd surface, until a peak Pd loading is reached. Taking into account of the SEM images (Figures 4-5 and Figure 4-6), the enrichment of Pd primarily in the outer shell of the polymer beads is likely the cause of the enhanced rates.

However, when the Pd coverage was further increased to 52.0 wt%, a decrease in reaction rate was observed. The activity drop can be attributed to the diminished accessible Pd sites in the outer shell when a layer or sheet of Pd particles is formed, or when surface accumulation of Pd disables the available reaction sites at excessive levels of Pd loading. Nutt et al. (2005) studied effect of Pd loading on TCE degradation rate with a Pd-on-Au bimetallic catalyst, and found formation of multiple layers of Pd particles at the support surface at elevated Pd loadings. The surface Pd layers may block the accessibility of the interior Pd sites of a porous support such as IRA-900 and IRA-958, which results in a decrease in the specific surface area and the overall catalytic activity at extremely high metal loadings. Furthermore, this behavior could be associated with deactivation of the catalysts due to degradation of the support at extraordinary high Pd content.

At the optimal Pd loading of 39 wt% Pd on IRA-900, the TCE degradation rate constant is $1.2\times$ and $215\times$ greater than those of the commercial Pd/Al$_2$O$_3$ and Pd black reported by Nutt et al. (2005).

4.6 Effect of Dissolved Organic Matter.

DOM (Dissolved organic matter) is prevalent in natural water. It's well known that the presence of DOM may inhibit the reaction rate as a result of competitive sorption onto the catalyst surface sites (Zhang et al. 2013).

Given the rather different porosity, pore size and hydrophobicity of the supporting resins (Table 3-1), DOM may interact with matrices in a different manner. IRA-958 has a more hydrophilic polyacrylic matrix than the polystyrene matrix of IRA-900, and thus, is expected to be more resistant to DOM clogging. However, based on the DOM sorption tests, only less than 2% of the 10mg/L was adsorbed by the two resin supports in 120min. On the other hand, IRA-900 has a much greater pore size compared with IRA-958. At the presence of DOM in water, the pores can be easily clogging by large molecule of DOM on the IRA-958 supported Pd catalyst (pore size smaller than 6.46nm), and thus, diminish the accessible palladium sites and retard the global reaction rate. Consequently, IRA-900 supported Pd catalysts offered better catalytic activity with DOM concentration of 3 mg/L and 10 mg/L. This assumption is in agreement with our results. At a TOC concentration of 3 mg/L, no significant impact was evident on the reaction rate for IRA900/Pd (PIRA900=0.880), while a decrease on the k_{app} value from 0.0696 min^{-1} to 0.0458 min^{-1} for IRA958/Pd; when the TOC concentration increased to10 mg/L, the k_{app} for IRA900/Pd was reduced to 0.0583 min^{-1} while no further decrease of k_{app} value was found for IRA958/Pd.
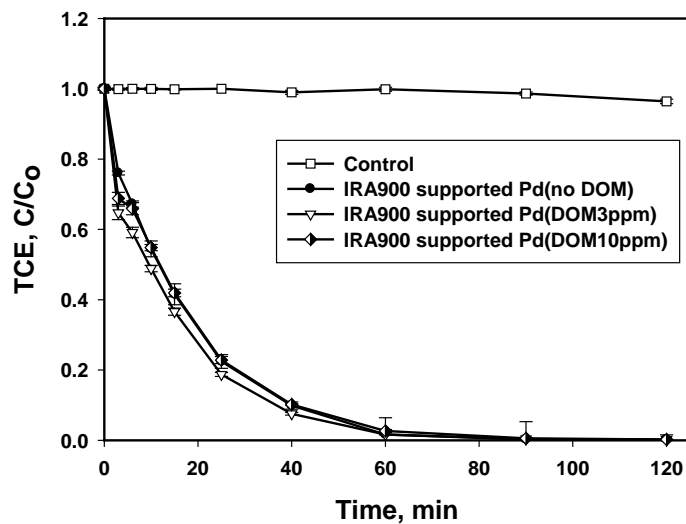
(a)
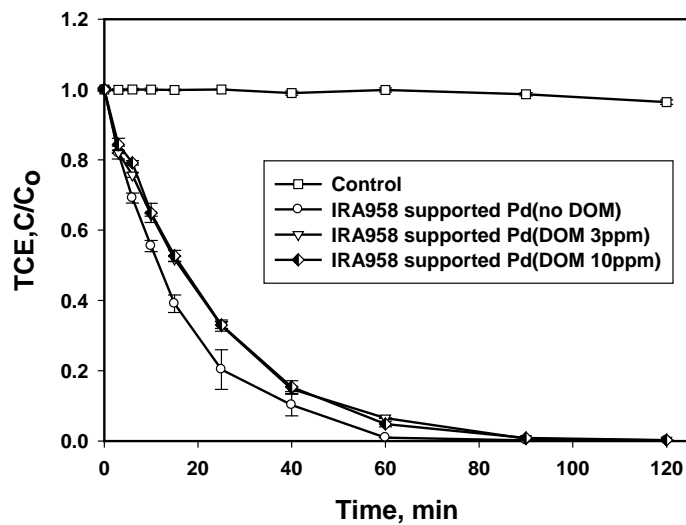
(b)

Figure 4-14. TCE hydrodechlorination in the presence of various concentration of dissolved organic

carbon using (a) IRA-900 supported Pd catalysts; (b) IRA-958 supported Pd catalysts. (TCE = 50 mg/L,

resin = 1g/L, Pd = 17.0 wt% of resin). Data plotted as mean of duplicates, error bars indicate deviation

from the mean.

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4.7 Effect of Physical Properties of the Resin Support.

Taking into account the hydrophobic natures of the two resin supports, it can be expected that TCE hydrodechlorination is more favorable with palladium catalysts on the more hydrophobic IRA-900 resins.

TCE adsorption indicated that the adsorption of TCE on both resin matrixes is less than 2 % with a resin concentration of 1 g/L as in TCE hydrodechlorination. When the resin concentration increased to 10 g/L, the IRA-900 resin adsorbed ~12 % of the total TCE while the IRA-958 rarely adsorbed TCE (~1 %). These results accord with the TCE hydrodechlorination kinetic data in Figure 4, where no significant difference was found with a low amount of the catalyst.

It has been suggested that the rapid sorption of TCE on the support may also result in less available TCE for the Pd and therefore limit the global rate (Zhang et al. 2012). However, considering the high Pd loading in the IRA-900 catalyst, this situation, which is favored by low Pd coverage, is not likely to occur in this case. It can be expected that the IRA-900 resin supported Pd catalyst would offer a more suitable environment for TCE hydrodechlorination.

In summary, the polystyrene IRA-900 resin supported Pd catalysts offered greater catalytic activity in water as well as with the presence of dissolved organic matter.

CHAPTER 5 CONCLUSION AND FUTURE STUDY

In this work, we investigated the potential of enhanced catalytic performance of Pd catalysts supported on two commercial strong basic anion (SBA) exchange resins. Knowledge of the catalytic activity, stability and reusability of the SBA resin supported Pd catalysts were studied. The influences of DOM, palladium content and support properties were also evaluated.

The analysis of the results originated the following conclusions:

- Palladium sorption equilibrium on the SBA resins can be fitted perfectly with the linearized Langmuir model.

- Given the same concentration of palladium complexes, the palladium sorption on these two SBA resins is favored with higher pH value.

- At the same initial condition, the IRA-900 resin gets higher palladium uptake than the IRA-958 resin.

- Egg-shell morphology was observed in the SBA resin supported Pd catalysts as a result of concentrate-gradient-driven Pd migration together with support degradation.

- At a Pd coverage of 17.0 wt.%, the SBA resin supported Pd catalyst can effectively catalyze rapid hydrodechlorination of TCE. The apparent rate constant, k_{app}, was determined to be 0.0807 min^{-1} for IRA900/Pd and 0.0696 min^{-1} for IRA958/Pd.

- The resin-based catalysts can be repeated use for at least nine times with negligible Pd bleeding ($< 0.1\%$).

- The SBA resin supported catalysts is stable without activity loss for more than three months.

- For the IRA-900 supported Pd catalysts, the apparent kinetic constant (k_{app}) increased from 0.0400 min^{-1} to 0.2651 min^{-1} as Pd loading increased from 13.6 to 39.0 wt%. For the IRA-958 supported Pd, the rate constant increased from 0.0470 min^{-1} to 0.2344 min^{-1} as Pd loading increased from 11.0 to 33.0 wt%.

- The TCE hydrodechlorination rate increases with an increase of metal content when the catalysts were repeated up to 3 times. Further increase in metal content can't improve the catalytic activity.

- IRA-900 supported Pd catalysts offered better catalytic activity with DOM concentration of 3 mg/L and 10 mg/L.

5.1 Future Studies

Future studies including a research on the more detailed properties resin catalysts (such as the change of BET surface area, pore size) before/after palladium loading are recommended. Increasing the ratio of resin catalysts mass to the volume of aqueous phase as well as increasing the DOM concentration is suggested since it could be provide more information for the effect of support hydrophobicity.

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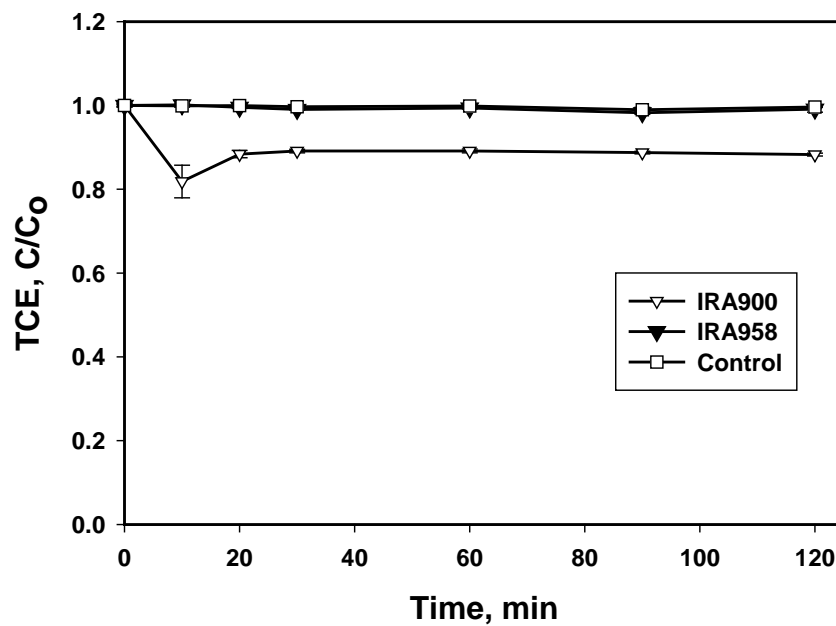
APPENDIX ADDITIONAL EXPERIMENTAL RESULTS

Figure A-1. TCE sorption tests with the two SBA resin supports.
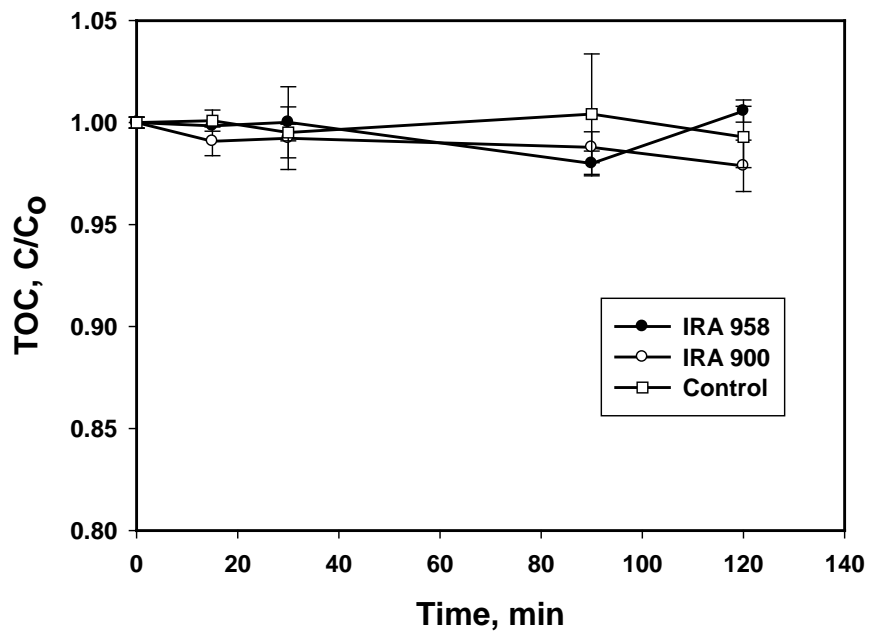(Initial TCE= 50 mg/L, resin = 10 g/L).

Figure A-2. DOM sorption tests with the two SBA resin supports.
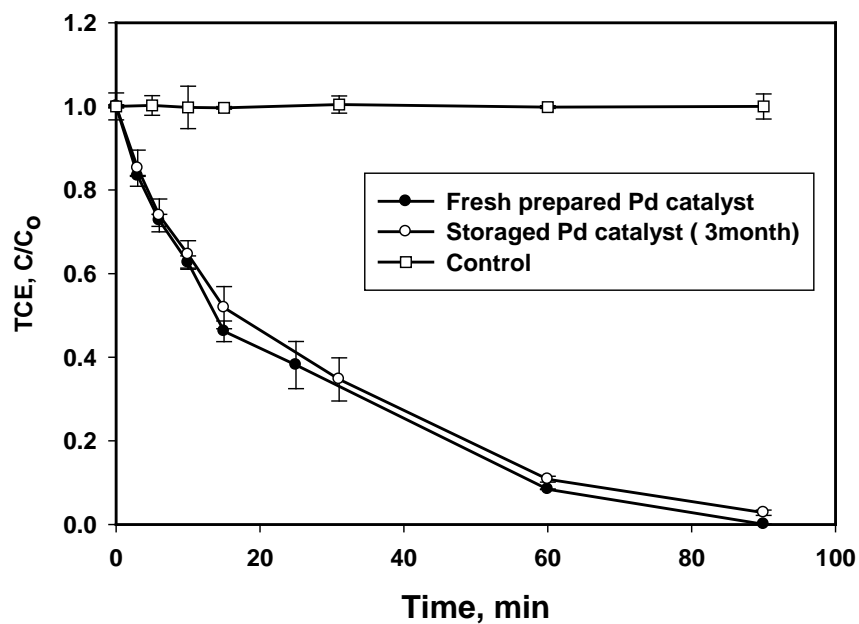Initial TOC= 10mg/L, resin=1g/L.

Figure A-3. Stability of the SBA supported Pd catalyst. The 17wt% IRA958/Pd was used in this test with initial TCE concentration of 50 mg/L and resin= 1g/L.