Direct Catalytic Hydrodechlorination of Toxic Organics in Wastewater

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The in-situ catalytic hydrodechlorination of chlorinated hydrocarbons in wastewater-generating HCl and a hydrocarbon-free chlorine is demonstrated as a viable wastewater remediation technique. Catalyst screening studies with a shaker-type hydrogenation reactor have shown that the commercial Pd/C catalyst is highly effective in hydrodechlorinating various chlorinated hydrocarbons in synthetic wastewater at room temperature and near atmospheric pressure. 1,1,2-trichloroethane hydrodechlorination experiments in an autoclave reactor shows that initial rates are well correlated with first-order dependence of the reactant hydrocarbon adsorbed on carbon. Initial rates are also independent of hydrogen pressure, and adsorption on the carbon support is Langmuir type. Activation energies calculated at different catalyst loadings varied from 29 to 38 MJ/mol.
1,1,2-trichloroethane hydrodechlorination activity is much lower for Pd/Al_2O_3 than Pd/C because the reactant hydrocarbon does not adsorb on alumina. When the carbon support does not readily adsorb the reactant hydrocarbon, the hydrodechlorination rate dropped significantly. These results confirm the role of the carbon support in providing the major path to reaction and thereby significantly increasing reaction rates compared to direct adsorption from solution onto the palladium.

Introduction

A number of industrial processes produce wastewater-containing chlorinated hydrocarbons (CHCs) (Surprenant et al., 1985), and a wide variety of methods, such as air stripping, carbon adsorption, and biological treatments, have been used to reduce their quantity in such discharge streams (Strier, 1980; Patterson, 1985). When the treatment method is a separation technique, such as air stripping or adsorption, the recovered CHC often requires further treatment. Catalytic incineration converts the CHC to carbon dioxide, hydrogen chloride, and water (Kosusko et al., 1988; Tichenor and Palazzolo, 1977). The noble metals, supported chromia and CuO (Subbanna et al., 1988), and vanadium oxide (Jin et al., 1989) have all been used to catalyze the gas-phase oxidation of CHCs. Berty (1991) has demonstrated that by using a unique catalyst system comprising a metal or a metal oxide in combination with an alkali or an alkali-earth carbonate, or an alkali-earth oxide and hydroxide, it is possible to trap the corrosive HCl formed in the oxidation of CHCs.

Chlorinated hydrocarbons often are quite soluble in liquid organic wastes; hydrodechlorination can be a practical treatment method in such cases. In this instance, the reaction products are the halogen-free (or less halogenated) hydrocarbon and hydrogen chloride. The overall reaction may be represented as:

$$C_xH_yCl_z + zH_2 \rightarrow C_xH_{y+z} + zHCl \quad (1)$$

A recent study has shown that for organic wastes such as PCB dielectric liquids and halogenated petrochemical by-products, hydrodechlorination, recycle, and recovery are more attractive economically than direct incineration (Kalnes and James, 1988). Noble metals are used commonly as hydro-

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dechlorination catalysts in the liquid phase for organic synthesis (Rylander, 1967) and have been used for the same purpose in gas-phase work (LaPierre et al., 1978; Coq et al., 1986). Nickel-molybdenum materials are also reported to be efficient dehalogenation catalysts at elevated temperatures in the gas phase (Hagh and Allen, 1990).

Among the attempts to directly treat CHCs in wastewater are wet air oxidation where the liquid-phase oxidation takes place with oxygen supplied by compressed air at high pressures and temperatures, supercritical water oxidation and chemical oxidation processes using UV radiation and oxidants such as ozone and hydrogen peroxide (Surprenant et al., 1988). These processes use either extreme conditions or large amounts of oxidants that are expensive (Lankford et al., 1988). Direct catalytic destruction of CHCs has also been achieved. Baker et al. (1989) report treatment of aqueous streams with nickel catalyst at 350°C to 400°C and 200 to 273 bar, which converts the CHCs to innocuous products. Another *in-situ* catalytic treatment of CHCs is photochemical oxidation on a titania catalyst (Ollis, 1985; Pellezzetti and Serpone, 1986).

Despite the attention hydrodechlorination has received for treating liquid organic wastes, there are no reports of attempts to directly treat CHCs in wastewater or groundwater by *in-situ* catalytic reaction with hydrogen. Organic hydrodechlorinations, however, may be carried out in aqueous solution. In the conversion of benzyl chloride to toluene, several solvents, including water, have been used; palladium, platinum, and rhodium may be used as catalysts with palladium exhibiting the greatest activity (Rylander, 1967).

Trichloroethylene, trichloroethane, and methylene chloride are among the most common CHCs found in contaminated groundwater. Hydrodechlorination is potentially an attractive method for the single-stage remediation of such pollutants because the gaseous hydrocarbon products of the dehalogenation are innocuous at the level corresponding to complete conversion of saturated aqueous solutions of the parent CHC. Their low solubility, about 1,000 ppm (W/W), also suggests that dissolution of hydrogen, often the rate-limiting step in other concentrated liquid-phase hydrogenation processes, would be relatively unimportant in groundwater treatment.

In this article, we describe the direct dechlorination of these CHCs in aqueous solution over noble metal catalysts using shaker and stirred autoclave reactors at mild reaction conditions, that is, near atmospheric pressure and 16–55°C temperature range. Reaction kinetics, mass transfer, catalytic activity, selectivity, and the role of carrier for the noble metal are considered.

Experimental Studies

Shaker reactor

Catalyst screening work was carried out in a Parr shaker hydrogenation reactor. The reactor consisted of a 500-mL glass vessel mounted on a bottle holder and connected to a shaker mechanism equipped with a heating mantle, thermocouple assembly, temperature controller, pressure gage, and valve assembly to pressurize or evacuate the system.

For most experiments that lasted three hours or longer, 50 μL of CHC and 0.005–0.5-g powdered carbon-supported noble metal catalyst were charged to the shaker bottle containing 400 mL of deionized water followed by the evacuation of air in the headspace of the reactor. For the experiments that lasted only 10 minutes, the CHC was first dissolved in 400 mL of deionized water by continuous agitation for an hour in the shaker bottle before charging the catalyst. Air evacuation was done primarily to remove the oxygen that was found to react with hydrogen on the noble metal catalyst. The reactor was then brought to the desired temperature (16–55°C), after which hydrogen was introduced until the desired pressure was obtained. After introducing the hydrogen, the reaction was initiated by starting the shaking mechanism that induces rapid agitation. The progress of the reaction was monitored from the pressure gage readings that reflected hydrogen consumption. When the shaker was stopped, the bottle was vented and the catalyst was recovered. The reaction mixture was analyzed for the chloride ion and occasionally for the CHC content. The shaker reactor did not have any provision for sampling during the course of the reaction.

The amount of hydrogen in the 100-mL headspace of the shaker-type reactor before and after completion of the reaction was calculated from the pressure reading allowing for the vapor pressure of water. The pressure drop is due both to hydrogen consumed in the reaction and hydrogen dissolved in water and adsorbed on the catalyst surface. The quantity of hydrogen dissolved and adsorbed was determined in separate experiments without the chlorinated hydrocarbon using only hydrogen and water, as well as hydrogen, water and the catalyst.

Loss of the chlorinated hydrocarbon to the 100-mL headspace was determined by measuring the CHC solution concentration before and after the shaking period of about one hour without the catalyst and hydrogen.

Autoclave reactor

Adsorption and reaction studies for 1,1,2-trichloroethane hydrodechlorination were performed using a Parr autoclave reactor. The reactor consisted of 1-L, Hastelloy C, stirred autoclave equipped with temperature and agitator speed (up to 700 rpm) controllers. For the data presented here, an agitator speed of 700 rpm was used. In adsorption experiments, aqueous solutions having different CHC concentrations were prepared by dissolving 1,1,2-trichloroethane in deionized water in a 2-L flask by continuously agitating the solution for two hours. The solution of desired concentration was transferred to the autoclave. The solution was sampled to determine the CHC content, after which 0.05 g to 1.0 g of adsorbent was added. Pd/C-ESC 110, Pd/C-ESC 12 and activated carbon were used for adsorption experiments. Adsorption equilibrium was achieved within half an hour at room temperature by continuously agitating the mixture.

For reaction studies, 30 to 70 μL of 1,1,2-trichloroethane was introduced into a slurry consisting of 550 mL of deionized water and catalyst followed by air evacuation. The contents of the reactor were continuously agitated for an hour. Periodic sampling of the slurry indicated complete dissolution of the CHC and attainment of adsorption equilibrium prior to the introduction of hydrogen. When the selected temperature was obtained, the reactor was pressurized with hydrogen to 2.74 bar. Hydrogen introduced while the reactor was being agitated initiated the reaction. Samples of 5-mL reaction mixture were collected during the reaction for analyses. It was found that the reaction continued in the sample that contained dissolved

Table 1. Catalysts Used in the Experiments

Catalyst	Metal on Carbon (%)	BET Surface Area (m^2/g)	Metal Dispersion* (%)	Mean Particle Size (μm)
Pd/C-110	5	950	34	38
Pd/C-12	5	1,350	—	27
Pd/C-111	5	950	—	28
Pd/C-103	5	850	—	21
Pd/C-11	5	950	—	28
Pt/C-23	5	1,350	—	27
Rh/C-30	5	950	—	28
Pd/Al_2O_3	5	91.5	24	—

* Determined from CO chemisorption data.

hydrogen unless the catalyst was immediately removed; this was accomplished by a filter in the sample line. The amount of catalyst collected in the filter was small relative to the total amount in the autoclave, less than 1%. Hence, no attempt was made to return the catalyst to the reactor. During sampling, some hydrogen loss occurred and the pressure drop was 0.14 bar. After each sampling, the pressure was restored to the level before sampling. The variation of reactor pressure during introduction of hydrogen and during sample collection was not considered a serious complication as the reaction rate was found to be independent of hydrogen pressure.

Loss of the chlorinated hydrocarbon to the headspace was determined by measuring the CHC solution concentration before and after the mixing period of about one hour without the catalyst and hydrogen. These experiments were carried out for headspace volumes of 300 mL and 450 mL.

Since the headspace volume in the autoclave reactor was much larger than that in the shaker reactor, the pressure change during the reaction was small, making it difficult to accurately monitor progress of the reaction by recording total pressure as a function of time. Hence, in the autoclave reactor, the reaction kinetics was based on the determination of the chloride ion generated during the course of reaction.

Analytical Methods

Chloride determination

Chloride ion was determined with the use of a commercial chloride-specific ion electrode calibrated against standard sodium chloride solutions. A number of reaction mixture samples were also analyzed using a turbidometric method (Boltz and Howell, 1978). Agreement between the two methods was excellent with less than 2% difference in the measured values.

Table 2. Catalyst Activity Study with Shaker-Type Reactor*

Catalyst	Wt. (gm)	Temp. (°C)	Conv.** (%)
Pd/C-ESC 110	0.05	25	46
Pt/C-ESC 23	0.05	25	9
Rh/C-ESC 30	0.05	25	8
Rh/C-ESC 30	0.05	40	22
Pd/C-ESC 103	0.05	40	46
Pd/C-ESC 110	0.05	40	50
Pd/C-ESC 11	0.50	55	42
Pt/C-ESC 23	0.50	55	8
Pd/C-ESC 111	0.50	55	86
Pd/C-ESC 110	0.50	55	87
Pd/C-ESC 12	0.50	55	89

* CHC: 1,1,2-Trichloroethane; liquid volume = 400 mL; headspace volume = 100 mL; amount of CHC = 50 μL; pressure = 2.74 – 3.77 bar; reaction time = 3 h.
** Based on the chloride ions generated.

Chlorinated hydrocarbon analysis

To identify and quantify the chlorinated hydrocarbon(s) in the reaction mixture, samples were sent to an outside analytical laboratory for testing using the GC-EPA Method 601. Concentrations of 1,1,2-trichloroethane and trichloroethylene were also determined in our laboratory. The aqueous liquid solution was analyzed for the CHC content with an HP-5890 GC equipped with an electron capture detector by directly injecting the liquid sample into the fused silica capillary column having a stationary phase of 5% diphenyl and 95% dimethyl polysiloxane.

Materials

The catalysts used in this work were all commercial products of Engelhard Corporation, Iselin, New Jersey. Except for one catalyst supported on alumina, other catalysts were supported on carbon. The carbon support was obtained from different natural sources with different types of activation. Catalyst metals were deposited according to proprietary procedures, and carbon was treated to vary the surface properties. Further information on these catalysts is listed in Table 1.

Results

Shaker reactor

Commercial catalysts used in the shaker reactor were palladium, platinum, and rhodium supported on various carbons. Since the CHC can be expected to adsorb on the carbon support of the catalyst, CHC conversions were calculated on the basis of measured chloride ion concentrations generated in conjunction with the stoichiometry of Eq. 1. Conversions for a variety of catalysts were obtained for an operating period of three hours. One experiment involving hydrodechlorination of 1,1,2-trichloroethane was continued for a period of 20 hours; the conversion was essentially the same as after the shorter period. The results are summarized in Table 2. Palladium on carbon is seen to be considerably more active than Pt/C and Rh/C. This general trend is often noted in hydrodehalogenations (Rylander, 1967). Conversions with Pt/C were very low, raising the question whether this may be due to low reactivity and whether conversion can be improved with longer operating periods. When the hydrodechlorination experiment was continued for 18 hours, there was no further increase in conversion. This suggests that under the relatively low temperature and pressure conditions used here, the Pt/C catalyst deactivates and/or is inhibited after only a modest period of reaction.

At room temperature and a catalyst loading of 0.5 g after three hours of reaction, no chlorinated hydrocarbon was detectable in the hydrodechlorination of both 1,1,2-trichloroethane and trichloroethylene on the Pd/C catalyst. On the other hand, with 0.5 g of activated carbon and other conditions being the same, there was a substantial amount of chlorinated hydrocarbon left in the solution; only 73% of those reactants were found to have adsorbed. It was also found that no chloride

Table 3. Catalyst Activity Study with Shaker-Type Reactor for Various Chlorinated Hydrocarbons*

Catalyst	Wt. (gm)	Temp. (°C)	Conv.** (%)
CHC: Trichloroethylene			
Pd/C-ESC 111	0.50	25	69
Pd/C-ESC 12	0.50	25	68
Pd/C-ESC 110	0.50	55	73
Pd/C-ESC 12	0.50	55	82
Pd/C-ESC 111	0.50	55	84
CHC: Chloroform			
Pd/C-ESC 12	0.30	55	70
Pt/C-ESC 22	0.30	55	38
Pd/C-ESC 111	0.34	25	80
CHC: Carbon Tetrachloride			
Pd/C-ESC 111	0.05	55	63
Pt/C-ESC 22	0.30	55	33
Pd/C-ESC 110	0.50	55	74
CHC: 1,2,4-Trichlorobenzene			
Pd/C-ESC 111	0.20	55	80
Pt/C-ESC 22	0.20	55	18
Pd/C-ESC 12	0.30	55	93
CHC: Dichloromethane			
Pd/C-ESC 111	0.50	55	17
Pd/C-ESC 11	0.50	55	30
Pt/C-ESC 22	0.50	25	3
Pd/C-ESC 111	0.50	55	70†

* Liquid volume = 400 mL; headspace volume = 100 mL; amount of CHC = 50 microliters; pressure = 2.74 – 3.77 bar; reaction time = 3 h.
** Conversion is based on the chloride ions generated.
† In the presence of basic media.

ion was liberated, confirming that carbon acts as an adsorbent and has, by itself, no catalytic activity.

Other experiments were performed with 0.5-g Pd/C catalyst but without hydrogen. Here no reaction was expected to occur, and indeed no chloride ions were detected; 40% of the CHC (1,1,2-trichloroethane) was found to adsorb on the catalyst surface.

Hydrodechlorination of 1,1,2-trichloroethane is given by the following stoichiometric reaction:

$$C_2H_3Cl_3 + 3H_2 \rightarrow C_2H_6 + 3HCl \qquad (2)$$

Based on the stoichiometry of the above reaction, the reactant

Table 4. Conversion of 1,1,2-Trichloroethane after 3 Hours of Reaction in the Shaker Reactor*

Catalyst wt. (g)	Conv.** (%)
0.005	45
0.01	59
0.04	75
0.08	79
0.10	82
0.20	85
0.50	91

* Amount of 1,1,2-trichloroethane = 50 μL; liquid volume = 400 mL; headspace volume = 100 mL; temperature = 55°C; pressure = 2.74 – 3.77 bar; reaction time = 3 h; catalyst type: Pd/C-ESC 110.
** Conversion is based on the chloride ions generated.

Table 5. Conversion of 1,1,2-Trichloroethane after 10 Minutes of Reaction in the Shaker Reactor*

Catalyst wt. (g)	Conv. (%)	CHC Conc. (ppm)	CHC Removal (%)
0.1	7	133	26
0.5	20	83	54
1.0	33	50	72
2.0	42	19	89

* Amount of 1,1,2-trichloroethane = 50 μL; liquid volume = 400 mL; headspace volume = 100 mL; temperature = 22°C; pressure = 2.74 – 3.77 bar; reaction time = 10 min; catalyst type: Pd/C-ESC 12.

CHC conversions were also calculated from hydrogen consumed during the reaction and were found to be in good agreement with the method based on chloride ion measurements. For example, for the conditions corresponding to Table 2, the pressure drop for 1,1,2-trichloroethane hydrodechlorination with Pd/C-ESCAT 110 catalyst was 0.61 bar after 3 hours of reaction. (The range of pressures in Tables 2–5 is for separate experiments.) At 23°C the pressure drop associated with hydrogen absorbed into solution and adsorbed on 0.5 g catalyst was 0.26 bar. Hence, one would estimate 0.35-bar pressure drop associated with hydrogen reacting with the CHC. Based on the stoichiometry of Eq. 2 and using the ideal gas law, the pressure drop equivalent of the number of moles required to completely hydrodechlorinate 50 μL of CHC at 23°C is 0.38 bar. This would indicate 92% conversion based on hydrogen consumed during the reaction as estimated from hydrogen consumption, which is in reasonable agreement with 87% conversion based on chloride ion generation at the same conditions, as shown in Table 2.

Table 3 shows conversions for the hydrodechlorination of trichloroethylene, chloroform, carbon tetrachloride, 1,2,4-trichlorobenzene, and dichloromethane; the catalysts used were Pd/C and Pt/C. Again, the Pd/C catalyst is seen to be distinctly superior. Dichloromethane conversions were lower than other chlorinated hydrocarbons. However, when the solution was made basic by adding CaO or MgO, conversion significantly increased. Bases are used frequently in catalytic dehalogenation reactions (Rylander, 1967); possible reasons suggested for the resulting improved activity are neutralization of the liberated acid and/or altering of the catalyst surface by the base.

Table 4 shows conversion vs. catalyst loading for 1,1,2-trichloroethane after three hours of operation at 55°C. At a catalyst loading of 0.5 g and at 55°C, the reaction is completed in less than 3 hours. (Reaction is completed in about 3 hours at room temperature.) However, Table 4 shows that the reaction is not complete at the end of the 3-hour period for lower catalyst loadings of 0.005 t 0.2 g.

Table 5 shows the 1,1,2-trichloroethane concentration in solution and the conversion based on the chloride ion generation after 10 minutes of reaction at different catalyst loadings. One observes that % CHC removed from the solution is considerably higher than % conversion based on the chloride ion. The difference is due primarily to adsorption on the carbon support. Some CHC is lost to the headspace, but is estimated to be only 4% of its prevailing concentration in solution. In view of this, it is important to base conversions on chloride ion rather than the CHC content in solution because of sig-

Table 6. 1,1,2-Trichloroethane Concentration vs. Time During Adsorption in the Autoclave Reactor*

Time (min)	CHC Conc. (ppm)	CHC Adsorbed (%)
	Catalyst: Pd/C-ESC 110	
0	176	0
1	88	52
5	77	57
10	76	57
20	74	58
60	74	58
	Catalyst: Pd/C-ESC 12	
0	178	0
10	161	10
30	155	13
60	147	18
90	145	19

* Liquid volume = 700 mL; headspace volume = 300 mL; $T = 25°C$, $P = 1$ bar; catalyst weight = 0.5 g.

nificant adsorption on carbon. It is also apparent that at the highest catalyst loading, at least after the 10th minute, CHC hydrodechlorination takes place following adsorption on carbon. This can happen by two different mechanisms: 1) migration of the CHC on the carbon support to the palladium sites where it reacts with hydrogen adsorbed on these sites; 2) reaction on the carbon support with the hydrogen atom that migrates to the support following dissociative adsorption on palladium (Tauster, 1992). The importance of adsorption on carbon relative to adsorption from solution onto palladium will be addressed quantitatively based on data obtained from autoclave experiments.

The data in Table 5 are based on Pd/C-ESC 12 catalyst. Based on the three-hour runs in Table 2, there is no significant difference in the performance of Pd/C-ESC 12, Pd/C-ESC 110 and Pd/C-ESC 111. It was found, however, that the hydrodechlorination activity of Pd/C-ESC 110 and Pd/C-ESC 111 catalysts, which have the same carbon, were significantly higher than that of the Pd/C-ESC 12 catalyst, which has a different carbon in the first ten minutes of the reaction. At a catalyst loading of 0.5 g, all other conditions being the same as in Table 5, conversion based on the chloride ion for the Pd/C-ESC 110 catalyst was 40% with 97% CHC removed from the solution. (For the Pd/C-ESC 12 catalyst, the chloride-ion-based conversion and CHC removed from the solution were 20% and 54%, respectively.) The performance of the Pd/C-ESC 111 catalyst was virtually identical to that of the Pd/C-ESC 110 catalyst. This again points to the importance of the nature of the carbon in determining the reaction rate.

Autoclave reactor

The rate and the extent of the CHC adsorption on Pd/C-ESC 110 and Pd/C-ESC 12 were determined by experiments conducted in the autoclave reactor. The results in Table 6 show that adsorption of the CHC on the Pd/C-ESC 110 catalyst is very rapid, and 52% of the CHC is adsorbed in the first minute with adsorption equilibrium achieved within 20 minutes with 58% of the CHC removed from the solution. (In separate experiments it was determined that the CHC loss to the 300-mL headspace of the autoclave reactor is 6% of the equilibrium

Table 7. Adsorption Equilibrium Data*

CHC Conc. in Solution, C_s (ppm)	CHC Conc. on Adsorbent, C_c (kg/kg)
Adsorbent: Pd/C-ESC 110	
17	0.078
30	0.101
40	0.120
69	0.156
80	0.151
145	0.203

* CHC: 1,1,2-trichloroethane; $T = 23°C$; $P = 1$ bar; liquid volume = 700 mL; headspace volume = 300 mL; adsorbent weight = 0.05 – 1.0 g; initial CHC concentration = 74 – 183 ppm.

CHC concentration in solution.) As for the Pd/C-ESC 12 catalyst, adsorption is considerably slower where adsorption equilibrium is essentially reached after 90 minutes with only 19% of the CHC removed from the solution. The fact that the carbon in ESC-12 has substantially higher surface area than ESC-110 points to the importance of the chemical nature of the support in determining adsorption and subsequent catalytic conversion rates. These observations are the key to understanding the higher hydrodechlorination activity of the Pd/C-ESC 110 catalyst relative to the Pd/C-ESC 12 catalyst.

To facilitate the analysis of initial rate data where adsorption equilibrium exists prior to the beginning of the reaction, adsorption equilibrium experiments were conducted for 1,1,2-trichloroethane on the Pd/C-ESC 110 catalyst. The adsorption equilibrium data are given in Table 7. The amount of reactant hydrocarbon adsorbed was determined from material balance accounting for the loss to the headspace.

Langmuir type of adsorption would predict the following relationship between the amount of CHC adsorbed on carbon per unit mass adsorbent, C_c, and its concentration in solution, C_s:

$$C_c/C_T = K_A C_s/(1 + K_A C_s) \tag{3}$$

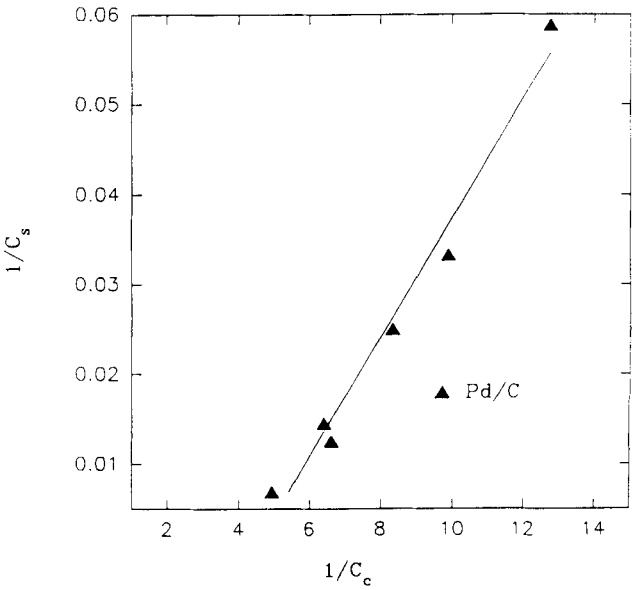

Figure 1. Adsorption isotherm data for Pd/C.

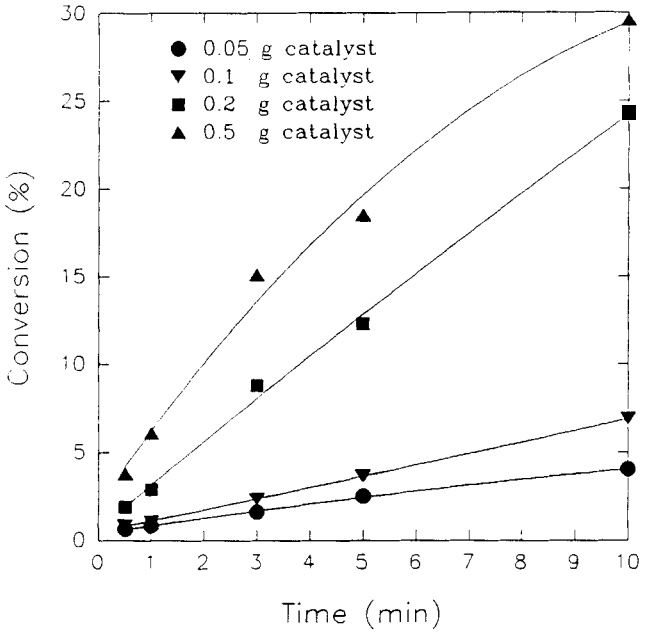

Figure 2(*a*). Conversion vs. time for the autoclave reactor at $T = 16°C$; 1,1,2-trichloroethane.

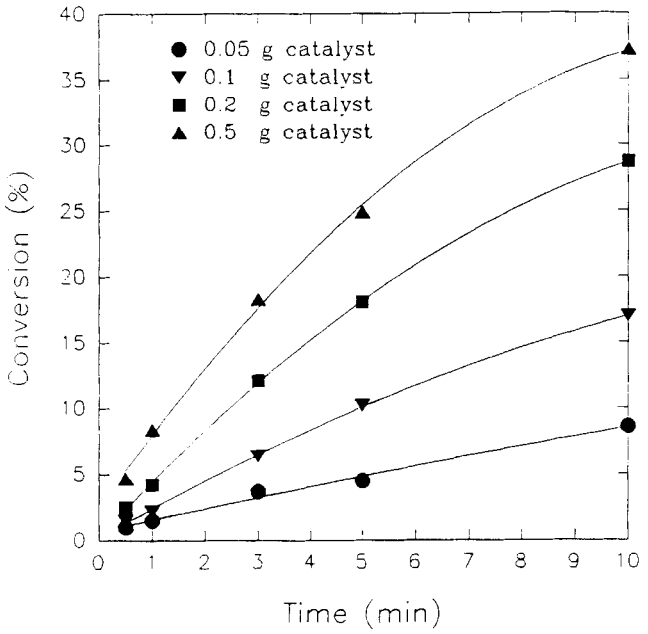

Figure 2(*b*). Conversion vs. time for the autoclave reactor at $T = 23°C$; 1,1,2-trichloroethane.

Equation 3 was rearranged as:

$$1/C_s = C_T K_A / C_c - K_A \tag{4}$$

Figure 1 shows the adsorption equilibrium isotherm plotted on the basis of Eq. 4 using the data from Table 7. The adsorption equilibrium constant, K_A, and the amount of hydrocarbon adsorbed per unit mass adsorbent at saturation, C_T, were obtained from linear regression using Eq. 4, where $1/C_s$ is the dependent and $1/C_c$ is the independent variable. K_A and

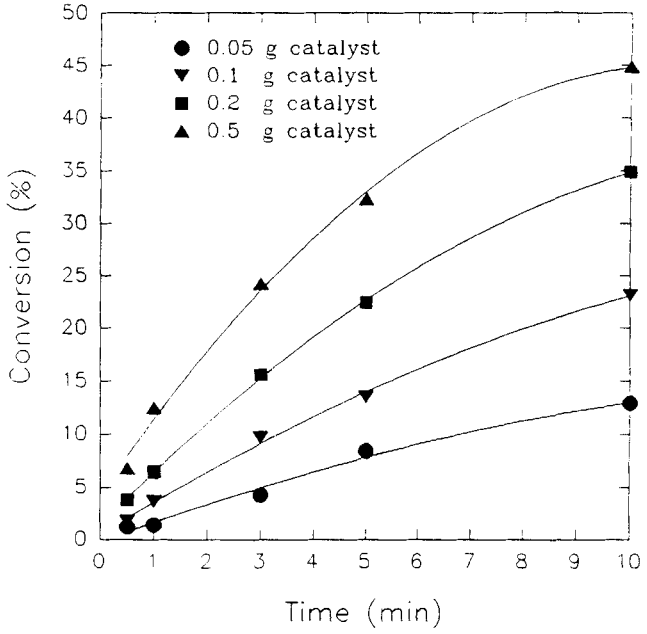

Figure 2(*c*). Conversion vs. time for the autoclave reactor at $T = 30°C$; 1,1,2-trichloroethane.

C_T were found to be 2.8×10^{-2} ppm and 0.23 kg(CHC)/kg(catalyst), respectively.

Kinetic studies for the hydrodechlorination of 1,1,2-trichloroethane were carried out in the temperature range of 16–30°C and at 2.74 bar. Pd/C-ESC 110, which had the highest activity in shaker reactor studies, was used as the catalyst. The same amount of CHC (70μL) was dissolved in a 550-mL slurry in these experiments. Reaction was started by admitting hydrogen into the autoclave after one hour of dissolution and equilibration period for the slurry. Reaction mixture samples were taken during the first 20 minutes and analyzed for their chloride ion and in some cases for the CHC. Figures 2a to 2c show such data at different catalyst loadings. The curves represent a second-order polynomial function constructed on the basis of best fit to the data.

Initial rates would typically be calculated from the slope of the conversion vs. time plot as time approaches zero:

$$R_i = C_o (dx/dt)_{t->o} \tag{5}$$

However, for the data collected here, a linear approximation to the plot of R_i vs. t for the first 1/2 minute was found to be satisfactory in evaluating the initial rates.

Table 8 shows that initial rates increase with temperature, as expected. Activation energies were calculated in the temperature range of 16 to 30°C; Figure 3 shows a plot of ln R_i vs. $1/T$. Activation energies calculated at different catalyst loadings in Figure 3 varied from 29 to 38 MJ/mol.

Hydrogen pressure was found to have no effect on the rate data. At 23°C and catalyst loading of 0.5 g, experiments were repeated at pressure levels of 1.5 and 1.8 bar and compared to those at 2.4 bar. Chloride levels measured after 1/2 minute and 3 hours of reaction were within the reproducibility of the experimental error which is estimated as 5% for the 1/2-minute data and 2% for the 3-hour data.

Table 8. Initial Rates at Different Temperatures in the Autoclave Reactor*

Catalyst wt. (g)	Initial Rate $(mol/m^3 \cdot s) \times 10^7$
Temperature = 16°C	
0.05	2.97
0.10	3.93
0.20	8.65
0.50	17.43
Temperature = 23°C	
0.05	4.56
0.10	6.88
0.20	11.45
0.50	21.50
Temperature = 30°C	
0.05	5.46
0.10	8.23
0.20	17.43
0.50	31.13

* Amount of 1,1,2-trichloroethane = 70 μL; liquid volume = 550 mL; headspace volume = 450 mL; catalyst type: Pd/C-ESC 110; pressure = 2.74 bar.

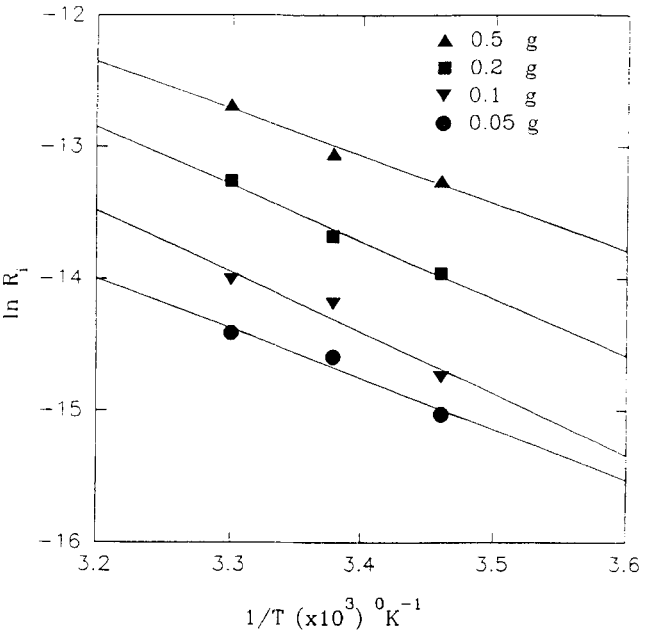

Figure 3. ln R_i vs. $1/T$ at different catalyst loadings.

It is reasonable to assume that during reaction the solution is saturated with hydrogen at all times because of the low reaction rates associated with low reactant CHC concentrations. Since the effect of the change in pressure on the saturation concentration is negligible (Perry and Green, 1984), the pressure level is not expected to affect hydrogen coverage of active sites. Unlike many hydrogenation reactions where the high reaction rate due to much higher CHC concentrations (often the liquid phase is pure hydrocarbon) gives rise to hydrogen mass-transfer limitations, hydrodechlorination reactions here apparently proceed in the absence of hydrogen mass-transfer effects.

Data were also collected at room temperature for different amounts of CHC dissolved in the autoclave. Table 9 shows the calculated initial rates as well as the CHC concentration on the catalyst surface and in the solution prior to the beginning of the reaction. At the time when hydrogen is admitted into the autoclave after the equilibration period, the conservation equation for the CHC in terms of concentrations can be written as follows:

$$C_o = C_s + \rho_{sl} C_c + C_h \tag{6}$$

where C_h represents the loss to headspace estimated as 8% of the solution concentration, C_s · C_c is the CHC concentration on the catalyst. These concentrations were calculated from Eqs. 3 and 6.

In Table 9 the total amount of CHC adsorbed on the catalyst is shown under the column $\rho_{sl} C_c$. The incentive for this listing

Table 9. Initial Rates for Different CHC Charges in the Autoclave Reactor*

Initial CHC Conc. (C_o) (ppm)	CHC Conc. in Solution (C_s) (ppm)	CHC Conc. on Catalyst (ppm) $\rho_{sl} C_c$	CHC Conc. on Catalyst $(kg/kg) \times 10^2$ C_c	Initial Rate (R_i) (ppm/min)	Initial Rate (R_i) $(mol/m^3 \cdot s) \times 10^7$
		Catalyst Weight = 0.05 g			
78	60	13	14.3	3.03	3.78
130	105	16	17.6	3.15	3.93
183	153	17	18.7	3.66	4.56
		Catalyst Weight = 0.10 g			
78	49	24	13.2	4.85	6.06
130	92	30	16.5	5.20	6.49
183	138	33	18.2	5.49	6.88
		Catalyst Weight = 0.20 g			
78	34	41	11.3	6.07	7.58
130	69	55	15.1	7.85	9.80
183	110	63	17.3	9.15	11.45
		Catalyst Weight = 0.50 g			
78	15	62	6.8	10.1	12.56
130	31	97	10.7	13.6	16.94
183	53	125	13.8	17.2	21.50

* CHC: 1,1,2-trichloroethane; temperature = 23°C; pressure = 2.74 bar; liquid volume = 0.550 L; headspace volume = 0.450 L; catalyst type: Pd/C-ESC 110.

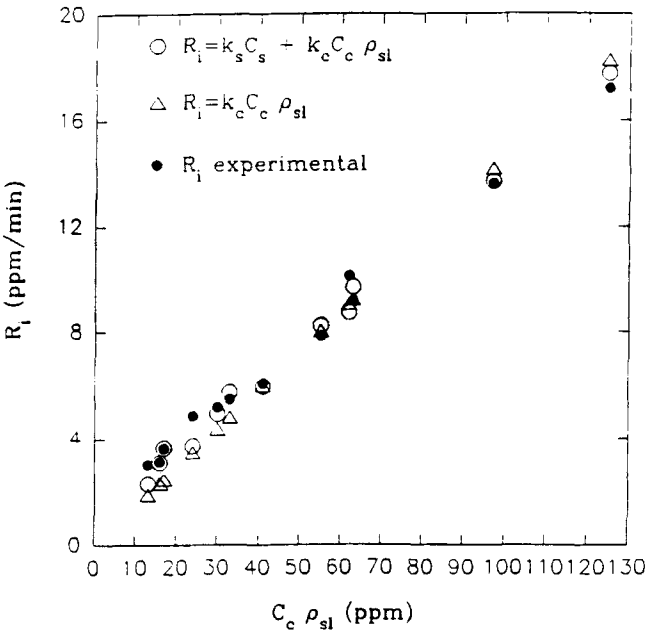

Figure 4. Correlation of initial rate data.

is to show the total amount of CHC absorbed on the catalyst when the catalyst loading changes. Table 9 indicates that initial rates correlate much better with $\rho_{sl}C_c$ than with C_s. The effect of CHC adsorbed on carbon relative to its concentration in solution on initial rates can be established quantitatively by using the following first-order empirical equation to correlate the initial rate data:

$$R_i = k_s C_s + k_c \rho_{sl} C_c \tag{7}$$

In Eq. 7 the first term represents the contribution of direct adsorption from solution on initial rate and the second term represents the contribution of adsorption on carbon.

If the contribution to initial rate by direct adsorption from solution onto the palladium can be neglected, one can write:

$$R_i = k_c \rho_{sl} C_c \tag{8}$$

The ability of Eqs. 7 and 8 to correlate the initial rate data was tested by carrying out the linear regression analysis. Initial rates and concentrations were obtained from Table 9. k_s and k_c values determined from regression analysis using Eq. 7 were 8.63×10^{-3} min $^{-1}$ and 0.139 min^{-1}, respectively, whereas k_c from Eq. 8 was 0.146 min^{-1}. Figure 4 shows how the predicted values for initial rates based on Eq. 7 and 8 compare with the experimental initial rates. The ability of Eq. 8 to correlate the initial rate data is almost as good as that of Eq. 7 for higher $\rho_{sl}C_c$ values. At lower $\rho_{sl}C_c$ values which correspond to higher values of C_s (lower catalyst loadings), the first term in Eq. 7 is no longer negligible and yet the the second term is still dominant. These results illustrate the importance of adsorption on carbon in determining initial rates. If one were to correlate initial rates with C_s alone, one would observe that initial rates are essentially independent of C_s at low catalyst loadings. This is because C_c (and consequently the dominant term $k_c\rho_{sl}C_c$) is mostly unaffected by the changes in C_s as illustrated for the 0.05-g data in Table 9.

Table 10. Change of 1,1,2-Trichloroethane Concentration with Time in the Autoclave Reactor*

Time (min)	CHC Conc. (ppm)	% Removal
1	59	68
4	34	81
9	15	92
14	9	95
20	3	98

* Amount of 1,1,2-trichloroethane = 70 μL; liquid volume = 550 mL; headspace volume = 450 mL; catalyst weight = 0.5 g; catalyst type: Pd/C-ESC 110; temperature = 23°C; pressure = 2.74 bar.

In the operation of a commercial autoclave reactor, since adsorption of the CHC on the catalyst is rapid, one would expect most of the CHC to be on the carbon support of the catalyst rather than in the solution (except perhaps during a very brief initial period), provided that the slurry has sufficient amount of catalyst. Therefore, Eq. 8 is a reasonable approximation which can be used for reactor design purposes.

Table 10 shows the CHC solution concentration as a function of time for the Pd/C-ESC 110 catalyst at room temperature. One observes that after 9 minutes of operation, 92% of the CHC is removed from the solution. At the same reaction conditions, it can be seen from Fig. 2b that conversion based on the chloride ion is 35% after 9 minutes of reaction. This confirms the earlier observation with the shaker-type reactor that the CHC depletion is solution is much faster than the chloride ion generation, indicating substantial accumulation of the CHC on the carbon support of the catalyst. We may note here again that at room temperature, the conversion based on chloride ion for the Pd/C-ESC 110 catalyst in the shaker reactor after 10 minutes was 40% with 97% CHC removal from the solution. Here the catalyst loading for the two reactors was the same (0.5 g); however, the liquid volume in the autoclave reactor was 550 mL compared to 400 mL for the shaker. Also the mixing in the two systems are considerably different. Despite these differences, the agreement between the two systems in % CHC removed and conversion based on the chloride ion is remarkably close.

To further understand the role of the carbon support in the rapid adsorption of chlorinated hydrocarbon, experiments were performed with 5% Pd/Al_2O_3, where the CHC is not expected to adsorb on the alumina support. In these experiments, 1,1,2-trichloroethane was first dissolved in a large flask containing deionized water and subsequently transferred to the bottles of two shaker reactors. Only one of the bottles contained the Pd/Al_2O_3 catalyst. The contents of the two bottles were agitated in the absence of hydrogen for 2 hours at room temperature after which they were analyzed for the CHC. This approach is more accurate than sampling before and after the adsorption experiment because it eliminates the uncertainty associated with the loss of the CHC to the headspace during the adsorption process. It was found that 1,1,2-trichloroethane concentrations in both bottles were the same indicating that 1,1,2-trichloroethane does not adsorb on either the palladium metal or the alumina support at the specified conditions.

Under reaction conditions (with hydrogen present), experiments were carried out in the autoclave and the CHC and chloride ion concentrations were calculated and compared. The

Table 11. 1,1,2-Trichloroethane Conversions in the Autoclave Reactor for the Pd/Al_2O_3 Catalyst*

Time (h)	CHC Conc. (ppm)	Chloride Conc. (ppm)	Conv.** (%)	Conv.† (%)
1	117	43	30	30
2	103	52	35	37
3	94	59	41	43
4	84	65	45	47
5	79	70	48	50

* CHC charge: 70 μL; liquid volume = 550 mL; headspace volume = 450 mL; catalyst weight = 0.5 g; catalyst type: Pd/Al; temperature = 23°C; pressure = 2.74 bar.
** Conversions based on the chloride ion concentration.
† Conversions based on the reactant hydrocarbon concentration.

difference between conversions based on the chloride ion generation and the CHC disappearance would be a measure of accumulation on the alumina support. The results in Table 11 show that conversions based on the CHC uptake from the solution are the same as conversions based on the chloride ion generation. Hence, one can conclude that the extent of 1,1,2-trichloroethane adsorption on the alumina surface, if any, is insignificant.

The reaction with the Pd/Al_2O_3 catalyst was found to be much slower than that with the Pd/C catalyst. For example, for the same reaction conditions as in Table 11, 1,1,2-trichloroethane conversion with the Pd/Al_2O_3 catalyst was 4.4% after 9 minutes of reaction compared to the 35% conversion with the Pd/C-ESC 110 catalyst. We also note here that the two catalysts have 5% palladium with similar metal dispersions (34% for Pd/C-ESC 110 and 24% for Pd/Al_2O_3). Table 11 also shows that after 5 hours of operation, reaction in the presence of Pd/Al_2O_3 catalyst continues. Under the same conditions, reaction with the Pd/C-ESC 110 catalyst was essentially complete in 3 hours.

For the Pd/Al_2O_3 catalyst where the alumina support does not adsorb the CHC, the path to reaction is by direct adsorption unto the palladium sites from solution. For the Pd/C-ESC 110 catalyst, we indicated earlier that contribution to reaction of direct adsorption from solution unto the palladium sites is smaller than that of adsorption on carbon. If it is also assumed that the reactivity of palladium on the alumina support is the same as on carbon, it is reasonable to expect that hydrodechlorination activity with the Pd/C catalyst will be higher than the Pd/Al_2O_3 catalyst because of the significant contribution of adsorption on carbon to reaction.

We earlier mentioned two possible mechanisms by which the CHC react following adsorption on carbon: 1) migration to the metals sites by surface diffusion followed by reaction with hydrogen adsorbed on the metal; 2) reaction on the carbon with hydrogen atoms which spill over to the support after dissociatively adsorbing on the metal. The latter mechanism has received considerable attention in the literature for palladium, platinum, and nickel catalysts on oxide supports (Levy and Boudart, 1974; Sermon and Bond, 1973). To our knowledge, however, hydrogen spillover has not been studied with carbon-supported catalysts.

In shaker and autoclave reactors, the observed conversions less than 100% based on chloride ion determination at long operating times when no CHC remained in solution suggest that a small fraction of the CHC could be remaining on the catalyst surface without reacting, presumably on carbon sites having the longest diffusion path to the metal. Indeed, for most palladium catalysts supported on different types of carbon conversions for long operating periods for a catalyst loading of 0.5 g are around 90%. The conversions are not expected to be identical because of the possible variations in adsorption properties of different carbon supports used. Loss to the headspace should not be a factor, as any CHC that may have escaped to the headspace in the beginning of the reaction is expected to be reabsorbed as its concentration in the liquid decreases with the progress of the reaction.

In other experiments using granular Pd/C catalyst in a fixed bed, the catalyst activity was essentially constant for 70 hours of operation, after which it decreased to 1/3 of its original level (Yu, 1991). The deactivated catalyst was regenerated to 85% of its original activity level by washing with NH_4OH solution following the procedure of Simone et al. (1991). Since this procedure is known to remove the chloride ions, the activity loss was attributed to the chloride ion buildup on the catalyst rather than hydrocarbon species that may have adsorbed and stayed on the catalyst without reacting.

Conclusions

Hydrodechlorination of a variety of chlorinated hydrocarbons (referred to as CHCs) such as 1,1,2-trichloroethane, trichloroethylene, chloroform, carbon tetrachloride, 1,2,4-trichlorobenzene, dichloromethane, and 1,1,1-trichloroethane have been carried out directly in aqueous solution using the shaker reactor. Adsorption and kinetic studies for 1,1,2-trichloroethane were also carried out with the autoclave reactor. For the hydrodechlorination of 1,1,2-trichloroethane and trichloroethylene with the shaker reactor at room temperature, near atmospheric pressure and reaction period of 3 hours, no residual reactant or any other chlorinated product was detected in the reaction mixture with up to 90% of the CHC hydrodechlorinated.

Although commercial Pt/C and Rh/C catalysts showed some initial activity, the hydrodechlorination reaction did not proceed beyond 10% conversion at the conditions tested. Shaker experiments were also performed for a 10-minute period where it was found that Pd/C-ESC 110 and Pd/C-ESC 111 catalysts are significantly more active than the Pd/C-ESC 12 catalyst in the hydrodechlorination of 1,1,2-trichloroethane. Adsorption experiments indicated that the rate and the extent of the CHC adsorption on the Pd/C-ESC 12 catalyst are significantly lower than those on the Pd/C-ESC 110 catalyst in spite of its higher surface area pointing out the importance of the surface chemistry of the two carbons.

Both shaker and autoclave experiments indicated that the uptake of 1,1,2-trichloroethane from solution is much faster than the chloride ion generation. This is primarily due to rapid adsorption and accumulation of the CHC on the carbon support. The observation that hydrodechlorination reaction continues even when no CHC is detectable in the solution suggests the following plausible mechanisms: 1) migration of the reactant hydrocarbon on the carbon support to the palladium where it reacts with the adsorbed hydrogen; 2) reaction on the carbon support with hydrogen that spills over to the carbon support after dissociatively adsorbing on palladium. Further studies indicated that adsorption on carbon contributes to reaction

significantly more than direct adsorption onto palladium from solution. For example, for the Pd/C-ESC 110 catalyst, the higher hydrodechlorination activity relative to the Pd/C-ESC 12 catalyst is due to much faster and larger extents of adsorption of the CHC on the carbon support of the ESC 110 material. Further confirmation of the key role played by the support was established from autoclave reaction experiments for 1,1,2-trichloroethane on the Pd/Al_2O_3 catalyst. Conversions based on the CHC consumption were found to be essentially the same as those based on the chloride ion generation at different time intervals, indicating the absence of CHC adsorption on the alumina support. Moreover, reaction rates with the Pd/Al_2O_3 catalyst were found to be much lower than those with the Pd/C-ESC 110 catalyst at the same operating conditions.

Autoclave reactor data for the hydrodechlorination of 1,1,2-trichloroethane showed that initial rates correlate well with first-order dependence of CHC concentration on the carbon support of the Pd/C-ESC 110 catalyst. Contribution to reaction by direct adsorption from solution onto palladium was found to be negligible at higher catalyst loadings. In estimating the CHC concentration on the carbon support, adsorption equilibrium data were used. 1,1,2-Trichloroethane adsorption isotherm with the Pd/C-ESC 110 catalyst was found to be of Langmuir type.

Initial rates were also found to be independent of hydrogen pressure. This was attributed to the solution being saturated with hydrogen at all times due to low reaction rates. Activation energies were calculated at different catalyst loadings in the temperature range of 16°C to 30°C and were found to vary, without trend, from 29 to 38 MJ/mol.

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Notation

C_c = concentration of CHC on the catalyst or absorbent after equilibration, kg/kg
C_h = loss of CHC to the headspace of the autoclave calculated as a fraction of C_s, ppm
C_o = mass of CHC divided by mass of solution in the autoclave reactor before reaction, ppm
C_s = concentration of CHC in solution after equilibration, ppm
C_T = mass of CHC adsorbed per unit mass adsorbent at saturation, kg·adsorbate/kg·absorbent
K_A = adsorption equilibrium constant, ppm^{-1}
k_C = velocity constants in Eqs. 7 and 8, min^{-1}
k_s = velocity constant in Eq. 7, min^{-1}
R_i = initial reaction rate based on the chloride ion generation for the autoclave reactor, ppm/min or $mol/m^3 \cdot s$
t = time, h, min or s
X = conversion based on the chloride ion generation

Greek letters

ρ_{sl} = mass of catalyst divided by the mass of solution, mg/kg

Literature Cited

Baker, E. G., L. J. Sealock, Jr., R. S. Butner, D. C. Elliott, and G. G. Neuenschwander, "Catalytic Destruction of Hazardous Organics in Aqueous Wastes: Continuous Reactor System Experiments," *Hazardous Waste and Hazardous Mat.*, **6**(1), 87 (1989).

Berty, J. M., "Catalyst for the Destruction of Toxic Organic Chemicals," U.S. Patent No. 5,021,383 (June 4, 1991).

Boltz, D., and J. Howell, *Colorimetric Determination of Nonmetals*, Wiley, New York (1978).

Coq, B., G. Ferrat, and F. Figueras, "Conversion of Chlorobenzene over Palladium and Rhodium Catalysts of Widely Varying Dispersion," *J. of Catal.*, **101**, 434 (1986).

Hagh, B. F., and D. T. Allen, "Catalytic Hydroprocessing of Chlorobenzene and 1,2-Dichlorobenzene," *AIChE J.*, **36**(5), 773 (1990).

Jin, L., and M. A. Abraham, "Destruction of 1,4-Dichlorobenzene through Heterogeneous Catalytic Reaction at Low Temperature," AIChE Meeting, San Francisco (Nov., 1989).

Kalnes, T. N., and R. B. James, "Hydrogenation and Recycle of Organic Waste Streams," *Environ. Prog.*, **7**(3), 185 (1988).

Kosusko, M., "Catalytic Oxidation of Groundwater Stripping Emissions," *Environ. Prog.*, **7**(2), 136 (1988).

Lankford, P. W., W. W. Eckenfelder, Jr., and K. D. Torrens, "Reducing Wastewater Toxicity," *Chem. Eng.*, **95**(16), 72 (Nov., 1988).

LaPierre, R. B., L. Guczi, and W. L. Kranich, "Hydrodechlorination of Polychlorinated Biphenyl," *J. of Catal.*, **52**, 230 (1978c).

Levy, R. B., and M. Boudart, "The Kinetics and Mechanism of Spillover," *J. of Catal.*, **32**, 304 (1974).

Ollis, D. F., "Contaminant Degradation in Water," *Environ. Sci. and Technol.*, **19**(6), 480 (1985).

Patterson, J. W., *Industrial Wastewater Treatment Technology*, Butterworth, Boston (1985).

Pelizetti, E., and N. Serpone, *Homogeneous and Heterogenous Photocatalysis*, D. Reidel Publishing Co., New York (1986).

Perry, R. H., D. W. Green, and J. O. Maloney, eds., *Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, New York (1984).

Rylander, P. N., *Organic Synthesis with Noble Metal Catalysts*, Academic Press, New York (1967).

Sermon, P. A., and G. C. Bond, "Hydrogen Spillover," *Catal. Rev.*, **8**(2), 211 (1973).

Simone, D. O., T. Kennelly, N. L. Brungard, and R. J. Farrauto, "Reversible Poisoning of Palladium Catalysts for Methane Oxidation," *Appl. Catal.*, **70**, 87 (1991).

Strier, M. P., "Pollutant Treatability: a Molecular Engineering Approach," *Environ. Sci. and Technol.*, **14**(1), 28 (1980).

Subbanna, P., H. Greene, and F. Desai, "Catalytic Oxidation of Polychlorinated Biphenyls in a Monolithic Reactor System," *Environ. Sci. and Technol.*, **22**, 557 (1988).

Surprenant, N., T. Nunno, M. Kravett, and M. Breton, *Halogenated-Organic Containing Wastes—Treatment Technologies*, Noyes Data Corp., Park Ridge, NJ (1985).

Tauster, S., private communication, Engelhard Corp. (Apr., 1983).

Tichenor, B. A., and M. A. Palazzolo, "Destruction of Volatile Organic Compounds via Catalytic Incineration," *Environ. Prog.*, **6**(3), 172 (1987).

Yu, G., "Hydrodechlorination of Trichloroethane and Trichloroethylene in a Trickle-Bed Reactor," MS Thesis, Stevens Inst. of Technol., Hoboken, NJ (1991).

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