Published in final edited form as:

J Hazard Mater. 2009 August 15; 167(0): 770–776. doi:10.1016/j.jhazmat.2009.01.059.

Thermocatalytic Destruction of Gas-Phase Perchloroethylene Using Propane as a Hydrogen Source

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Abstract

The use of propane in combination with oxygen to promote the destruction of perchloroethylene (PCE) over a platinum (Pt)/rhodium (Rh) catalyst on a cerium/zirconium oxide washcoat supported on an alumina monolith was explored. Conversions of PCE were measured in a continuous flow reactor with residence times less than 0.5 s and temperatures ranging from 200 to 600°C. The presence of propane was shown to increase significantly the conversion of PCE over oxygen-only conditions. Conversions close to 100% were observed at temperatures lower than 450°C with 20% oxygen and 2% propane in the feed, which makes this process attractive from a practical standpoint. In the absence of oxygen, PCE conversion is even higher, but the catalyst suffers significant deactivation in less than an hour. Even though results show that oxygen competes with reactants for active sites on the catalyst, the long-term stability that oxygen confers to the catalyst makes the process an efficient alternative to PCE oxidation. A Langmuir-Hinshelwood competitive adsorption model is proposed to quantify PCE conversion.

Keywords

PCE destruction; Catalytic dechlorination; Redox conditions; Reduction; Oxidation

1. Introduction

While perchloroethylene (PCE) has long proven to be a useful solvent for many applications, its widespread use has resulted in the compound being found at thousands of contaminated sites throughout the United States, often in conjunction with trichloroethylene (TCE). According to the Department of Health and Human Services, both of these compounds are suspected carcinogens [1], while a recent study [2] indicates that PCE is the most frequently detected solvent in ground water at concentrations above the maximum contaminant levels (MCL, 5 µg/L) [3]. For this reason, substantial efforts have been made towards the remediation of ground water and soil contaminated with halogenated organic solvents.

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Removal of the solvents from soils through soil vapor extraction (SVE), followed by treatment with activated carbon, is a widely used technology in remediation efforts [4], but suffers from a major shortcoming in that it is a non-destructive technology that simply transfers contaminants to a different phase. An environmentally-sound alternative is the thermocatalytic destruction over metal catalysts, provided that the reactions convert the chlorinated compounds into harmless products. A variety of metals has been studied for the catalysis of halogenated solvents under oxidizing or reducing conditions. The method and catalyst of choice depends on the nature of the carbon-halogen and carbon-carbon bonds in the target molecule [5]. Our group recently described the conversion of PCE on three-way Pt/Rh catalysts under mixed reducing and oxidizing conditions [6]. A gas stream of H₂, O₂ and PCE was treated at moderate temperatures (<475°C), resulting in near complete destruction of PCE with residence times less than 1 s. No other chlorinated compounds were obtained as products, and the catalyst was stable during long-term operation. Utilization of H₂, however, affects the economic competitiveness of the process due to the relative high costs of hydrogen, as compared with other possible hydrogen sources.

Alternative sources of hydrogen such as hydrocarbons and water also may promote the conversion of chlorinated volatile organic compounds (CVOCs). Water, hexane and toluene may aid catalytic CVOC destruction [7]; decane and hexane enhance the catalytic destruction of chlorobenzene [8]; and hexane, toluene, ethanol and acetone promote TCE conversion [9]. In each case, enhanced process kinetics was attributed to HCl formation, which liberated sites on the catalytic surface. Although the addition of steam is generally beneficial, it was concluded that hydrocarbons can be better hydrogen sources [8]. Unsaturated hydrocarbons enhance catalytic destruction of CVOCs more than saturated hydrocarbons, as noted by Musialik-Piotrowska [9]. Hydrocarbons containing at least one double bond are better adsorbed on the catalyst surface [10, 11]. Vesper et al. [11] described a reactivity order of propane > i-butane > ethane > methane among the saturated hydrocarbons, while ethylene was a better promoter of CVOC destruction than propylene. Heptane, decane, butane, methane and toluene were shown to initiate the destruction of CVOCs on a variety of catalysts [7, 9].

To better understand the effectiveness of hydrocarbons in the destruction of CVOCs, it is important to consider the oxidation of hydrocarbons using a noble metal catalyst such as the Pt/Rh mixture in three-way catalysts. The combustion of propane over a three-way catalyst is among the reactions used to model the destruction of unburned hydrocarbons in automobile exhaust gases by a catalytic converter. Bennett et al. [12] reported that the catalytic combustion of propane follows pseudo first-order kinetics in the reaction-controlled kinetic regime, while Lee and Aris [13] showed that the conversion of propane followed a Langmuir adsorption model with competition between oxygen and propane for active sites. At high oxygen concentrations, the surface can be saturated with oxygen [10, 11, 14]. Cerium and zirconium oxides have often been added to three-way catalysts to increase oxygen storage capacity [15].

Conversion of hydrocarbons often increases sharply as a function of catalyst temperature. The steep part of the curve conversion vs. temperature represents an ignition or light-off point, which is often defined as the catalyst temperature at which 50% of the reactant is converted. The ignition temperature decreases with increasing hydrocarbon chain length and fuel-to-oxygen ratio and lower noble metal-oxygen bond energy [10, 11, 16-19]. The chain length of the hydrocarbon governs both C-H bond strength and affinity for the catalytic surface. For alkanes, C-H bond dissociation energy and activation energy in combustion reactions decrease with chain length.

Hydrocarbon affinity for the catalytic surface is a function of chemical species and catalyst type, as well as pressure and temperature. Hydrocarbon chain length is positively correlated to the heat of adsorption [11, 14, 20]. Furthermore, unsaturated hydrocarbons are more readily oxidized than saturated hydrocarbons due to greater affinity for the catalyst surface and an ability to donate an electron from their double bond [10, 11, 18].

The lower explosive limit (LEL) is the smallest amount of fuel that may be present in the gas to yield an explosion. The fuel-to-oxygen ratio needed for auto thermal (catalytic) oxidation is similar in concept. The fuel concentration can also be too high, leading to incomplete oxidation, product deposition on the catalyst surface and catalyst poisoning. The hydrocarbon-to-oxygen ratio needed for auto thermal oxidation over a noble metal catalyst is lower than the LEL. When the fuel-to-oxygen ratio provides an oxidizing environment, the combustion of propane and other hydrocarbons yields carbon dioxide and water [21]. Under such conditions, hydrocarbon oxidation proceeds primarily via reaction with hydroxyl ($\text{HO}\cdot$) and superoxide ($\text{HO}_2\cdot$) radicals. Radicals are produced via direct reaction of adsorbed propane with adsorbed oxygen or from the dissociation of water molecules. Under net reducing conditions, oxygen is consumed before the hydrocarbon is exhausted. In the absence of molecular oxygen, water reacts with uncombusted hydrocarbons and carbon monoxide. These water reactions are steam reforming (slow reaction) and the water gas shift (fast reaction). Gas-phase oxygen prevents water from reacting in this manner [22]. Both water reactions result in hydrogen production, typically at catalyst temperatures greater than 400 °C [23]. It follows that the amount of hydrogen produced is related to the hydrocarbon-to-oxygen ratio. That is, the amount of hydrogen produced is directly related to excess hydrocarbon above that required for consumption of molecular oxygen [22].

The catalytic destruction of hydrocarbons is usually hindered by the presence of CVOCs due to competition for active sites between hydrocarbon, CVOC and oxygen. The inhibition is directly related to the number of chlorine atoms as opposed to other aspects of CVOC structure [9], since the C-Cl bond has a lower bond dissociation energy than the C-H bond.

This work focuses on the use of propane in the destruction of PCE under mixed redox conditions over an alumina-supported Pt/Rh catalyst. In our previous work [6], hydrogen gas was effective as the reducing agent. However, the catalytic system described is envisioned as an alternative to current remediation technologies, and hydrogen could prove to be prohibitively expensive in full-scale remediation efforts. Preliminary data have shown that PCE conversion increases with increasing alkane chain length for methane through n-butane (Figure 1). Here, conversion is defined by

$$\% \text{Conversion} = 100 \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}} \right) \quad (1)$$

where C_{in} and C_{out} are inlet and outlet concentrations of the target compound, respectively (PCE in this case). Even though n-butane performs better than propane, the lower cost and wider availability of the latter makes it more attractive from a practical standpoint. Independent variables investigated in order to establish process feasibility are catalyst temperature and influent reactant concentrations (PCE, propane and oxygen). Kinetic reaction models are explored in an attempt to develop mechanistic understanding of the process.

2. Experimental

2.1 Catalyst

The catalyst is a commercial Pt/Rh three-way catalyst, used in automobile catalytic converters. Catalyst monoliths (2.54 cm OD $\times$ 2.54 cm length cylinder) were cut from an 820 cm³ catalyst honeycomb block. The Pt/Rh ratio is 3:1 wt/wt, deposited on a support comprised of cordierite (90%) and a washcoat (10%) containing cerium and zirconium oxides, and other trace constituents. A scanning electron microscope image of the catalytic surface can be seen in Figure 2. Elemental analysis was obtained using an energy dispersive spectroscopy (EDS) detector. The analysis shows that the dark areas in Figure 2 are alumina and the light areas are the cerium and zirconium oxide washcoat containing the Pt/Rh catalyst. The figure shows that the washcoat is uniformly distributed over the alumina surface, with a wide particle size distribution, including particles reaching a few microns in size: some of the particles in Figure 2 reach about 10 μ m. The honeycomb monolith contains 0.185 mg total metal/cm³ with a cell density of 62 cells/cm². Each cell has a cross section of dimensions 1 mm $\times$ 1 mm. The catalyst total and void volumes are 12.87 cm³ and 9.36 cm³, respectively. The void volume was determined by immersion of a blank catalyst monolith in heptane. The commercially available (Applied Ceramics, Inc., Doraville, Georgia) unamended alumina support, the monolithic honeycomb, exhibited little reactivity: a standard experiment with 1% propane and 250 ppmv PCE in air at 1 L/min yielded <5% PCE conversion over the temperature range 425 to 650 $^{\circ}$ C.

2.2 Reactor System

Experiments were carried out in a tubular reactor. The reactor is a 50 cm (long) by 2.54 cm (inner diameter) quartz tube (ACE Glassware), containing the 2.54 cm $\times$ 2.54 cm cylindrical catalyst monolith. The tubular reactor is housed in a single-zone tube furnace (Thermolyne 21100), aligned at a 45 $^{\circ}$ angle, and equipped with temperature control. The length of the furnace is 38 cm. The honeycomb is located inside the reactor tube, approximately 20 cm from the upstream end of the furnace. This allows the flowing gas stream to reach the furnace temperature before entering the honeycomb structure. Temperature is measured in two places using thermocouples: a K-type thermocouple (Omega Engineering) is placed at the center of the inlet face of the honeycomb (the thermocouple is directly in contact with the solid surface of the honeycomb) and a Type Platinel II thermocouple is located at the furnace inner wall above the honeycomb (set point for temperature control). Independent measurements verified that the gas temperature at the entrance of the honeycomb block was approximately equal to the furnace temperature at the operating conditions employed in this work and that the temperature of the gas at the exit of the honeycomb was equal to the entrance gas temperature, which means that the reactor operates isothermally in all cases.

In a typical experiment, a well-mixed gas stream consisting of propane, O₂, N₂, and PCE was fed to the reactor. Propane (99.9% Airgas), oxygen (99.9%, Air Liquide) and nitrogen (99.99%, The University of Arizona Cryogenics & Gas Facility) were used as obtained. Flows were regulated using Aalborg (Orangeburg, New York) mass flow controllers. Liquid PCE (Aldrich, 99.9+%) was placed in a U-tube located in a temperature-regulated water bath (4 $^{\circ}$ C). Nitrogen was passed over the surface of the PCE, entraining the vapor phase, which was then mixed with propane, O₂ and N₂ at experiment-dependent ratios. The total flow rate was 1 L/min at room temperature, and concentrations of PCE were <600 ppmv. Residence times in the reactor ranged from 0.6 s (catalyst at room temperature) to less than 0.2 s (catalyst at 400 $^{\circ}$ C and above). Breathable air (The University of Arizona Cryogenics Facility, 21% O₂, 78% N₂, 1% Ar) was substituted for nitrogen and oxygen when experimental objectives permitted.

2.3 Analytical

An HP 5890 gas chromatograph equipped with a flame ionization detector (FID) was used to analyze the influent and effluent streams. Gas samples were injected into the GC using Hamilton gas-tight syringes. A 0.53-mm wide-bore capillary column (J&W DB-624, 30 m $\times$ 0.53 mm $\times$ 3.0 mm) was used to measure hydrocarbons and chlorinated hydrocarbons. The temperatures of the injector and the detector were typically 200 °C and 250 °C, respectively.

2.4 Experiments

To begin a typical experiment, the catalyst temperature was adjusted to 350°C under N₂ and O₂. Propane was always added after oxygen to avoid coke deposition on the catalyst surface. At that point, PCE was added into the system, and the temperature was gradually ramped across the temperature range of the experiment. Inlet and outlet concentrations of propane and/or PCE were measured every 20 to 25°C (the inlet concentration was constant throughout all experiments reported.) At high propane concentrations, the temperature sometimes increased rapidly due to propane “light-off”. When this occurred, inlet and outlet samples were taken as frequently as possible. After every 40 hours of operation, the catalyst was cleaned for 8 hours under 2% O₂ in N₂ (1 L/min) at 500 °C. Temperature changes along the temperature ramp occurred after steady state was reached so that each measurement in a typical conversion vs. temperature experiment corresponds to a steady state conditions. More details about verification of steady state are given elsewhere [6].

3. Results and Discussion

3.1 Advantages of Mixed Redox Conditions

The advantages of mixed redox conditions relative to strictly oxidative or reductive conditions for conversion of gas-phase chlorinated solvents were investigated in a previous work [6]. Briefly, purely reductive conditions (H₂ in the feed) induced initially relatively high conversions of PCE, but rapid deactivation of the catalyst occurred. On the other hand, purely oxidative conditions led to poor PCE conversion levels below 450°C (e.g. oxygen-only curve in Figure 1.) Figure 1 illustrates the ability of propane to promote conversion of PCE over oxygen only conditions. At temperatures above 400°C, the addition of 2% propane to the influent gas stream consisting of 200 ppmv PCE in air greatly enhanced the conversion of PCE. The conditions correspond to excess oxygen for propane oxidation (stoichiometric ratio 5:1 oxygen:propane). Similar experiments, with H₂ gas as the hydrogen source instead of propane, resulted in complete conversion of PCE in the same temperature range [6].

Propane and PCE conversions are presented as a function of time at a constant catalyst surface temperature of 425°C in Figure 3. The experiment was initiated under mixed redox conditions (20% O₂, 1% propane). Conversion of PCE was steady at 25%, and propane conversion was 10% for the first 20 minutes of operation. These conversion levels can be maintained for several hours without change (results not shown). After 20 minutes, the oxygen stream was eliminated, creating reducing conditions within the reactor. PCE conversion rose immediately to more than 95%, suggesting that oxygen presence interferes with propane and/or PCE adsorption on catalytic sites. However, deactivation of the catalyst started almost immediately, decreasing the PCE conversion to <10% after additional 60 minutes. Similar observations were obtained in a previous work using H₂ as reductant [6]. The results indicate that, even though oxygen adsorption reduces reaction rates for PCE destruction, it protects the catalyst from deactivation. In a pilot scale study [24], complete PCE and TCE destruction from an SVE gas over the same catalyst and in the presence of oxygen and propane were maintained for almost 240 days without catalyst deactivation.

Analysis of the effluent in experiments using oxygen and propane reveals that the only chlorinated organic present in the products is remaining PCE; that is, no chlorinated methanes, ethanes or ethenes were detected in the whole range of temperatures and concentrations used here. In addition, measurement of chloride ion in the product using ion chromatography, after bubbling the effluent through an alkaline aqueous solution, showed that the amount of chloride ions produced was consistent with the chlorines liberated by the PCE destroyed. This suggests that the main route for PCE destruction was reductive dehalogenation.

3.2 Propane and Oxygen Effects

Figure 4 shows temperature-dependent PCE conversions at 10% and 20% influent O₂ and influent propane contents ranging from 0.25% to 2.0%. At 10% O₂ (Figure 4a), PCE conversion is approximately independent of propane concentration at the lower propane contents (0.25% and 0.5%), but increases when the propane content is 1.0%. At 20% O₂ (Figure 4b), PCE conversion remains independent of propane content at 0.5% and 1% propane levels, but again increases when the propane content reaches 2.0%. There is consistency between results at the two influent oxygen contents in that PCE conversions are < 40% at 450°C when the influent O₂/C₃H₈ ratio is above 10 v/v. Similar levels of conversion were reported previously under oxygen-only conditions on the same catalyst [6].

The trends observed suggest the possibility of different reaction regimes. At relatively high oxygen-to-propane ratios, it appears that catalytic oxidation of PCE dominates. The second regime, at lower ratios, occurs when catalytic reduction initiates the bulk of the conversion. It would be convenient to assign a cutoff point for regime transition, but the transition point depends on oxygen concentration. At 5% O₂ (data not shown), the reaction regime change happened at a 5:1 O₂/C₃H₈ ratio, while at 10% and 20% O₂, it occurred at 10:1. It is clear that, while the relative amount of propane in the system affects conversion, the absolute concentration also plays a role. To verify these observations, experiments were performed at 1% propane and oxygen contents that varied from 20% to 1% (Figure 5). The data indicate that maximum conversion of PCE is achieved at an O₂/C₃H₈ ratio of around 5, which coincides with the stoichiometric ratio for complete oxidation of propane. Conversion of PCE drops in the reducing regime, O₂/C₃H₈ < 5, which might be a consequence of catalyst deactivation. Each data point represents an average conversion over approximately 40 minutes of operation. The large error bars in the reducing regime are a result of steadily decreasing conversions, confirming that deactivation begins to occur within this time frame. It is also evident that propane continues to promote the conversion of PCE at high concentrations of oxygen, since only 15% conversion was observed in the absence of a gas phase reductant.

Figure 4b has implications for remediation system design, since the influent O₂ concentration (20%) is close to atmospheric conditions at many sites where soil-vapor extraction is the selected remediation technology. These results suggest that 2% propane addition might be good enough under many field conditions. As mentioned above, an SVE pilot study in which the SVE gas contained PCE, TCE and DCE, as well as diesel and water, yielded complete conversion of the chlorinated compounds for 240 days of operation, using 2% propane [24].

The conversion of propane offers insights into the reaction mechanism and competition among gas-phase species for surface sites. Propane conversion is provided as a function of catalyst surface temperature and the influent propane content for influent O₂ contents of 10 and 20% in Figure 6. Propane conversion is lower than PCE conversion (compare with Figure 4). In most cases, there is <50% propane conversion at 500°C. Exceptions to this general observation occurred at 10% O₂/1% propane and 20% O₂/2% propane, both at a

10:1 O₂/C₃H₈ ratio, for which propane conversion was much greater than 50%. PCE conversion under those conditions was also nearly complete. A comparison of Figures 6a and 6b reveals that, at low propane contents for the conditions shown, oxygen content does not seem to affect propane conversion significantly, although the departure from the low propane content behavior occurs at lower propane content when the oxygen level decreases.

The fact that propane conversion increases with propane content is not consistent with a first-order apparent kinetics for propane consumption except at low propane contents (see section 3.4). In addition, a full Langmuir-Hinshelwood model accounting for competition for the same sites from propane and oxygen would not explain the observation. In previous studies, kinetic orders with respect to propane in propane oxidation have been reported to be greater than one, using similar catalysts [21,25], a fact that is consistent with the results presented here. The slow step for alkane oxidation has been postulated to be the dissociative chemisorption of the alkane on the catalyst surface, induced by the breakage of the weakest C-H bond [21]. Since propane occupies several active sites on the surface of the catalyst, and its dissociation liberates hydrogen, this process might lead to a higher apparent reaction order, as shown by calculations reported by Frennet et al. [26]. An increase in the rate of adsorption/dissociation of propane with propane concentration also explains the increase in PCE conversion with propane content: it is likely that PCE follows a reductive dehalogenation path reacting with the hydrogen produced on the surface by the dissociation of propane.

3.3 PCE Concentration Effects

Conversion of PCE decreases significantly as the influent PCE content increases, in the temperature range 350-500°C (Figure 7). The dependence of conversion on influent concentration was strongest at 350°C and influent PCE contents in the range 50-200 ppmv. Clearly, PCE transformation kinetics are not first order in PCE concentration, and the functional dependence that is evident suggests that surface saturation effects are possible, particularly at the low catalyst temperatures in these experiments (see below).

3.4 Modeling

3.4.1 Propane Oxidation Model—It is known that oxygen sorption on three-way catalysts is much stronger than alkane sorption. For these reasons, reported reaction orders with respect to oxygen for alkane oxidation are usually near zero or negative [21]. In this work, oxygen and propane contents do not seem to affect propane conversion, as long as the O₂/C₃H₈ influent ratios are greater than 10 (Figure 6). We interpret this result as meaning that oxygen is so much in excess on the surface that its concentration has no impact on propane destruction kinetics. Based on these observations, we propose a simple first order kinetic model for propane consumption:

$$\frac{dC_p}{dt} = -k_p C_p \quad (2)$$

where C_p is propane concentration, t is the residence time along the reactor, and k_p is the apparent first-order reaction constant for propane consumption, which is related to temperature by the Arrhenius equation:

$$k_p = k_{p,0} \exp\left(-\frac{E_{a,p}}{RT}\right) \quad (3)$$

where $E_{a,p}$ is the apparent activation energy. Equation (2) assumes that the reactor behaves as a plug flow reactor. In addition, we will consider that the temperature is uniform along the reactor (which was verified experimentally), and that propane consumption is kinetically controlled (i.e. there are no mass transfer limitations.) The assumption of first-order kinetics for propane conversion breaks down as the ratio of oxygen to propane becomes equal to 10 (Figure 6), where a clear effect of propane concentration on conversion is seen. Therefore, the previous equations are only applicable to conditions in which oxygen is clearly in excess with respect to propane. A more detail discussion on the validity of these assumptions is reported in a previous work [6]. Integration of equation (2) yields

$$C_{p,out} = C_{p,in} \exp(-k_p \theta) \quad (4)$$

where θ is the residence time in the reactor at the reaction temperature. Since we have kept constant the volumetric flow rate of inlet gas measured at room temperature ($T_a = 298$ K) (and thus the residence time measured at room temperature, θ_a), the ideal gas equation yields the following expression for the residence time:

$$\theta = \frac{T_a}{T} \theta_a \quad (5)$$

Values of k_p were obtained from the experimental data in Figure 6 for $O_2/C_3H_8 > 10$, as a function of catalyst temperature. The results are shown as an Arrhenius plot in Figure 8. Predicted propane conversions vs. temperature are shown in Figure 6.

3.4.2 PCE Conversion Model—The drop in PCE conversion with PCE content (Figure 7) suggests that surface sites available for PCE decrease with PCE concentration in the range explored in this work. In addition, PCE conversion increases with propane content for $O_2/C_3H_8 < 10$. At high oxygen-to-propane ratios and the conditions explored here (Figure 4), PCE conversion is approximately independent of both oxygen and propane content. For this specific regime, we postulate that PCE reacts according to a Langmuir-Hinshelwood kinetic expression, which assumes that adsorption of PCE is fast enough to be an equilibrium process, and reaction of PCE on the surface is first order in PCE concentration. In this case, the rate of consumption of PCE can be expressed as

$$\frac{dC_c}{dt} = - \frac{k_c C_c}{K_c + C_c} \quad (6)$$

where k_c is the maximum apparent rate constant for PCE destruction (i.e., it is the rate constant when PCE has saturated the surface,) and K_c is the equilibrium constant for PCE desorption. Details on the derivation of equation (6) can be found elsewhere (e.g. [27]).

Integration of equation (6) leads to

$$K_c \ln \frac{C_{c,out}}{C_{c,in}} + C_{c,out} - C_{c,in} = -k_c \theta \quad (7)$$

where C_c is PCE concentration. The apparent rate constant is represented by an Arrhenius equation,

$$k_c = k_{c,0} \exp\left(-\frac{E_{a,C}}{RT}\right) \quad (8)$$

Similarly, the desorption constant is related to temperature by

$$K_C = K_{C,0} \exp\left(\frac{-\Delta H_r}{RT}\right) \quad (9)$$

where ΔH_r is the molar enthalpy of desorption. The concentrations in equation (7) must be evaluated at the reaction's temperature, using the ideal gas law:

$$C_c = \frac{P}{RT} y_c \quad (10)$$

where $P=1$ atm, and y_C is the mole fraction of PCE.

The kinetic model for PCE transformation contains four fitting parameters ($K_{C,0}$, ΔH_r , $E_{a,C}$, and $k_{c,0}$). These parameters were obtained by fitting the experimental data presented in Figure 7, which are within the regime $O_2/C_3H_8 > 10$. The fitting procedure consisted of finding values of K_C and k_c for each temperature by fitting equation (7) to the data (solid lines in Figure 7), and then fitting equations (8) and (9) to find the four fitting parameters. The values obtained were: $K_{C,0} = 4.99 \times 10^{-3}$ mol/L, $\Delta H_r = 52.5$ kJ/mol, $E_{a,C} = 65.4$ kJ/mol, $k_{c,0} = 0.691$ mol/L s. Afterwards, equation (7) was used to generate the predictions shown in Figure 4. Note that the predictions are adequate, but the data seem to change more rapidly with temperature.

The main purpose for the application of the model developed here was to show that a Langmuir-Hinshelwood model can account for the dependence of PCE conversion of PCE inlet concentration. However, in the whole range of data presented in this work, it is evident that propane affects PCE conversion at low O_2/C_3H_8 ratios. In addition, oxygen eventually may inhibit PCE conversion, as evidenced by the low PCE conversions for the oxygen only curve in Figure 1. No attempts were made to extend the model to these conditions, due to the large number of fitting parameters that would be generated.

4. Conclusion

Propane is effective at promoting the conversion of PCE on alumina-supported Pt/Rh catalysts under mixed redox conditions, providing high conversions at moderate temperatures ($< 600^\circ\text{C}$) and short residence times (0.5 s), as well as long-term catalyst stability. Results presented in this work show that 2% propane can achieve high conversions of PCE without the presence of measurable side products in a stream containing 20% oxygen. This suggests that this system could prove to be an effective alternative to current remediation technologies of soil vapor extraction gases.

Acknowledgments

The work described here is supported by grant number P42 ES04940 from the National Institute of Environmental Health Sciences (NIEHS), National Institutes of Health (NIH). The views of authors do not necessarily represent those of the NIEHS, NIH. The authors are grateful to Mr. Jilei Shan for his help with SEM/EDS analysis.

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Figure 1.

PCE conversion in the presence of O_2 (21%, Δ), and mixtures of O_2 (21%) with CH_4 (5%, $\bullet$), C_2H_6 (3%, $\blacksquare$), C_3H_8 (2%, $\blacklozenge$) and $n\text{-}C_4H_{10}$ (1.5%, $\circ$). The PCE content in the influent was within the range of 175 – 200 ppmv. Flow rate: 1.0 L/min (room temperature residence time: 0.5 s). The carrier gas was N_2 . Dots are experimental data, while solid lines are results of a first-order kinetic model in which the activation energy is a linear function of C-H bond dissociation energy [24]. The reactor and other conditions used in these experiments are the same as those described in this work. *Pending reprint permit from the New York Academy of Sciences.*

Figure 2. Scanning electron microscopy image of the Pt/Rh catalyst surface. Dark gray areas are the alumina support while light gray areas represent the washcoat. At this scale of magnification, other areas of the catalyst surface looked similar.

Figure 3. PCE (◆) and propane (□) conversions as functions of time for a constant catalyst surface temperature of 425 °C. The influent PCE content was 250 ppmv. The influent O₂ and propane contents were 20% and 1%, respectively. After 20 minutes, O₂ was turned off. The total gas flow rate was 1.0 L/min (0.5 s residence time) at 25 °C.

Figure 4.

PCE conversion as a function of catalyst surface temperature for (a) 10% O₂, (b) 20% O₂. The PCE content in the influent was 500 ppmv. The total gas flow rate was 1.0 L/min (0.5 s residence time) at 25 °C. Legend: (◆) 0.25% propane; (□) 0.5% propane; (▲) 1.0% propane; (○) 2.0% propane. Lines are model results (section 3.4).

Figure 5. PCE (◆) and propane (□) conversions as functions of the influent O₂/C₃H₈ ratio. The catalyst surface temperature was 440°C, and the influent PCE content was 500 ppmv. The influent propane content was 1%, and the total gas flow rate 1.0 L/min at 25 °C. Error bars represent plus and minus one standard deviation.

Figure 6.

Propane conversion as a function of catalyst surface temperature for (a) 10% O₂, (b) 20% O₂. The influent PCE content was 500 ppmv and the total gas flow rate was 1.0 L/min at 25 °C. Legend: (◆) 0.25% propane; (□) 0.5% propane; (▲) 1.0% propane; (○) 2.0% propane. Lines are model results (section 3.4).

Figure 7.

PCE conversion as a function of the inlet PCE contents and catalyst surface temperature. The influent oxygen and propane contents were 20% and 1%. The total gas flow rate was 1.0 L/min at 25 °C. Legend (catalyst surface temperature): (◆) 350 °C; (□) 425 °C; (▲) 500 °C. Lines are model results (section 3.4).

Figure 8.

Arrhenius plot for the data in Figure 7 with $\text{O}_2/\text{C}_3\text{H}_8 > 10$. The PCE content in the influent stream is 500 ppmv, and the total gas flow rate is 1.0 L/min at 25 °C. The line shown gives values for the Arrhenius parameters of $k_{p,0}=4.9\times 10^8 \text{ s}^{-1}$ and $E_{a,p}=127 \text{ kJ/mol}$.