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Palladium-catalyzed hydrodehalogenation of 1,2,4,5-tetrachlorobenzene in water–ethanol mixtures

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Abstract

Palladium-catalyzed hydrodehalogenation (HDH) was applied for destroying 1,2,4,5-tetrachlorobenzene (TeCB) in mixtures of water and ethanol. This investigation was performed as a critical step in the development of a new technology for clean-up of soil contaminated by halogenated hydrophobic organic contaminants. The main goals of the investigation were to demonstrate the feasibility of the technology, to determine the effect of the solvent composition (water:ethanol ratio), and to develop a model for the kinetics of the dehalogenation process. All experiments were conducted in a batch reactor at ambient temperature under mild hydrogen pressure. The experimental results are all consistent with a Langmuir–Hinshelwood model for heterogeneous catalysis. Major findings that can be interpreted within the Langmuir–Hinshelwood framework include: (1) the rate of hydrodehalogenation depends strongly on the solvent composition, increasing as the water fraction of the solvent increases; (2) the HDH rate increases as the catalyst concentration in the reactor increases; (3) when enough catalyst is present, the HDH reaction appears to follow first-order kinetics, but the kinetics appear to be zero-order at low catalyst concentrations. TeCB is converted rapidly and quantitatively to benzene, with only trace concentrations of 1,2,4-trichlorobenzene appearing as a reactive intermediate. The results obtained here have important implications for the further development of the proposed soil remediation technology, and may also be important for the treatment of other hazardous waste streams.
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1. Introduction

Halogenated hydrophobic organic compounds (HHOCs) are commonly found at many contaminated sites on the National Priorities List in the United States [1,2]. Chlorinated benzenes, chlorinated phenols, and polychlorinated biphenyls (PCBs) belong to this category of pollutants. Most of these HHOCs tend to reside preferentially in soil and sediment, rather than water or air, because they have low aqueous solubility and only semi-volatile characteristics. Therefore, effective methods are needed to clean up soils contaminated by HHOCs.

Unfortunately, the biodegradation rates of HHOCs in soil are often very slow, requiring months or years for adequate remediation [3]. Incineration of contaminated soil is feasible, but high energy consumption is required to reach the necessary temperatures, and hazardous by-products such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) can be generated from the combustion of HHOCs [4]. Therefore, solvent extraction followed by activated carbon sorption is popularly employed for treating soils contaminated by HHOCs [5]. The main problem with this treatment method is the generation of a secondary waste because the target contaminants are not destroyed, merely transferred into another phase. Thus, further treatment or disposal of the waste is required, leading to additional cost and/or possible exposure to future populations. Therefore, it is desirable to develop a cost-effective method for destroying HHOCs in soils without generating a secondary waste stream.

Catalytic hydrodehalogenation (HDH) with noble metals has previously been recognized as a potential means of treating halogenated organic compounds in water and/or *liquid* waste streams [6–10]. In particular, palladium is the most commonly used transition metal for the HDH of chlorinated organic compounds in engineering practice [11]. Pd-catalyzed HDH treatment has

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been successfully applied for the treatment of water or liquid waste streams contaminated by chlorinated benzenes [8,12–16], chlorinated phenols [17–19], and PCBs [20–22]. The general stoichiometry of the HDH reaction is

$$R\text{–}X_n + nH_2 \xrightarrow{\text{Pd catalyst}} R\text{–}H_n + nH^+ + nX^-$$
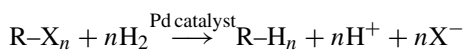
where X represents a halogen atom such as chlorine.

Therefore, we now propose a new treatment method for contaminated soils in which HHOCs are extracted from the soil by a solvent, then destroyed by Pd-catalyzed HDH reaction. We call this process remedial extraction and catalytic hydrodehalogenation, or REACH. In the REACH process, the solvent plays a critical role in both the extraction and the HDH reaction. Mixtures of water and ethanol are good candidates for the choice of solvent, because these mixtures have been shown to be effective solvents for extraction at the laboratory scale [23] and field scale [24], and previous research has shown the potential for HDH in water/ethanol mixtures [17,25]. In this paper, we focus on the Pd-catalyzed HDH of 1,2,4,5-tetrachlorobenzene (TeCB) in water/ethanol mixtures, thereby simulating the solvent streams likely to be treated in practice. We focus on TeCB because it is one of 31 priority chemicals targeted by the United States Environmental Protection Agency (US EPA) for waste reduction [26]; also, TeCB has physical and chemical properties similar to those of many other HHOCs of concern. It is worth noting that, of the 31 priority chemicals identified by US EPA, about half fall into the category of halogenated hydrophobic organic contaminants, and would therefore be candidates for clean-up by the technology proposed here.

The long-term goal of our research is to develop the REACH process for full-scale application at contaminated sites. The first critical step is to develop a sufficient understanding of the HDH reaction in water/ethanol mixtures. Therefore, the main goals of the research described herein were (1) to assess the potential for hydrodechlorination of the target contaminant, (2) to determine the effect of the solvent composition (i.e., the water:ethanol ratio), and (3) to develop a model for the kinetics of the dehalogenation process. These goals have been accomplished through a series of batch kinetic experiments, in which TeCB was spiked into mixtures of water and ethanol, then destroyed via Pd-catalyzed hydrodehalogenation in a batch reactor. Results of the experiments are interpreted with a Langmuir–Hinshelwood conceptual model for heterogeneous catalysis.

2. Materials and methods

2.1. Chemicals and catalyst

The chemicals employed in this research are summarized in Table 1. Mixtures of water and ethanol were prepared using de-ionized water and 200 proof (99.5%) ethanol. Commercially available 1 wt.% Pd-on-Al$_2$O$_3$ catalyst was employed, and the palladium content of the catalyst specified by the manufacturer is assumed to be accurate. Detailed physical properties of the catalyst can be found elsewhere [27]. The

Table 1
Chemicals and catalyst used in experiments

Chemical or catalyst	Specification	Source
1,2,4,5-Tetrachlorobenzene (TeCB)	98%	Sigma–Aldrich
2,5-Dibromotoluene (internal standard)	98%	Sigma–Aldrich
Ethanol	99.5%	Sigma–Aldrich
Hexane (for GC analysis)	HPLC grade, 98.5%	EMD Chemicals
Pd-on-Al$_2$O$_3$ catalyst	1% Pd by weight	Sigma–Aldrich
De-ionized water	>17.5 MΩ cm	See below

De-ionized water was produced in the laboratory with use of a Barnstead water purification system.

catalyst was used in the HDH reactions without further treatment. No special effort was given to prevent the catalyst from contacting air. A stock solution of 1,2,4,5-tetrachlorobenzene with concentration 5000 mg/L was prepared by dissolving 0.1 g of TeCB into 20 mL ethanol in a 20-mL clear borosilicate glass vial. The vial containing the stock solution was closed using a PTFE-lined septum and kept in a freezer to minimize volatilization.

2.2. Pd-catalyzed hydrodehalogenation reaction studies

In this research, all Pd-catalyzed hydrodehalogenation (HDH) reactions were carried out in a Parr 3911 hydrogenation apparatus (Parr Instrument Company, Moline, IL, USA). The experiments were conducted as follows.

A desired mixture of deionized water and ethanol was pre-mixed in a glass beaker and then transferred to a 500-mL reaction bottle. The total volume of solvent (water/ethanol mixture) in the reaction bottle was approximately 300 mL for all experiments; for instance, a 50/50 mixture consisted of 150 mL water and 150 mL ethanol mixed and then added to the reaction bottle. (The slight negative volume change of mixing for water and ethanol means that the final volume may have been less than 300 mL, but the effect is small enough to neglect.) After adding the solvent, the desired amount of catalyst and the desired amount of TeCB stock solution were also added to the reaction bottle. The bottle was then placed in the hydrogenation reactor, and air in the headspace was removed by filling the bottle with hydrogen gas up to 0.31 MPa and venting it. Pressurizing and venting were repeated three times. After venting, the reactor headspace was filled with hydrogen gas to 0.21 MPa, and shaking of the reaction bottle was started. The hydrogenation reactor is designed to shake at 200 rpm to ensure complete mixing. After shaking for the desired amount of time, the reactor was stopped, and a sample was collected for analysis. Experiments were conducted at room temperature (22 ± 3 °C).

Four sets of experiments were conducted, each requiring that different experimental conditions be tested, as summarized in Table 2. For each experimental condition, kinetic data were obtained for six or seven different reaction times, which required repeating the experimental process once for each reaction time. Each experiment was conducted in duplicate.

Table 2
Experimental conditions for Pd-catalyzed hydrodehalogenation reactions

Initial concentration of TeCB in reactor (mg/L)	Concentration of catalyst (g/L)	Solvent composition (v:v, before mixing) (% water:% ethanol)
Determine effect of solvent composition		
2.0	0.17	67:33
2.0	0.17	50:50
2.0	0.17	33:67
5.0	0.33	67:33
5.0	0.33	50:50
5.0	0.33	33:67
Determine effect of catalyst concentration		
5.0	0.17	50:50
5.0	0.33	50:50
5.0	0.67	50:50
10.0	0.17	50:50
10.0	0.33	50:50
10.0	0.67	50:50
Determine effect of initial concentration of TeCB		
5.0 (January 2005)	0.33	50:50
10.0 (January 2005)	0.33	50:50
5.0 (November 2005)	0.33	50:50
10.0 (December 2005)	0.33	50:50
Determine transformation products and mass balance		
5.0 (23 µM)	0.33	50:50

2.3. Sampling and analysis

At the end of each HDH run, the shaker was stopped and an appropriate amount of sample was collected using a syringe. Any fine catalyst was immediately separated from the sample using a 0.2-µm membrane filter. An aliquot of the filtered sample was placed in an extraction vial with hexane, and the vial was vigorously shaken for 1 h to transfer TeCB (and any reaction products) to the hexane. Duplicate samples were collected from the reactor and extracted into hexane. The hexane contained a known concentration of 2,5-dibromotoluene as an internal standard. TeCB concentrations in the hexane were determined using gas chromatography (GC) with electron capture detection (ECD). Prior to analysis, the GC was calibrated using standard solutions of TeCB in hexane, prepared by dilutions of the TeCB stock solution. Blank samples were analyzed between each standard to verify that TeCB was eluting properly from the GC and not bleeding from one analysis to the next.

For a set of mass balance studies (described in more detail subsequently), the samples were analyzed by Advanced Technologies & Testing Laboratories (Gainesville, Florida) through the EPA purge-and-trap method 8260 [28].

2.4. Control experiments

Two kinds of control tests were conducted to verify that any observed disappearance of TeCB was due to catalytic hydrodehalogenation (HDH), rather than any other mechanism (e.g., volatilization or sorption). The first type of control experiments were conducted in exactly the same fashion as described above, with the exception that no catalyst was added to the reaction bottles. This determines the loss of TeCB due to volatilization.

The second type of control experiments was performed using nitrogen gas instead of hydrogen gas, with all other experimental conditions the same as described above. This determines the loss of TeCB due to sorption onto the catalyst surface.

For a solvent composition of 67% water, significant volatilization of TeCB was observed: we recovered only 43–47% of the TeCB after venting and 30 minutes of shaking (without catalyst present). For other solvent compositions, no significant loss was observed due to volatilization, with TeCB recoveries from 92 to 103%.

In the sorption control experiments, recoveries of TeCB were 32–64% when a solvent composition of 67% water was used. This is consistent with the results of the volatilization controls, and it is believed that the main mechanism of TeCB loss was due to volatilization, not sorption. In solvent compositions of 50:50 and 33:67 of water/ethanol, recoveries of TeCB for the sorption controls were in the range 86–88% and 103–107%, respectively. This indicates that sorption onto the catalyst support is only a minor loss mechanism. Therefore, with the exception of TeCB in 67% water, we trust that any observed removal of TeCB is due to catalytic HDH.

3. Conceptual and mathematical model

To interpret the results of the Pd-catalyzed HDH experiments, we adopt a Langmuir–Hinshelwood model for the catalytic reaction. According to this framework, the hydrodehalogenation of TeCB occurs via the following steps [29]: (1) mass transfer of the reactants (i.e., TeCB and hydrogen) from the water/ethanol solvent to the catalyst surface; (2) adsorption of the reactants to the catalyst surface; (3) reaction on the surface of the catalyst; (4) desorption of the reaction products from the surface; (5) mass transfer of the reaction products back into the bulk water/ethanol solvent. This framework enables us to develop a mathematical model to interpret the experimental data, as follows.

First, we assume that the HDH reaction on the catalyst surface follows a simple kinetic expression:

$$r = k_r C_{TeCB}^{cat} C_{H_2}^{cat} \qquad (1)$$

where r is the rate of disappearance of the TeCB (mass of TeCB reacted per mass of catalyst per time). C_{TeCB}^{cat} and $C_{H_2}^{cat}$ represent the concentration of TeCB sorbed on the catalyst surface and the concentration of H_2 sorbed on the catalyst surface, respectively.

Next, we assume that the rate-limiting step for the HDH reaction is surface reaction (step 3 in the list above), not mass transfer or sorption/desorption. The mass transfer processes are sure to be sufficiently fast because the reaction bottle is shaken vigorously, and we here assume that sorption and desorption are fast compared to the surface reaction. Thus, the sorbed concentrations are in equilibrium with the dissolved concentration in the solvent. We further assume that these equilibrium sorption relationships are described by Langmuir isotherms. The hydrogen concentration is in the high region of the Langmuir isotherm, such that $C_{H_2}^{cat}$ is a constant. (We have verified with experiments that the HDH reaction is not sensitive to the H_2 pressure in the reaction vessel as long as the pressure is at least 0.17 MPa; this

finding supports the assumption that C_{H2}^{cat} is constant under the experimental conditions considered here.) Therefore, Eq. (1) can be replaced by

$$r = k_r^* C_{TeCB}^{cat} \tag{2}$$

where k_r^* is an apparent first-order rate constant for the reaction on the catalyst surface, and is given by $k_r^* = k_r C_{H_2}^{cat}$.

Next, we apply a mass balance for TeCB in the entire reaction vessel:

$$M^{cat} \frac{dC_{TeCB}^{cat}}{dt} + V^{solvent} \frac{dC_{TeCB}^{solvent}}{dt} = -M^{cat} r \tag{3}$$

where M^{cat} and $V^{solvent}$ are the mass of catalyst and the volume of solvent, respectively. Combining Eqs. (2) and (3) yields the following:

$$M^{cat} \frac{dC_{TeCB}^{cat}}{dt} + V^{solvent} \frac{dC_{TeCB}^{solvent}}{dt} = -M^{cat} k_r^* C_{TeCB}^{cat} \tag{4}$$

Next, we consider that the sorption of TeCB onto the catalyst surface follows a Langmuir isotherm:

$$C_{TeCB}^{cat} = q_{max} \frac{K C_{TeCB}^{solvent}}{1 + K C_{TeCB}^{solvent}} \tag{5}$$

In the low-concentration range (i.e., $C_{TeCB}^{solvent} \ll 1/K$), this Langmuir isotherm reduces to

$$C_{TeCB}^{cat} = q_{max} K C_{TeCB}^{solvent} = K_d C_{TeCB}^{solvent} \tag{6}$$

where K_d is an apparent linear partitioning coefficient describing the equilibrium between the dissolved concentration and the sorbed concentration of TeCB. In other words, K_d is the ratio of the sorbed concentration of TeCB to the concentration of TeCB in the solvent, $K_d = C_{TeCB}^{cat}/C_{TeCB}^{solvent}$, assuming that the sorption is at equilibrium and that the concentrations are linearly related at low values of $C_{TeCB}^{solvent}$. In this case, Eq. (4) can be reduced to the following:

$$\frac{dC_{TeCB}^{solvent}}{dt} = -k_r^* \frac{M^{cat} K_d}{M^{cat} K_d + V^{solvent}} C_{TeCB}^{solvent} \tag{7}$$

For our experiments, we generally have the condition that $V^{solvent} \gg M^{cat} K_d$, such that Eq. (7) reduces further to

$$\frac{dC_{TeCB}^{solvent}}{dt} = -k_r^* \frac{M^{cat}}{V^{solvent}} K_d C_{TeCB}^{solvent} \tag{8}$$

Thus, when $C_{TeCB}^{solvent}$ is in the low-concentration range, the kinetics of the hydrodehalogenation reaction should be first-order with respect to the concentration of TeCB in the liquid solvent. For ease of notation we can re-write Eq. (8) as follows:

$$\frac{dC_{TeCB}^{solvent}}{dt} = -k_1 C_{TeCB}^{solvent} \tag{9}$$

where the apparent first-order rate constant k_1 is given by $k_1 = k_r^* K_d M^{cat}/V^{solvent}$.

In the high-concentration range (i.e., $C_{TeCB}^{solvent} \gg 1/K$), the Langmuir isotherm reduces to

$$C_{TeCB}^{cat} = q_{max} \tag{10}$$

and Eq. (4) becomes the following:

$$\frac{dC_{TeCB}^{solvent}}{dt} = -k_r^* \frac{M^{cat}}{V^{solvent}} q_{max} \tag{11}$$

Thus, when $C_{TeCB}^{solvent}$ is in the high-concentration range, the kinetics of the hydrodehalogenation reaction should be zero-order with respect to the concentration of TeCB in the liquid solvent. For ease of notation we can re-write Eq. (11) as follows:

$$\frac{dC_{TeCB}^{solvent}}{dt} = -k_0 \tag{12}$$

where the apparent zero-order rate constant k_0 is given by $k_0 = k_r^* q_{max} M^{cat}/V^{solvent}$.

In summary, according to this conceptual and mathematical model, the rate of disappearance of TeCB in the liquid phase should follow first-order kinetics when the concentration is low (Eq. (9)), and should follow zero-order kinetics when the concentration is high (Eq. (12)). In either case, the apparent rate constant should increase with increasing catalyst concentration in the reactor, $M^{cat}/V^{solvent}$. Furthermore, the apparent first-order rate constant k_1 depends upon the equilibrium partitioning coefficient K_d. This is significant because K_d is likely to depend upon the solvent composition, with higher ethanol concentrations favoring the TeCB remaining in solution rather than sorbing onto the catalyst surface. Thus, the apparent first-order rate constant k_1 is expected to depend upon the solvent composition.

As shown in Table 2, we designed different sets of experiments to test the validity of this conceptual model. Results are reported below.

4. Results and discussion

4.1. Effect of solvent composition on the Pd-catalyzed hydrodehalogenation rate

The effect of solvent composition on the Pd-catalyzed hydrodehalogenation (HDH) kinetic rate of 1,2,4,5-tetrachlorobenzene (TeCB) over time in a batch reactor is presented in Fig. 1. The results show clearly that the Pd-catalyzed HDH rate increases as the fraction of water increases in the solvent. This was observed for both sets of experimental conditions (2 mg/L initial concentration of TeCB with 0.17 g/L catalyst, and 5 mg/L initial concentration of TeCB with 0.33 g/L catalyst). The apparent first-order rate constants k_1 for each solvent composition are given in the legend of Fig. 1 and are summarized in Table 3. Similar effects of solvent composition have been reported for the dehalogenation rate of polychlorinated biphenyls treated by bimetallic Pd/Fe [25], and for perchloroethylene treated by zero-valent iron [30]. We attribute this to the effect of the solvent composition on the sorption of TeCB to the catalyst surface. As ethanol fraction increases in the solvent, the contaminant partitioning coefficient K_d decreases and the apparent first-order kinetic constant k_1 decreases, thereby resulting in a decrease in the overall HDH rate, as predicted by Eqs. (7) and (8). Conversely, as the

Table 3
Summary of apparent rate constants and recoveries in control experiments

Initial concentration of TeCB (mg/L)	Solvent composition (v:v, before mixing) (% water:% ethanol)	Concentration of catalyst (g/L)	Apparent zero-order rate constant, k_0 (mg/(L min))	Apparent first-order rate constant, k_1 (min^{-1})	TeCB recovery in controls	
					Volatilization control (%)	Volatilization/sorption control (%)
Determine effect of solvent composition						
2.0	67:33	0.17		0.24	43	
2.0	50:50	0.17		0.081	95	
2.0	33:67	0.17		0.040	103	
5.0	67:33	0.33		0.40	47	32–64
5.0	50:50	0.33		0.099	95	86–88
5.0	33:67	0.33		0.051	99	103–107
Determine effect of catalyst concentration						
5.0	50:50	0.17	0.039			
5.0	50:50	0.33		0.094	95	86–88
5.0	50:50	0.67		0.36		
10.0	50:50	0.17	0.032			
10.0	50:50	0.33		0.025	92	
10.0	50:50	0.67		0.082		
Determine effect of initial concentration of TeCB						
5.0 (January 2005)	50:50	0.33		0.099	95	86–88
10.0 (January 2005)	50:50	0.33		0.087	92	
5.0 (November 2005)	50:50	0.33		0.094	95	86–88
10.0 (December 2005)	50:50	0.33		0.025	92	

Volatilization controls were conducted with no catalyst addition; volatilization and sorption controls were conducted with catalyst addition but using nitrogen gas instead of hydrogen gas; see text for more details.
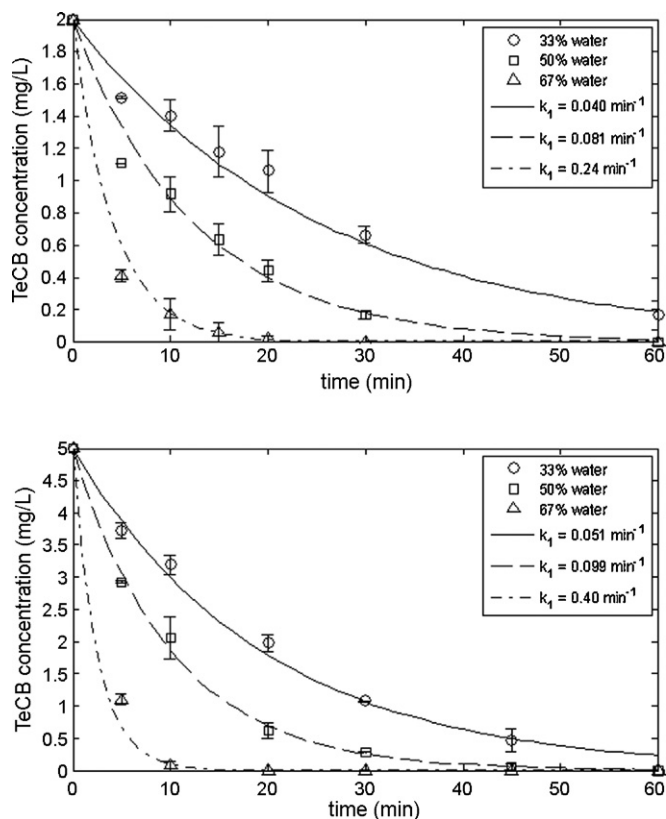
Fig. 1. Effect of solvent composition on the rate of Pd-catalyzed hydrodehalogenation (HDH) of tetrachlorobenzene (TeCB) in a batch reactor. Symbols represent experimental data and lines represent first-order kinetic degradation model. Top panel: catalyst concentration = 0.17 g/L and initial TeCB concentration = 2 mg/L. Bottom panel: catalyst concentration = 0.33 g/L and initial TeCB concentration = 5 mg/L.

water fraction increases in the solvent, the amount of TeCB sorbed on the catalyst surface increases, and a higher kinetic rate is observed. These observations are consistent with the Langmuir–Hinshelwood framework adopted above.

Furthermore, the data shown in Fig. 1 appear to follow first-order kinetics, as predicted by Eq. (9). The first-order kinetic model fits the data sets in Fig. 1 with R^2 values ranging between 0.985 and 0.999 (based on linear regression of $\log(C_{TeCB}^{solvent})$ versus t). Therefore, the results shown in Fig. 1 are consistent with the conceptual and mathematical model we have developed above.

It is worth noting that, for a solvent composition of 67% water, the control experiments indicated poor recovery of TeCB, as described previously. We believe that some TeCB is lost due to volatilization for the experiments in 67% water. The data are included in Fig. 1, but should be interpreted appropriately. Despite this, we believe that there is a very clear trend indicating the strong effect of the solvent composition on the HDH kinetics.

From Fig. 1, it can be seen that the apparent first-order rate constants k_1 are higher for the bottom panel than for the top. This is because the experiments shown in the bottom panel were conducted at a higher concentration of catalyst. Therefore, in the next sub-section, we examine the effect of catalyst concentration on the rate of hydrodehalogenation.

4.2. Effect of catalyst concentration on the Pd-catalyzed hydrodehalogenation rate

The effect of catalyst concentration ($M^{cat}/V^{solvent}$) on the Pd-catalyzed HDH rate is shown Fig. 2. The top half of Fig. 2 is for an initial TeCB concentration of 5 mg/L, and the bottom half is for an initial concentration of 10 mg/L. All experiments represented in Fig. 2 were conducted in a 50:50 solvent composition. Fig. 2 shows clearly that an increase in catalyst concentration increases the HDH rate. This behavior is predicted by Eqs. (8) and (11), and it indicates that the availability of Pd surface sites is a rate-limiting factor for the overall removal of TeCB under the experimental conditions we tested.

As can be seen from Fig. 2, the first-order kinetic model is a good descriptor for four of the six data sets, yielding R^2 values between 0.990 and 0.999 (based on linear regression of $\log(C_{TeCB}^{solvent})$ versus t). However, when the catalyst concentration is 0.17 g/L, the data are not well described by the first-order kinetic model, Eq. (9). Therefore, we tested a zero-order kinetic model, Eq. (12), as shown in Fig. 3. The zero-order model appears to fit the data quite well for $t > 10$ min, and appears to
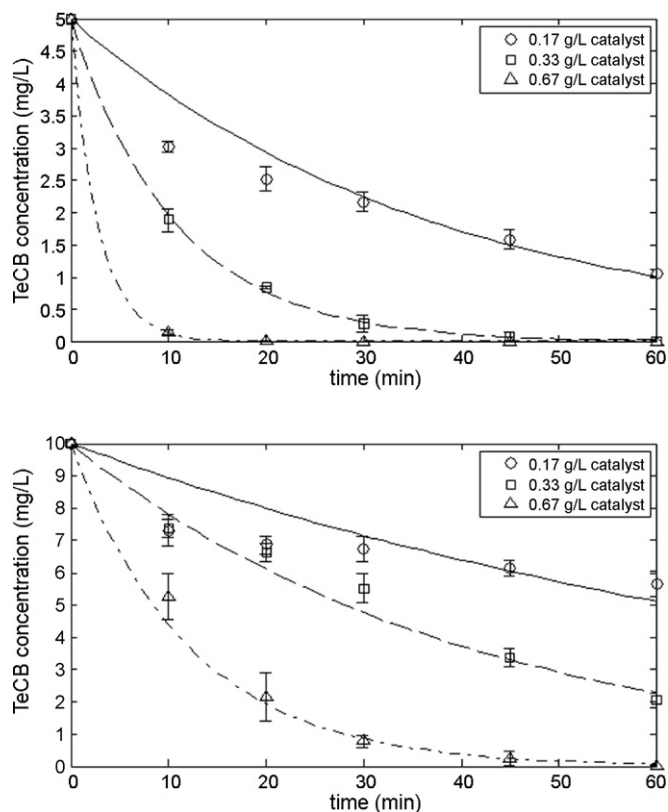

Fig. 2. Effect of catalyst concentration on the rate of Pd-catalyzed hydrodehalogenation of TeCB. Symbols represent experimental data and lines represent first-order kinetic degradation model. Top panel: initial TeCB concentration = 5 mg/L; apparent first-order rate constants k_1 are 0.027 min^{-1}, 0.094 min^{-1}, and 0.36 min^{-1} for 0.17 g/L catalyst, 0.33 g/L catalyst, and 0.67 g/L catalyst, respectively. Bottom panel: initial TeCB concentration = 10 mg/L; apparent first-order rate constants k_1 are 0.011 min^{-1}, 0.025 min^{-1}, and 0.082 min^{-1} for 0.17 g/L catalyst, 0.33 g/L catalyst, and 0.67 g/L catalyst, respectively. For all experiments, the solvent composition was a 50:50 mixture (v/v, before mixing) of deionized water and ethanol.
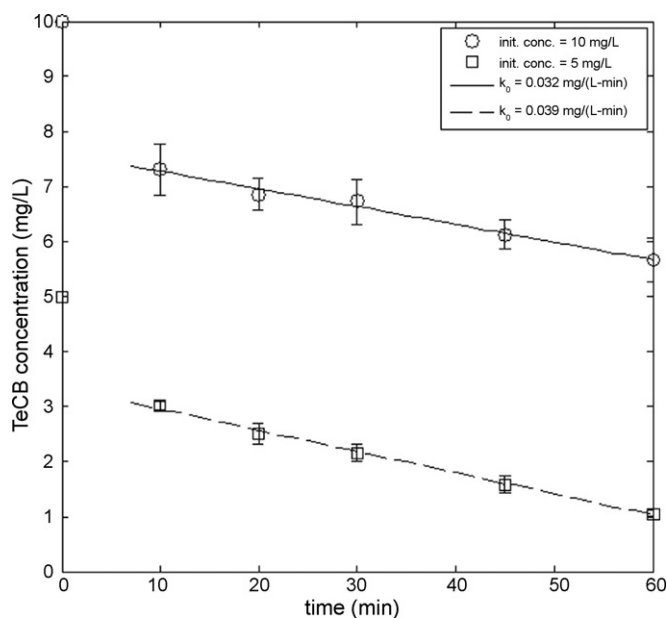
Fig. 3. Zero-order kinetic model fit to TeCB dehalogenation data with 0.17 g/L catalyst. The solvent composition was a 50:50 mixture (v/v, before mixing) of deionized water and ethanol.

fit the data better than the first-order model. In Section 3, we demonstrated that zero-order kinetics are to be expected when the TeCB concentration is sufficiently high. The data in Fig. 3 suggest that a zero-order kinetic model is appropriate when the ratio of TeCB concentration to catalyst concentration is roughly 30 mg/g or higher. The zero-order rate constant k_0, as defined by Eq. (12), appears to be in the range 0.03–0.04 mg/(L min) for the experimental conditions used here.

It appears that the zero-order model is valid for $t > 10$ min, but not valid for $t < 10$ min. It may be that the assumption of rapid sorption equilibrium is not valid within the first few minutes of the experiment.

4.3. Effect of initial concentration of TeCB on the Pd-catalyzed HDH rate

If the reaction kinetics are first-order, as described by Eq. (8) and (9), then the apparent first-order reaction rate constant k_1 should not depend upon the initial concentration of TeCB in the reactor. To test this hypothesis, we compared the results for two initial concentrations of TeCB: 5 and 10 mg/L. In both cases, a 50:50 mixture of water/ethanol was used, and the catalyst concentration was 0.33 g/L. Two experiments were run for $C_0 = 5$ mg/L, and two experiments were run for $C_0 = 10$ mg/L, for a total of four experiments. Results are shown in Fig. 4. The normalized concentration of TeCB (C/C_0) is graphed versus time for the four experiments. For three of the four, the normalized concentrations coincide very closely. The apparent first-order rate constants for those three experiments are not statistically different at the 95% confidence level, and as seen in Fig. 4, all three sets of data are described quite well by an apparent first-order rate constant $k_1 = 0.09$ min^{-1}.
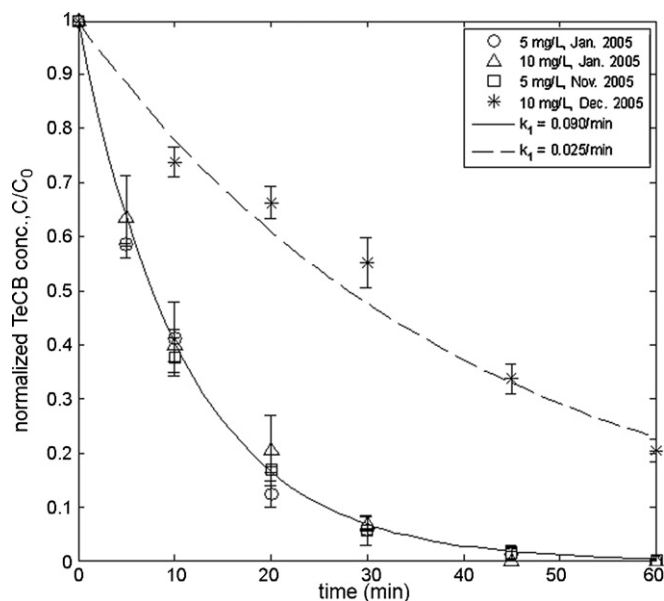

Fig. 4. Effect of initial TeCB concentration on the rate of Pd-catalyzed hydrodehalogenation of TeCB. Two experiments were conducted with $C_0 = 5$ mg/L, and two with $C_0 = 10$ mg/L; all experiments were conducted with 0.33 g/L catalyst concentration and a solvent composition of 50:50 (v/v, before mixing) water:ethanol. Symbols represent experimental data, and lines represent first-order kinetic model. Data are presented as normalized concentration, C/C_0, in order to facilitate comparison between experiments with different initial concentrations.

However, one of the four experiments gave quite different results from the other three. We note that it was the last (by date) of the four experiments performed. Our hypothesis is that, because the Pd-on-Al$_2$O$_3$ catalyst was exposed to air over a prolonged period of time, the catalyst had lost some of its activity by the time the last experiment was run. Hence, slower kinetics were observed. An argument against this hypothesis is that data from November 2005 and December 2005 exhibit different kinetics, and the catalyst might not have lost so much activity in one month's time. However, additional data from June 2006 (presented below) appear to corroborate the hypothesis that the catalyst was slowly losing its activity between late 2005 and mid-2006. Thus, overall, we believe that the rate constant k_1 is essentially independent of initial TeCB concentration, as originally hypothesized.

4.4. Transformation of TeCB by the Pd-catalyzed hydrodehalogenation

The experimental data presented in Figs. 1–4 show clearly that the concentration of TeCB in the water/ethanol solvent decreases over time. However, one might still question whether the observed disappearance of TeCB is due to Pd-catalyzed hydrodehalogenation, or due to some other process (e.g., slow volatilization into the reactor head space, slow sorption onto the catalyst surface). A mass balance is required to ascertain that the observed disappearance of TeCB is due to conversion to a reaction product. Furthermore, for development of the full-scale REACH process, it is important to know the chemical products of the HDH reaction. For instance, do chlorinated
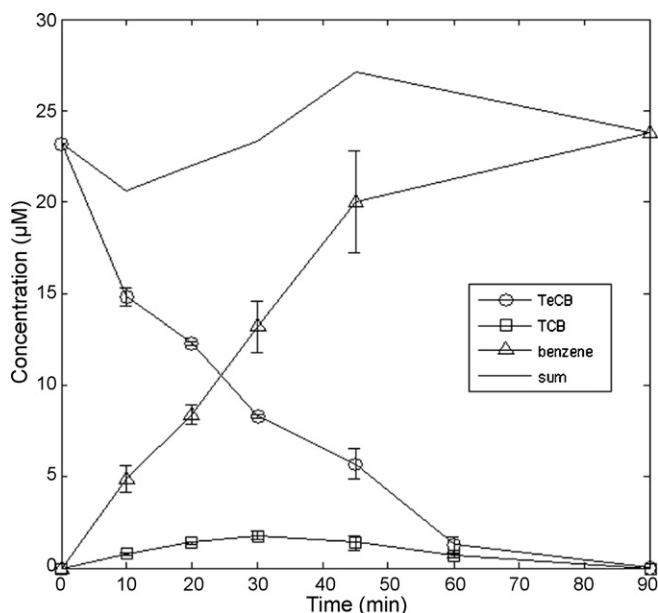
Fig. 5. Transformation of 1,2,4,5-tetrachlorobenzene (TeCB) to 1,2,4-trichlorobenzene (TCB) and benzene. The solvent composition was a 50:50 mixture (v/v, before mixing) of deionized water and ethanol, the initial concentration of TeCB was 23 μM, and the catalyst concentration was 0.33 g/L. Symbols represent experimental data.

by-products accumulate in the system? To answer these questions, and to determine a proposed reaction pathway, a mass-balance study was performed. Experiments were conducted as described above, but samples were analyzed by purge-and-trap gas chromatography (GC) with mass spectrometry (MS) detection in order to quantify the concentrations of all reaction products. The GC/MS work was performed by an outside commercial laboratory (Advanced Technologies & Testing Laboratories, Gainesville, FL) through the EPA purge-and-trap method 8260 [28].

Experimental results are presented in Fig. 5. Minor amounts of 1,2,4-trichlorobenzene (TCB) as an intermediate chlorinated by-product were formed, but the TCB did not persist or accumulate. The concentration of benzene, which is the end product of the HDH reaction, increased as the TeCB was removed. This finding is consistent with that of previous research [9–11]. Fig. 5 shows excellent closure of the mass balance, meaning that all TeCB originally present in the system is accounted for by conversion to TCB or to benzene. This verifies that any observed loss of TeCB is due to hydrodehalogenation, not due to any other loss process.

The experiment shown in Fig. 5 was performed in June 2006. The kinetics exhibited in Fig. 5 are slower than the kinetics exhibited under identical reaction conditions tested earlier (as shown in Figs. 1, 2 and 4, and summarized in Table 3). This corroborates our hypothesis that the catalyst was losing its activity between November 2005 and June 2006. Therefore, the kinetics exhibited in Fig. 5 are probably slower than would be observed with fresh catalyst. With fresh catalyst, it is possible that even less trichlorobenzene would be formed as an intermediate. In general, the amount of TCB formed as a reactive intermediate is essentially negligible.

A possible reaction pathway for the transformation of TeCB to benzene by the Pd-catalyzed HDH method is

$$1,2,4,5\text{-TeCB} \xrightarrow{k^*} 1,2,4\text{-TCB} \xrightarrow{k^{**}} \text{benzene}$$
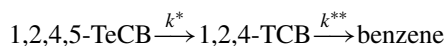
where k^* and k^{**} are kinetic constants, and k^{**} is much larger than k^*. Accordingly, an intermediate product is formed, but it reacts very quickly, so effectively it appears that 1,2,4,5-TeCB is converted to benzene via a direct transformation.

In certain circumstances, conversion of TeCB to benzene might be considered a significant improvement, because dechlorination generally renders compounds less toxic. However, benzene is a regulated contaminant. In future investigations, we will likely employ both palladium catalyst and rhodium (Rh) catalyst, because Rh is known to catalyze hydrogenation of the aromatic ring [12]. Hence, we expect that TeCB could be converted to cyclohexane, which might represent a preferable environmental endpoint.

5. Conclusions

The long-term goal of this research is to develop a new technology for cleaning soils contaminated by halogenated hydrophobic organic compounds (HHOCs). The proposed technology is called remedial extraction and catalytic hydrodehalogenation, or REACH. Towards that goal, we have investigated the Pd-catalyzed HDH of a selected target contaminant, 1,2,4,5-tetrachlorobenzene (TeCB), in mixtures of water and ethanol.

The goals of this investigation were (1) to assess the potential for hydrodechlorination of the target contaminant, (2) to determine the effect of the solvent composition (i.e., the water:ethanol ratio), and (3) to develop a model for the kinetics of the dehalogenation process. These goals were accomplished through a series of experiments conducted in a batch reactor.

We found that TeCB can be completely dehalogenated at room temperature under mild hydrogen pressure (0.21 MPa). Therefore, we believe that the proposed REACH technology may be technically and economically feasible for treatment of soils contaminated by HHOCs. Other significant findings of this study are:

- The rate of hydrodehalogenation depends strongly on the solvent composition, decreasing as the ethanol fraction of the solvent increases.
- The HDH rate increases as the catalyst concentration in the reactor increases.
- When enough catalyst is present, the HDH reaction appears to follow first-order kinetics, but the kinetics appear to be zero-order at low catalyst concentrations.

These experimental results are all consistent with a Langmuir–Hinshelwood model for heterogeneous catalysis, which we have developed herein.

TeCB was converted stoichiometrically to benzene by the Pd-catalyzed HDH reaction. We observed low concentrations of a transient intermediate, 1,2,4-trichlorobenzene (TCB). The

disappearance of TCB was rapid enough that we may consider TeCB is converted directly to benzene. Future work will involve the use of both Pd catalysts and Rh catalysts to convert the benzene to cyclohexane, which is less toxic than benzene.

Overall, the findings of this study are important towards the full development of the proposed REACH process. These findings may also be useful to the treatment of other liquid waste streams containing TeCB or other halogenated hydrophobic organic contaminants.

Acknowledgements

References

[1] National Research Council, Alternatives for Ground Water Cleanup, National Academy Press, Washington, DC, 1994.

[2] U.S. Environmental Protection Agency, Common Chemicals Found at Superfund Sites, http://www.epa.gov/superfund/resources/chemicals.htm, updated March 1, 2006.

[3] G.E. Speitel, F.B. Closmann, Chlorinated solvent biodegradation by methanotrophs in unsaturated soils, J. Environ. Eng. ASCE 117 (1991) 541–548.

[4] K. Tuppurainen, I. Halonen, P. Ruokojarvi, J. Tarhanen, J. Ruuskanen, Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review, Chemosphere 36 (1998) 1493–1511.

[5] U.S. Environmental Protection Agency, A Citizen's Guide to Solvent Extraction, Publication EPA-542-F-01-009, 2001.

[6] T.N. Kalnes, R.B. James, Hydrogenation and recycle of organic waste streams, Environ. Progr. 7 (1988) 185–191.

[7] F. Gioia, Detoxification of organic waste liquids by catalytic hydrogenation, J. Hazard. Mater. 26 (1991) 243–260.

[8] S. Kovenklioglu, Z. Cao, D. Shah, R.J. Farrauto, E.N. Balko, Direct catalytic hydrodechlorination of toxic organics in wastewater, AIChE J. 38 (1992) 1003–1012.

[9] F. Alonso, I.P. Beletskaya, M. Yus, Metal-mediated reductive hydrodehalogenation of organic halides, Chem. Rev. 102 (2002) 4009–4091.

[10] E.N. Balko, E. Przybylski, F. von Trentini, Exhaustive liquid-phase catalytic hydrodehalogenation of chlorobenzenes, Appl. Catal. B 2 (1993) 1–8.

[11] F.J. Urbano, J.M. Marinas, Hydrogenolysis of organohalogen compounds over palladium supported catalysts, J. Mol. Catal. A 173 (2001) 329–345.

[12] B. Coq, G. Ferrat, F. Figueras, Conversion of chlorobenzene over palladium and rhodium catalysts of widely varying dispersion, J. Catal. 101 (1986) 434–445.

[13] C. Schuth, M. Reinhard, Hydrodechlorination and hydrogenation of aromatic compounds over palladium-on-alumina in hydrogen-saturated water, Appl. Catal. B 18 (1998) 215–221.

[14] C. Schuth, S. Disser, F. Schuth, M. Reinhard, Tailoring catalysts for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater, Appl. Catal. B 28 (2000) 147–152.

[15] F. Murena, F. Gioia, Catalytic hydrotreatment of water contaminated by chlorinated aromatics, Catal. Today 75 (2002) 57–61.

[16] D. Fritsch, K. Kuhr, K. Mackenzie, F.-D. Kopinke, Hydrodechlorination of chloroorganic compounds in ground water by palladium catalysts. Part 1. Development of polymer-based catalyst and membrane reactor tests, Catal. Today 82 (2003) 105–118.

[17] J.B. Hoke, G.A. Gramiccioni, E.N. Balko, Catalytic hydrodechlorination of chlorophenols, Appl. Catal. B 1 (1992) 285–296.

[18] V. Felis, P. Fouilloux, C. De Bellefon, D. Schweich, Three-step catalytic detoxification process of wastewater containing chlorinated aromatic compounds: experimental results and modeling issues, Ind. Eng. Chem. Res. 38 (1999) 4213–4219.

[19] G. Yuan, M.A. Keane, Liquid-phase catalytic hydrodechlorination of 2,4-dichlorophenol over carbon-supported palladium: evaluation of transport limitations, Chem. Eng. Sci. 58 (2003) 257–267.

[20] Y. Ukisu, S. Iimura, R. Uchida, Catalytic dechlorination of polychlorinated biphenyls with carbon-supported noble metal catalysts under mild conditions, Chemosphere 33 (1996) 1523–1530.

[21] P. Forni, L. Prati, M. Rossi, Catalytic dehydrohalogenation of polychlorinated bipheyls. Part II. Studies on a continuous process, Appl. Catal. B 14 (1997) 49–53.

[22] Y. Noma, M. Ohno, S. Sakai, Pathways for the degradation of PCBs by palladium-catalyzed dechlorination, Fres. Environ. Bull. 12 (2003) 302–308.

[23] A.P. Khodadoust, M.T. Suidan, C.M. Acheson, R.C. Brenner, Solvent extraction of pentachlorophenol from contaminated soils using water–ethanol mixtures, Chemosphere 38 (1999) 2681–2693.

[24] J.W. Jawitz, R.K. Sillan, M.D. Annable, P.S.C. Rao, K. Warner, In-situ alcohol flushing of a DNAPL source zone at a dry cleaner site, Environ. Sci. Technol. 34 (2000) 3722–3729.

[25] N.E. Korte, O.R. West, L. Liang, B. Gu, J.L. Zutman, Q. Fernando, The effect of solvent concentration on the use of palladized-iron for the stepwise dechlorination of polychlorinated biphenyls in soil extracts, Waste Manag. 22 (2002) 343–349.

[26] U.S. Environmental Protection Agency, Priority Chemicals and Fact Sheets, http://www.epa.gov/epaoswer/hazwaste/minimize/chemlist.htm, Last updated on June 28, 2006.

[27] G.V. Lowry, M. Reinhard, Hydrodehalogenation of 1- to 3-carbon halogenated organic compounds (HOCs) in water using a palladium catalyst and hydrogen gas, Environ. Sci. Technol. 33 (1999) 1905–1910.

[28] U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods—SW846, third ed., Rev. 2, U.S. Government Printing Office, Washington, DC, 1996.

[29] H.S. Fogler, Elements of Chemical Reaction Engineering, 3rd ed., Prentice-Hall Inc., Upper Saddle River, NJ, 1999.

[30] C.J. Clark, P.S.C. Rao, M.D. Annable, Degradation of perchloroethylene in cosolvent solutions by zero-valent iron, J. Hazard. Mater. 96 (2003) 65–78.