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Catalytic dechlorination of gas-phase perchloroethylene under mixed redox conditions

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Abstract

The validity of a new method to destroy gas-phase perchloroethylene (PCE) is demonstrated at bench scale using a fixed-bed reactor that contains a Pt/Rh catalyst. Hydrogen and oxygen were simultaneously fed to the reactor together with PCE. The conversion efficiencies of PCE were sensitive to H_2/O_2 ratio and reactor temperature. When the temperature was $\geq 400\ ^{\circ}C$ and H_2/O_2 was ≥ 2.15, PCE conversion efficiency was maintained at $\geq 90\%$. No catalyst deactivation was observed for over 2 years, using only mild, convenient regeneration procedures. It is likely that PCE reduction steps precede oxidation reactions and that the importance of oxidation lies in its elimination of intermediates that would otherwise lead to catalyst poisoning. In practice, this catalytic dechlorination method holds potential for low-cost, large-scale field operation.

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

1. Introduction

Acyclic, short-chain halogenated organics are useful solvents, the principal representatives being tetrachloroethylene (PCE), trichloroethylene (TCE) and methylene chloride. Because of their widespread use such as in dry cleaning and metal degreasing, chlorinated compounds are found at thousands of contaminated sites in the United States. In particular, PCE and TCE are among the top 31 Priority Hazardous Substances that are determined to pose the most significant potential threat to human health by the Department of Health and Human Services (DHHS) [1,2]. A recent nationwide study [1] ranks PCE and TCE as the first and third most frequently detected solvents in ground water at concentrations greater than their respective Maximum Contaminant Levels (MCLs) [3]. The same study indicates that PCE and TCE comprise the most frequently occurring mixture of solvents in ground water. Alarmingly, both PCE and TCE are reasonably anticipated to be human and animal carcinogens according to the DHHS and several research institutions [2]. There is thus substantial interest in the development of efficient, economic methods for remediating ground water and soils contaminated with halogenated organic solvents.

At U.S. Superfund sites, incineration and solidification have been traditionally employed as remediation technologies to treat chlorinated solvents. More recently, soil vapor extraction (SVE) and pump-and-treat methods have been used at many Superfund sites [4]. However, all of these technologies can be expensive. In addition, they can lead to other environmental problems (such as air pollution in the case of incineration) or they merely separate contaminants into a different phase rather than destroy them. Abiotic transformations, such as reduction and oxidation reactions, are the most studied alternatives to separation technologies for treatment of chlorinated solvents. The method of choice depends mainly on the nature of the carbon–halogen and carbon–carbon bonds in the target molecule [5]. A variety of metals have been used to catalyze the destruction of halogenated solvents under either oxidizing or reducing condition.

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1.1. Catalytic oxidation reactions

Catalyzed oxidative dehalogenation occurs when an organochlorine compound is oxidized to CO_2 in the presence of oxygen. Upon oxidation, chlorinated VOCs yield HCl in addition to CO_2 and H_2O. Formation of incomplete oxidation products such as dioxins and furans is an important consideration due to their toxicity. In addition, formation of Cl_2 has been observed, such as in the catalytic oxidation of CH_3Cl over α-Cr_2O_3/Al_2O_3 [6] and in the oxidation of TCE and 1,1-dichloroethylene over a similar catalyst [7].

Commercially available catalysts fall into three broad categories: base metal oxides (e.g. Cu, Cr, and Mn); supported noble metal catalysts (e.g. Pt, Pd); and noble metal/metal oxide combinations [8–12]. Detailed kinetics of catalytic oxidation on noble metals is not firmly established, but may follow either a Langmuir–Hinshelwood type of mechanism (reaction between adsorbed oxygen and an adsorbed reactant) or an Eley–Rideal mechanism (reaction between adsorbed oxygen and a gas-phase reactant molecule) [13]. Platinum on various oxide supports is commonly used to catalyze oxidative dehalogenation reactions. Unfortunately, Pt is typically poisoned by chlorinated compounds, so deactivation is an important performance characteristic. Deactivation can be minimized by controlling the state and loading of Pt in the catalyst [9,14] or choosing an appropriate temperature range [15,16].

Since some chlorinated hydrocarbon molecules contain more chlorine than hydrogen atoms, some research has focused on methods for providing hydrogen in order to convert all the chlorine to hydrogen chloride (HCl) and prevent the accumulation of unwanted products [9–11,17,18]. Hexane, water and toluene [11]; methane and water [10,17]; and propane [9] have been studied as the hydrogen source. Gonzalez-Velasco et al. [11] observed that complete catalytic oxidation of TCE over alumina-supported Pt or Pd occurred at an accelerated rate in the presence of hexane or toluene. Water did not alter the catalytic activity of the Pd catalyst, while TCE oxidation on the Pt catalyst was enhanced by water vapor at low temperatures (<400 °C) but inhibited at higher ones. Production of HCl was improved for both catalysts by adding a hydrogen source. There have been several successful field applications of catalytic oxidation for the destruction of VOCs, although relatively little of this work is described in the literature [19–21].

1.2. Catalytic hydrodechlorination reactions

In catalytic hydrodechlorination, halogenated compounds are commonly reduced to corresponding hydrocarbons on a catalyst surface using H_2 as the reducing agent,

$$R{-}Cl + H_2 \xrightarrow{\text{catalyst}} R{-}H + HCl \qquad (1)$$

Table 1
Previous investigations of catalytic hydrodechlorination

Catalysts	Reactants	References
$NiMo/Al_2O_3$ (sulfided)	Chlorinated benzenes	[22]
$NiMo/Al_2O_3$ (sulfided)	Chloropyridinols	[23]
Ni/Mo-γ-alumina (sulfided)	Dichloromethane, 1,1,1-TCA, TCE, PCE	[24]
Pd/C (w/sodium hypophosphite)	1,2,4,5-Tetrachlorobenzene	[25]
Nickel loaded silica and exchanged Y-zeolite	Chlorophenols, dichlorophenols, trichlorophenols, pentachlorophenol	[26]
Pd/Al_2O_3, Rh/Al_2O_3	Chlorobenzene	[27]
Pt/C, Pd/γ-Al_2O_3	4-Chloro-2-nitrophenol	[28]
Rh/SiO_2	Dichloroethane (DCA), TCE	[29]
Pt/Al_2O_3	Dichloroethylene (DCE)	[30,31]
Pd on carbon	Chlorofluorocarbons	[32]
Pt on various support,	Carbon tetrachloride (CCl_4)	[33]
Pt/γ-Al_2O_3	Carbon tetrachloride	[34]
Pt/MgO	Carbon tetrachloride	[35]
Pd oxide on γ-Al_2O_3	1,1,2-Trichlorotrifluoroethane	[36]
Ni on Y zeolites	Carbon tetrachloride	[37]
Pd–Cu–Sn on carbon	PCE	[38]
Pt–Cu–Ag–Au on carbon	1,2-Dichloropropane	[39]
Ni on ZSM-5 and Al_2O_3	TCE and TCA	[40]
Pd on carbon	Aqueous TCE, TCA, and chlorobenzene	[41]
Pd on Al_2O_3, fluorinated Al_2O_3 and AlF_3	1,1-Dichlorotetrafluoroethane, dichlorodifluoromethane	[42]
Group VIII noble metals	Dichlorodifluoromethane	[43]
Pd, Rh, Pt, on alumina	PCE	[44]
Pd on silica	1,1,1-Trichloroethane (TCA)	[45]
$NiMo/Al_2O_3$	PCE, TCE, 1,1-dichloroethylene, *cis*-dichloroethylene and *trans*-dichloroethylene	[46]
Pd/γ-Al_2O_3	CF_2-Cl_2 (CFC-12)	[47]
Ni-Raney, Ni on SiO_2, Pd/Al_2O_3, Pt/Al_2O_3,$Pt/Rh/Al_2O_3$, Ru/Al_2O_3 and sulfided Ni–Mo on Al_2O_3	Dichloromethane, chloroform, carbon tetrachloride, 1,1,1-TCA, TCE and PCE	[48]
Pt on various alumina supports	TCA	[49]
Pt and Pd on Vycor, Al_2O_3, C, AlF_3,	Chloromethanes, chlorobenzene	[50]