5-31-1991

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Recommended Citation

Yu, Tai-Chiang, "Catalytic oxidation of chlorinated compounds over PdO/Al2O3 on a monolith" (1991). *Theses*. 1882.
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CATALYTIC OXIDATION OF CHLORINATED COMPOUNDS OVER PdO/Al_2O_3 ON A MONOLITH

by

Tai-Chiang Yu

Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology
in partial fulfillment of the requirements for
the degree of
Master of Science in Chemical Engineering
1991

APPROVAL SHEET

Title of Thesis: Catalytic Oxidation of Chlorinated Compounds over PdO/Al_2O_3 on a Monolith

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Master of Science in Chemical Engineering, 1991

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ABSTRACT

Title of thesis : Catalytic Oxidation of Chlorinated Compounds over PdO/Al_2O_3 on a Monolith

Tai-Chiang Yu : Master of Science in Chemical Engineering, 1991

Thesis directed by : Dr. Henry Shaw
Professor of Chemical Engineering

The catalytic oxidation of trichloroethylene(TCE) and dichloromethane (DCM) was investigated over a catalyst containing 4% PdO on Al_2O_3 washcoat and on a cordierite monolith with 400 channels per in^2. Reactivity and selectivity of the catalyst for the destruction of 200 ppm C_2HCl_3 and 500 ppm CH_2Cl_2 in air was evaluated over the temperature range 250 to 550 ^oC. This research was conducted in a tubular reactor system at space velocities of 4,000 to 24,000 v/v/hr. It was found that complete ox:idation occurs at 500 ^oC for DCM and 550 ^oC for TCE. In addition to the expected products of combustion from DCM, CH_3Cl, $CHCl_3$, and CCl_4 were also found. CHCl3 was found at low temperatures and was destroyed above 500^{o}C. The only chlorinated product produced in oxidation of TCE was C_2Cl_4 and was destroyed above 550^{o}C. No significant CO formation was observed above 500 ^oC for either compound. It was found that reaction temperature predicts conversion of the chlorocarbons and space velocity affects product distribution.

Varying the oxygen concentration over a factor of 4 showed no effect on rate, thus allowing representation of the destruction process as a first order rate law in TCE oxidation. The Arrhenius activation energy is 34 kcal/mole. The HCl selectivity in the presence of 1.5% water or 0.5% methane was also investigated. It was found that the water and methane enhance the HCl selectivity and inhibit the formation of Cl_2. These two hydrogen sources also inhibited the formation of C_2Cl_4.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to his advisor, Professor Henry Shaw for his guidance, encouragement, and enlightening discussions.

My special thanks go to Dr. Robert J. Farrauto and Dr. Ching R. Huang, for their thoughtful advice, helpful suggestions and ideas for conducting this research.

The author acknowledges support from NJIT/ Hazardous Waste Management Research Center for this study.

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I. INTRODUCTION

Chlorinated hydrocarbons are widely used in dry cleaning and degreasing operations, organic chemicals manufacturing, automotive painting operations, etc. Chlorinated hydrocarbons emitted into the atmosphere affect stratospheric ozone and when disposed in the ground can cause water pollution which affects human health because many chlorocarbons are carcinogenic. Also, because of the chemical stability of chlorinated hydrocarbons, it is necessary to use high temperature incineration to destroy the chlorinated hydrocarbons into non-toxic products. As a consequence of using high temperatures, expensive materials of construction and additional fuel are needed, making this method of destruction very expensive (Bond, 1974).

Catalytic oxidation is a combustion process in which the chlorinated hydrocarbons air stream is preheated and passed through a catalyst bed usually containing metal oxides or noble metals. The catalyst allows the oxidation to occur rapidly and at lower temperatures than required for thermal incineration (Palazzolo, 1987). This reduced temperature requirement translates to a potential cost advantage for catalytic systems.

The object of this research is to understand the fundamental of catalytic oxidation processes for chlorinated hydrocarbons. This includes rate measurements for catalytic destruction of low concentrations of chlorinated hydrocarbons, the effect of catalyst type and support, the effect of active metal concentration, the effect of different space velocities and feed concentrations , and process operating conditions.

Since some chlorinated hydrocarbons contain more chlorine atoms than hydrogen atoms, they produce Cl_2 in addition to the more desirable HCl. HCl is easy scrubbed in an alkaline medium. A desirable research objective is therefore to find a means of introducing additional hydrogen in order to convert all the chlorine to hydrogen chloride. We have examined the possibility of supplying the additional hydrogen required with the feed in the form of either water or methane. The exothermicity of the catalyzed combustion of methane increases the temperature at which a chlorinated molecule might acquire hydrogen atoms (either directly from a hydrocarbon molecule, or from hydrogen atoms residing temporarily on the catalyst surface, or even directly from water) to achieve production of hydrogen chloride. The carbon atoms of the chlorinated molecule are essentially converted to carbon dioxide.

There are considerable advantages in using catalyzed combustion instead of high temperature incineration. Although, incinerators can meet current EPA regulations for effluent emissions, they may have operational problems with combustion stability and high destruction efficiencies in the face of the flame-inhibiting properties of halogenated compounds. Many conventional combustion systems (Palazzolo, 1985) require back mixing (swirling) auxiliary fuel, staged burning, high temperature of operation (producing NO_x), and long average residence times (requiring large reactor volumes and consequent high capital costs). A catalytic combustor can avoid halogen flame inhibition sufficiently to permit plug flow combustion (i.e., without significant back mixing). With combustor size requirements significantly reduced, capital and operating costs can also be brought down and on-site or mobile incineration made more economical (Wang, 1991).

II. BACKGROUND

A. Review of the Literature

Chlorinated hydrocarbons (CHCls) are widely used in dry-cleaning and in degreasing operations, and as solvents in the pharmaceutical industry, but their vapors are toxic to human beings because of damage they cause to the liver (Bond, 1973). Dichloromethane (DCM) and trichloroethyene (TCE) were used in this research as representation solvents used in industry.

In recent years , TCE has been discovered in ground-water and in aquafers used for potable water throughout the United States. It has become the subject of extensive governmental regulations and a target chemical in perhaps hundreds of environmental litigations (Schaumburg, 1990) These two compounds, according to " Hazardous Substance Fact Sheet " (NJ Dept. Health, 1986), may be cancer causing agent in humans. There may be no safe level of exposure for a carcinogen, so all contact should be reduced to the lowest possible level.

Catalytic incineration (oxidation) is an energy efficient method of destroying chlorinated hydrocarbons (Lester, 1990). Such a process involves contacting the waste gas stream with a catalyst in the presence of excess oxygen at a temperature below about 600 ^{o}C. Chlorinated hydrocarbons are usually destroyed by thermal incineration at temperature of at least 1100 ^{o}C (Bose et al. , 1983; Senkan et al., 1986; Lee et al., 1990). Therefore, there is a need for a catalyst which can oxidize chlorinated hydrocarbons at lower temperatures. However, the chlorine can react with the catalytic metal and poison its activity.

Numerous metal catalysts have been evaluated for their potential for oxidizing hydrocarbons and chlorocarbons. These metals are usually divided into noble metal catalysts and transition metal oxide catalysts. The activity of metal oxide catalysts for the complete oxidation of chlorinated compounds was summarized by Ramanathan et al., (1989) as follows:

Co, Cr > Mn > Cu > Ni > Pt > V > Mo

Some studies have involved noble metal catalyst to treat chlorinated hydrocarbon compounds. U.S. patent 1485375 (Bond, 1973) showed that 0.8 to 1.5 wt% Pt on Al_2O_3 catalysts are effective in treating a number of chlorinated compounds, such as CH_2Cl_2, CCl_4, $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4, and have good performance in the presence of propane. The percent destruction of chlorinated compounds is above 95% but the selectivity to HCl was not investigated.

Pope et al., (1978) studied the oxidation of 1,1,1-trichloroethane in a mixture of gases by a platinum-honeycomb catalyst. They compared the destruction efficiency of Co_3O_4 with Pt catalysts. The Co_3O_4 catalyst proved to be more effective in the presence of chlorinated fuels. Hung et al., (1989) investigated a Cr_2O_3/Co_3O_4 binary catalyst. This binary catalyst performed better than Pt catalyst in oxidizing CH_3Cl, CH_2Cl_2 in the presence of propane. The product distribution, as a function of temperature, was not investigated.

Some investigators evaluated transition metal oxides catalysts on supports. A chromium oxide impregnated catalyst on a support was used in the oxidation of chlorinated compounds which treated CH_3Cl (Senkan et al., 1986), 1,1-dichloroethane (Ramanathan et al., 1989) , hexachlorobezene and hexachlorobutadiene (Johnston, 1976), and PCB's (Novinson, 1989). It was shown that Cr_2O_3 catalysts have good activity for chlorinated compounds destruction. However, the undesirable product, Cl_2, can not be effectively removed. In a study by K. Ramanathan et al., (1989), the selectivity to chlorine from catalytic oxidation of 1,1-Dichloroethane was determined to be 50% at 500^oC.

Hydrated nickel oxides, manganese oxides, cobalt oxides (Lavanish et al., 1976; Sare et al., 1977) and titania catalysts (Tanguay, 1989) were evaluated for the catalytic oxidation of C_2-C_4 halogenated hydrocarbons, and dichloromenthane. Conversions of 45 to 90 percent were obtained for vinyl chloride (VCM), vinylidene chloride (VDCM) and trichloroethane over the nickle oxides (II) and (II and III). At temperatures over 450 ^oC, nickle oxide catalysts started to deactivate by thermal sintering. For initial concentration of 46.5 ppm of VCM or VDCM at 107 ^oC, 99% conversion was measured with the cobalt oxide (II) catalyst. Cobalt oxides (II) catalysts deactivated by reacting with Al_2O_3 support to form $CoAl_2O_4$ at temperature over 850 ^oC. The destruction of CH_2Cl_2 on titania catalyst showed poor activity.

A catalyst's overall effectiveness depends on the selectivity for products from practical detoxications. Previous research in the heterogeneous catalytic oxidation of low concentrations of chlorinated hydrocarbons with air has focused on identifying highly active catalysts and final reaction products at temperatures high enough to achieve essentially complete oxidation. In general, reaction conditions are chosen that result in complete oxidation to H_2O, CO_2, and HCl.

In recent years, a number of catalytic processes were being developed for destroying hazardous organics in aqueous waste stream. Baker et al., (1989) develop a catalytic process which can treat wastes that are too dilute in organic material to incinerate and are too toxic for biotreatment . The aqueous streams are treated with a reduced nickel catalyst at 350 ^oC to 400 ^oC and 3000 to 4000 psig, which converts the organics to innocuous gases.

Olfenbuttel (1991) developed new technologies for cleaning up contaminated ground water. The ground water containing volatile organic compounds (VOC's) can be treated by air stripping and catalytic destruction techniques. The technique originally was targeted to clean up tars and oils that often coat the walls and piping of wood and agriculture waste gasifiers and foul downstream processing equipment.

Test results show more than 90 % of incoming tars and oils in the gasifier products can be destroyed in a single catalytic step.

B. Basic Principles of Catalysis

1. General Description of a Catalyst

The basic concept of a catalyst is that of a substance that affects the rate of a reaction but emerges from the process unchanged. Many commercial heterogeneous catalysts are composed of an active material and a support. The active component is normally a metal or metal oxide, and the support is a ceramic or metal monolith. Molecules vary in size and chemical structure. So, different catalysts are necessary for different reaction processes. The optimization of a catalyst is specific for each reaction and requires selection of appropriate operating condition. Therefore, determination of performance of a catalyst is dependent on empirical results.

2. Catalytic Processes and Kinetic Characterization

In a catalytic process, reactants must interact with the "active site" on the catalyst, the term "active site" is thought to be that site (or sites) on the catalyst surface in which chemisorption and reaction occur. Basically, a catalytic process includes:(Augustine, 1988; Du, 1990)

1. Bulk diffusion: reactants must pass through stagnant film from the gas or liquid phase.

2. Pore diffusion: reactants diffuse or are transported through pore structures to active sites.

3. Chemisorption: a reactant chemically adsorbs on active sites i.e., by bonding.

4. Chemical reaction: a reactant converts to a product on the active sites.

5. Desorption: products desorb from the active sites.

6. Product diffusion: products diffuse through pore from the active sites.

7. Product diffusion: products diffuse through the film to the bulk gas or liquid phase.

Steps 1 and 7 are controlled by mass transfer limitation; steps 2 and 6 are controlled by pore diffusion limitations ; and steps 3,4 and 5 are controlled by chemical reaction limitations. The physical and chemical properties of catalysts and operating condition that control the rate of reaction should be carefully chosen.

Much research is required to optimize the properties of a catalyst and the conditions for its practical use. The effect of rate limiting phenomena is correlated with the Arrhenius expression from which activation energies are determined.

A general plot depicting the three rate regimes in catalysis is shown in Figure 1. Figure 2 illustrates a conversion versus temperature profile. The relationship used in plotting Figure 1, normally Ln k versus 1/T, is determined from the Arrhenius expression as follows:

$$k = A \exp(-E/RT)$$

$$\ln k = \ln A - (E/R)*(1/T)$$

where,

k = rate constant,

A = Pre-exponential constant,

E = activation energy (kcal/mole),

R = gas constant (kcal/mole*K),

T = absolute temperature (K).

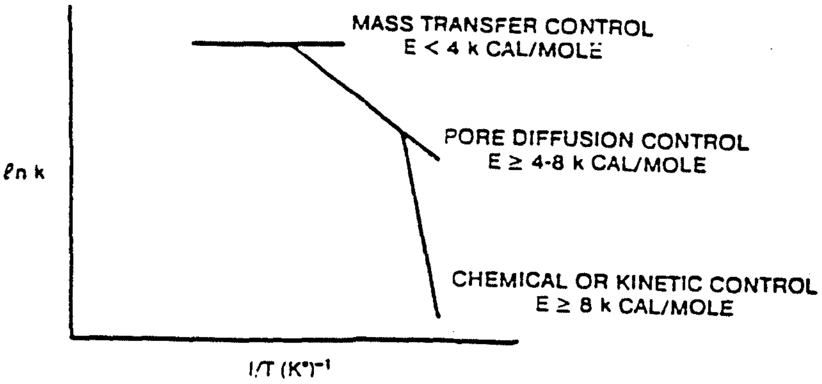


Figure 1 Arrhenius Equation

The calculation of the activation energy, E, from the slope of the Arrhenius plot allows an assessment of the rate limiting step. From Figure 2, it is evident that reactions controlled by chemical kinetics are most sensitive to temperature, while mass transfer controlled reaction are essentially temperature independent.

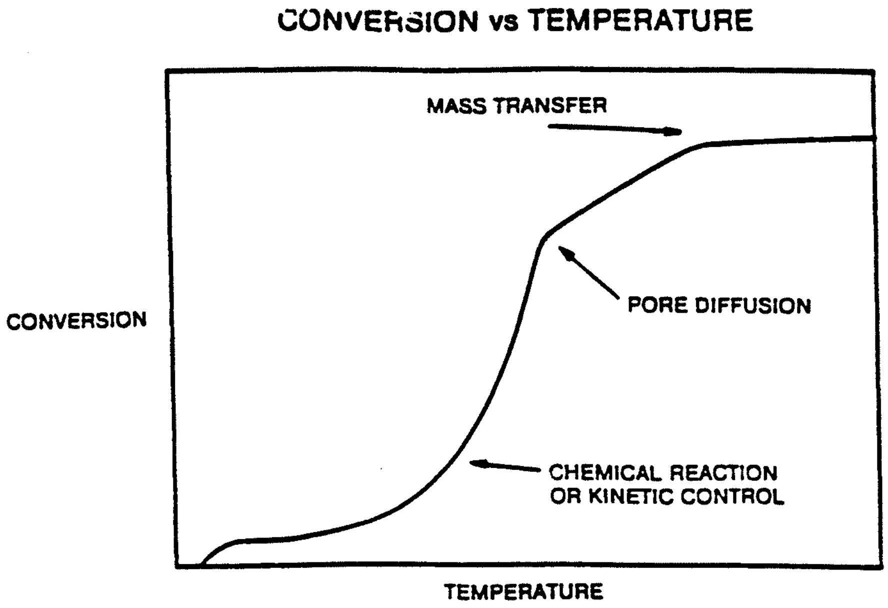


Figure 2 Conversion of reactant as a function of temperature showing rate controlling regions

3. Catalyst Deactivation

A catalyst may loose its activity or its selectivity for a wide variety of reasons. The causes may be grouped into:

1. poisoning
2. fouling
3. reduction of active area by sintering or migration
4. loss of active components.

A catalyst poison is an impurity present the feed stream that reduces catalyst activity. For oxidation of chlorinated hydrocarbons, a catalyst can be poisoned by chloride. It may poison a metal by forming a surface metal chloride, or it may enhance sintering via the formation of volatile metal chloride (Satterfield, 1980). Therefore, development of a chloride tolerant catalyst or an additives which can react with the chloride, thus avoiding catalyst poisoning is an important aspect for commercializing catalytic oxidation of chlorinated hydrocarbons.

III. EXPERIMENTAL APPROACH

A. Experimental Apparatus

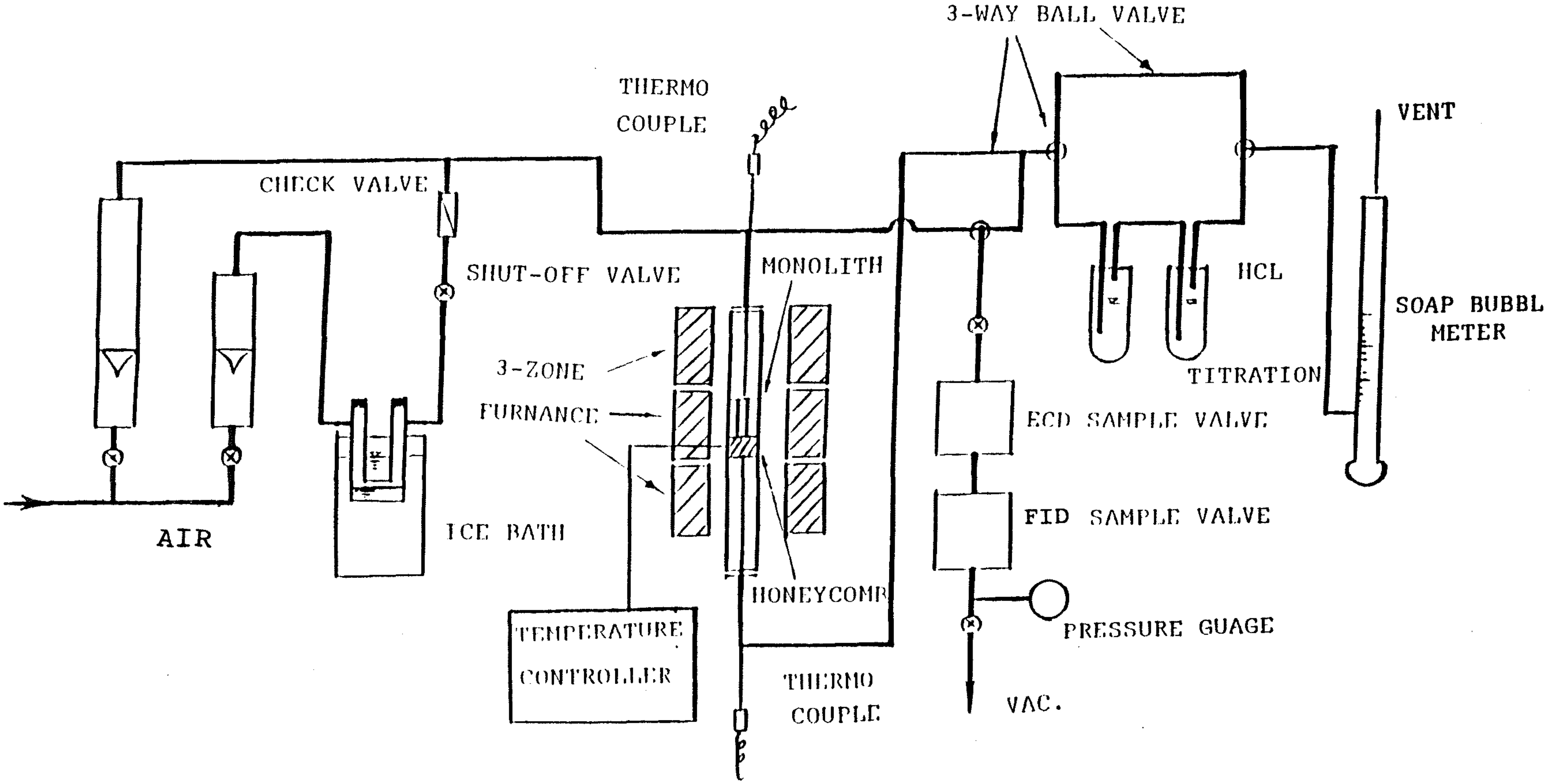
The experimental apparats flow schematic is shown in Figure 3. A tubular flow reactor is shown in Figure 4. This system consists of a quartz tube reactor (Kontes Scientific Glassware, Inc.) residing in a vertical three zone controlled furnace (Applied Test System, Inc.) containing known volumes of PdO honeycomb or powder catalyst.

A glass U-tube containing C_2HCl_3 (TCE) or CH_2Cl_2 (DCM) (Aldrich Chemicals, Co., 99.9%) feed in liquid form was placed in an ice-bath. The U-tube allows a portion of the air to bubble through the devise before mixing with the rest of the air and feeding the mixture to the reactor. In order to change the concentration of DCM or TCE, the split in the amount air or 20% O_2 in Helium (i. e., for improved thermal conductivity detection, (TCD), sensitivity) was varied into the reactant bubbler gas, with the rest of the air mixed at a junction after the bubbler. All gases were purchased from Liquid Carbonic, Inc. and were research grade purity, 99.95%. The flow rate of inlet gases were measured with two calibrated rotameters (Cole Parmer Co.).

The reactor temperatures were monitored by two Chromel-Alumel (K-type) thermocouples (Omega Engineering, Inc.) which were placed in both sides of the honeycomb catalyst. The reported temperature readings are based on average of inlet and outlet temperatures. Since the reaction

Figure 3

FLOW SCHEMATIC OF CATALYTIC OXIDATION UNIT



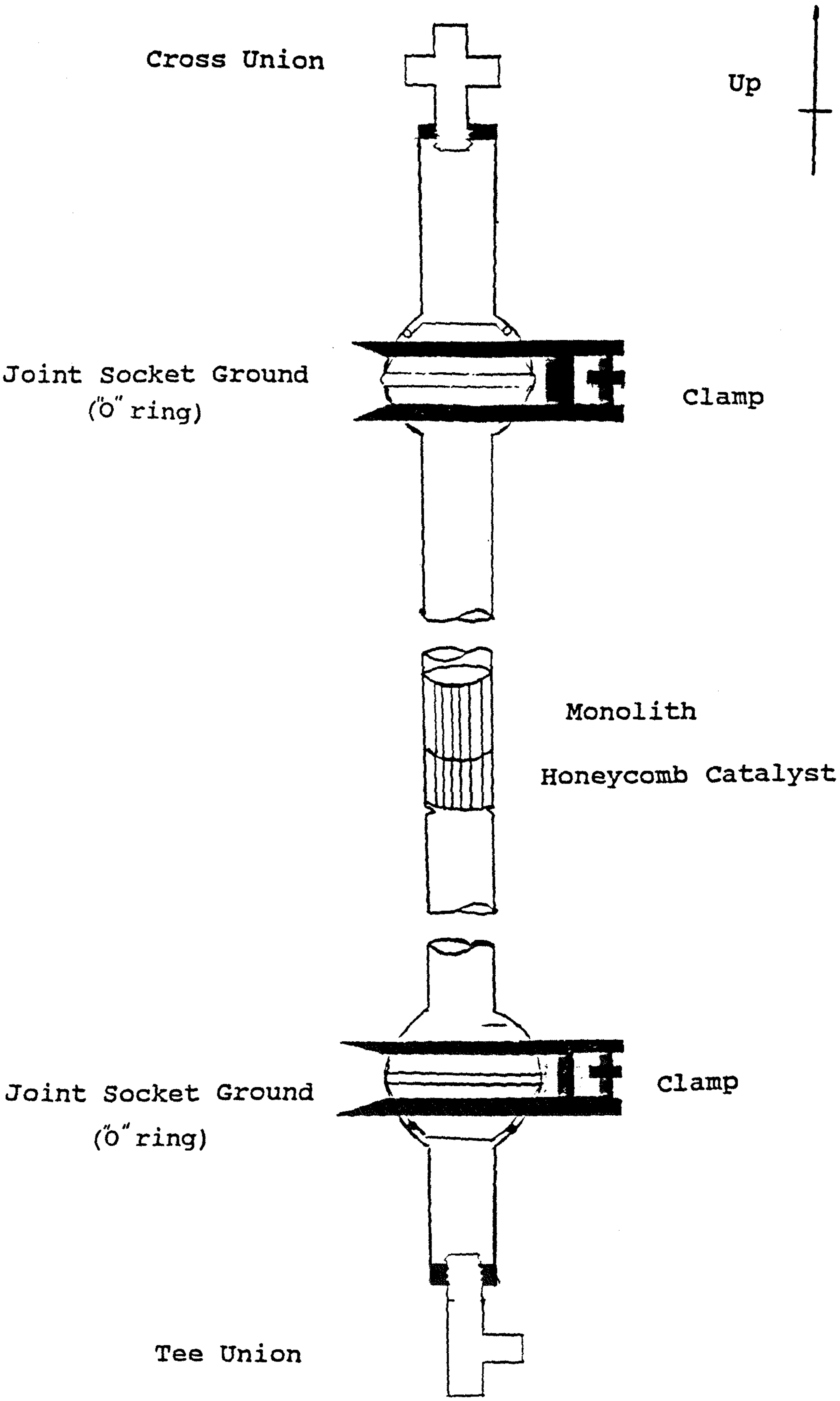


Fig. 4 Design for quartz tube reactor.

temperature was sufficiently low, no correction was made for radiation.

The product gas was analyzed by gas chromatography (GC) to determine the concentration of chlorinated hydrocarbons, CO, and CO_2. In addition, the product gas was bubbled through to a scrubber to absorb HCl gas in order to determine the concentrations of HCl. Drager gas color-detector tubes were employed to verify the concentrations of HCl and Cl_2. These tubes were supplied by SKC, Inc. The effluent gases from the scrubber, Drager tubes, and gas chromatographies were discharged to a laboratory hood.

B. Instrumental Analysis

Part of the effluent product stream, pulled by a vacuum pump, flowed through a six points gas sampling valve, from which it was picked up by the carrier gas to an on-line gas chromatograph. The GC operating conditions are as follows:

GC1 : for chlorinated hydrocarbons

Detector : ECD, HP 5890
Detector Temperature : 250 °C
Injection Temperature : 200 °C
Column Temperature : 40 °C
Carrier Gas : N_2, 30 ml/min
Column Packing Materials : 2% SE30 on Chromosorb GAW 80/100,1/8"x10′,ss (Alltech Associates, Inc.)
Integrator : HP 3396A
Chart Speed : 1 cm/min

GC2 : for CH_4, CO and CO_2

The CH_4, CO and CO_2 were analyzed by either flame ionization detector (FID) or thermal conductivity detector (TCD). Due to the limitations of TCD sensitivity, the sample gas is introduced into a nickel hydrogenation catalytic reactor to produce methane allowing the use of the very sensitive FID system. Figure 5 illustrates the flow schematic for the methanation reactor in the GC.

Detector : FID, HP 5890
Detector Temperature : 200 °C
Injection Temperature : 150 °C
Column Temperature : 40 °C
Carrier Gas : Helium, 5 ml/min
Auxiliary carrier gas : Helium, 30 ml/min
Packing Materials : Porapak Q 80/100,1/8"x6′ ss (HP)
Ni catalyst reaction Temperature : 350 °C
Air : 400 ml/min
H_2 : 35 ml/min
Integrator : HP 3396A
Chart Speed : 1 cm/min

Figure 6, 7 and 8 show typical peak resolution and retention times for the reactants and products.

The concentrations of HCl were determined by absorbing it in a bottle of 0.01 N NaOH solution with phenolphthalein indicator, and subsequently back titrating the solution with 0.01 N HCl solution. Also, the concentrations of HCl were double checked with Drager gas color-detector tubes. The

Figure 5 Nickle Hydrogenation Catalyst System

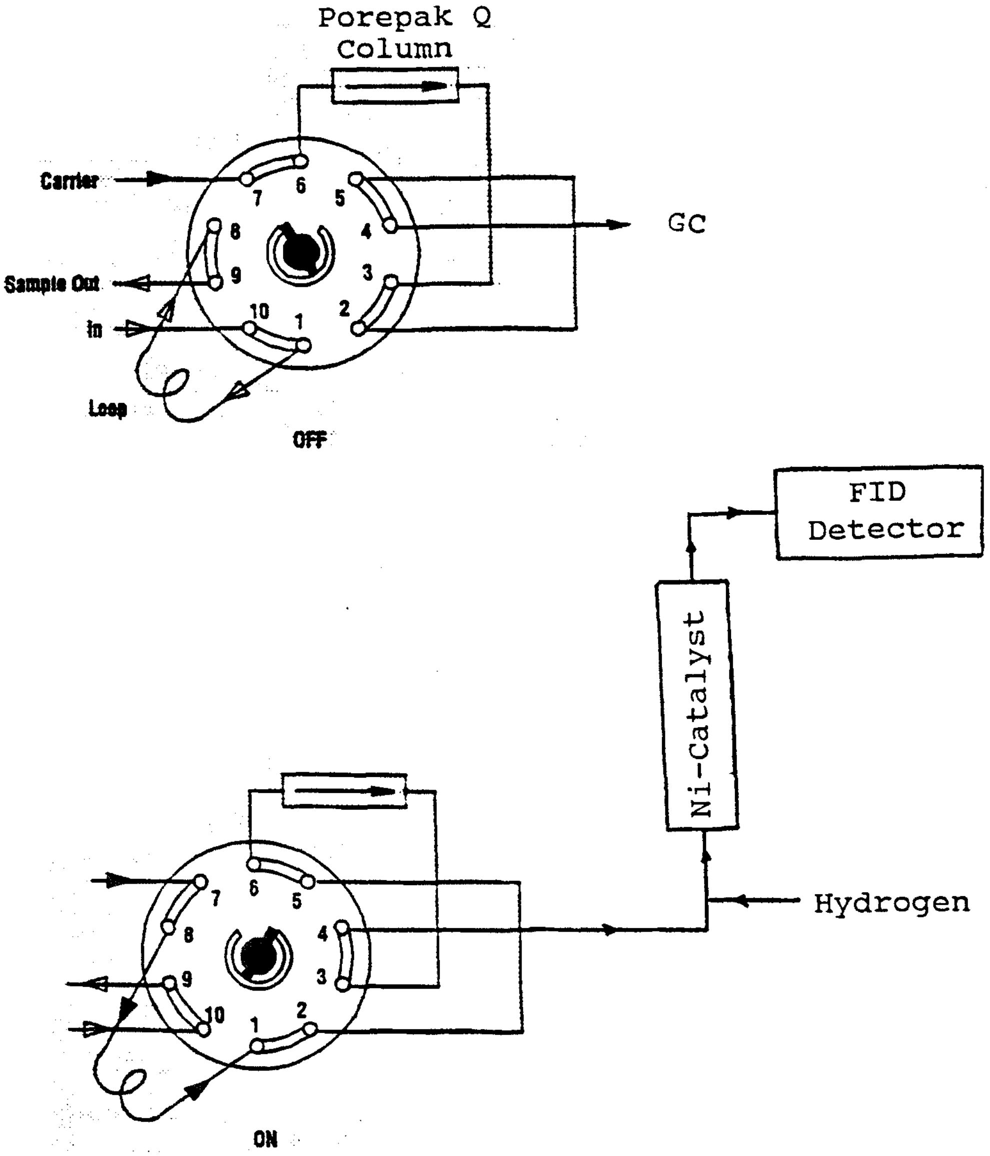


Figure 6 Peak resolution and retention times for chlorocarbon products from TCE oxidation.

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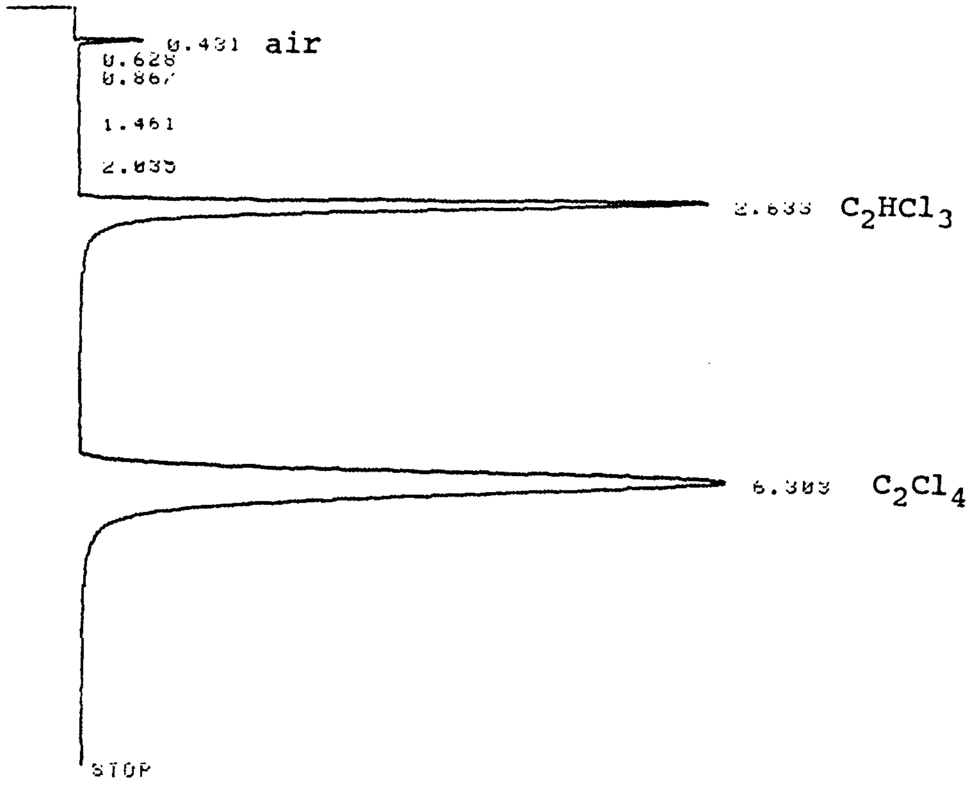

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    .628        995   BP    .028      .00127
    .867       1292   PV    .061      .00165
   1.461       3366   BP    .091      .00431
   2.035       5402   PP    .125      .00691
   2.633   22898672   PB    .164    29.29571
   6.303   54746240   PB    .383    70.04032

TOTAL AREA=7.8164E+07
MUL FACTOR=1.0000E+00
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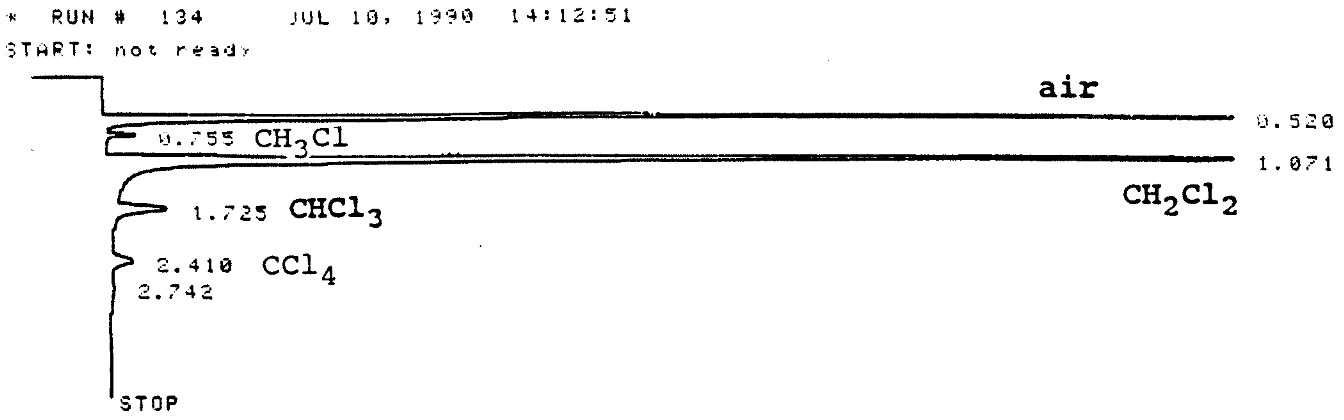
Figure 7 Peak resolution and retention times for chlorocarbon products from DCM oxidation.



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START: not ready
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    .755      71881   PB   .042      .76977
   1.071    4548787   PB   .065    48.71278
   1.725     309727   BB   .106     3.31685
   2.410     155338   BP   .126     1.66351
   2.742       3506   PB   .014      .03755

TOTAL AREA=9.3380E+06
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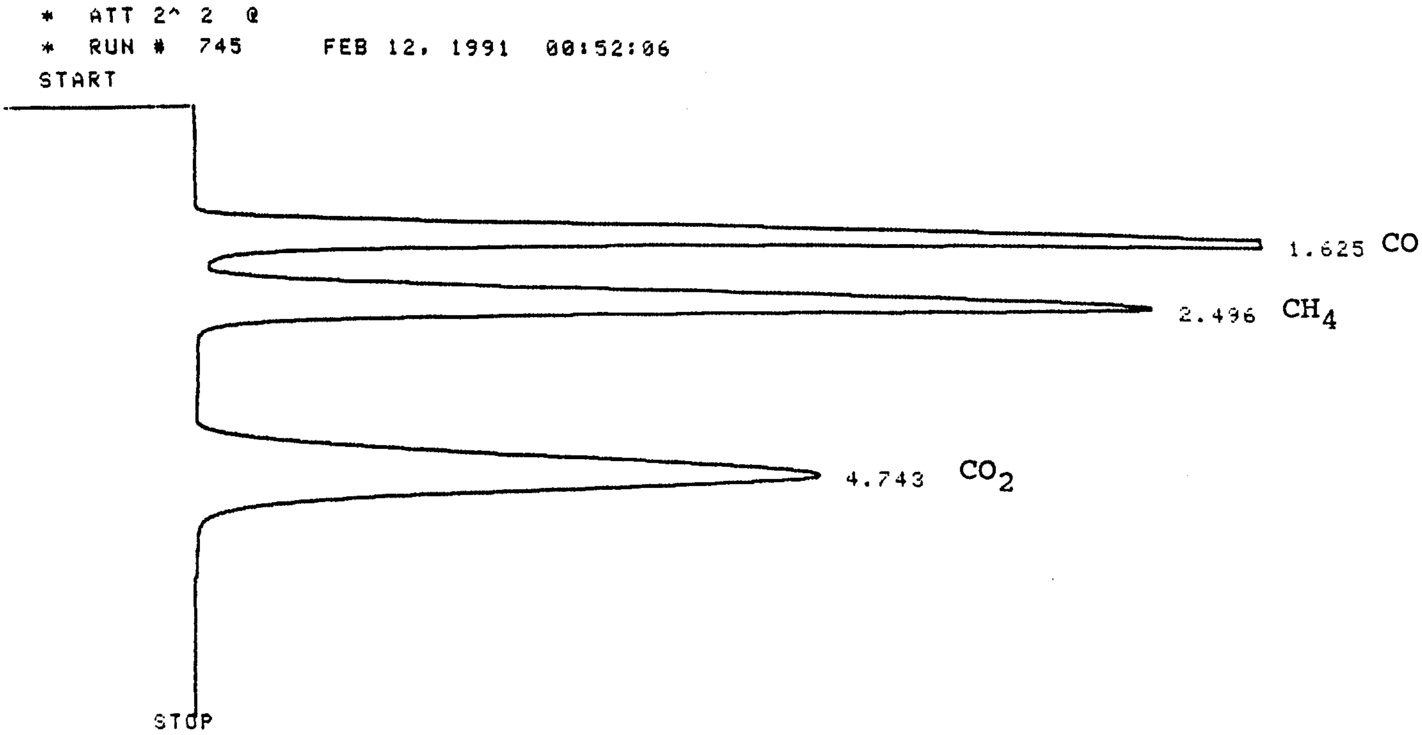
Figure 8 Peak resolution and retention times of CO_2, CO and CH_4 on FID.



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START
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   2.496     534768   VV   .327    33.23320
   4.743     561577   VP   .522    34.89925

TOTAL AREA=1609138
MUL FACTOR=1.0000E+00
```

concentrations of Cl_2 were determined by using Drager gas color-detector tubes. This method of analyses was reported to be accurate within 10 percent according to the manufacturer.

C. Catalyst Materials

The catalysts used in this study were provided by Engelhard. Those catalysts were supplied as either a powder catalysts (50-150 mesh) PdO content of (0.5%, 1%, 2%, and 4%) on alumina, or PdO over alumina on 400 cells per square inch cordierite monolith.

D. Experimental Procedures

1. Catalyst Characterizations

a. Temperature Programmed Reduction (TPR) and chemisorption (Huang et al., 1989; Hurst et al., 1982)

(1). Load 0.01 g powder catalyst into U-tube.

(2). Install U-tube on the Altamira Catalyst Characterization Instrument (Altamira Instruments, Inc.)

(3). Set operating parameters:

Step1:

Temperature: 40 °C,

Carrier gas: Ar, 30 ml/min

Step2:

Temperature: programmed temperature, 40°C to 350°C, ramp rate 10 °C/min

Carrier gas: 5% H_2 in argon

Step 3:

Hold on the Temperature at 350 ^{o}C for 5 minutes.

Step 4:

Cool down to room temperature and shift carrier gas to argon.

Inject adsorbate gas, CO, for 20 pulses.

Step 5:

Calculate total volume of CO which adsorbed on the surface of catalyst.

Step 6:

Repeat step 1-5 varied with the content of PdO on catalyst.

b. Activity Test

(1). Weigh 0.01 g catalyst and dilute with 0.1 g alumina.

(2). Pack in a tubular reactor.

(3). Set operating conditions:

flow rate: 960 ml/min,

feed concentration: 200 ppm,

reaction Temperature: 340 ^{o}C.

(4). Repeat 1-3 varied with the content of PdO on catalyst.

2. Catalytic Oxidation of Chlorinated Hydrocarbons

a. Dichloromethane (DCM)

(1). Feed concentration : 500 ppm.

(2). Oxidant: 20% O_2 in helium.

(3). Space velocity: 6000-34000 v/v/hr.

(4). Reaction Temperature: 250-550 °C

(5). Catalyst: 4% PdO/alumina/400 cpsi cordierite.

b. Trichloroethylene (TCE)

(1). Feed concentration: 200 ppm.

(2). Oxidant: 20% O_2 in helium or air.

(3). Space Velocity (SV): 4000-24000 v/v/hr.

(4). Reaction Temperature: 250-550 °C.

(5). Catalyst: 4% PdO/alumina/400 cpsi cordierite.

(6). Water effect: 1.5% water is added in the feed line (Heras et al., 1988).

(7). Methane effect: 0.5% methane is added in the feed line (Simone et al., 1991).

IV. RESULTS

A. Catalyst Characterization Analysis

Temperature programmed reduction (TPR) experiments were run with powdered catalysts containing 0.5 to 4 % PdO. The results are summarized in Figure 9. Only one peak appears on every plot at 72°C and this peak represents hydrogen consumption on the catalyst surface. It is determined that this metal oxide catalyst consumes hydrogen to reduce PdO to Pd and has one oxidation state, PdO. A linear relationship is obtained in Figure 10 indicating that the metal surface area of the catalyst is proportional to PdO content on catalyst and indicate that this peak is not caused by hydrogen dissolved in palladium. It is further observed that dispersion is not affected significantly when content of Pd is increased from 0.5% to 4%. Activity tests were run at the same operating condition which were summarized in the experimental procedure on page 23 (D.1-b). Figure 11 shows that conversion of TCE is proportional to PdO content on the catalyst. It is concluded that catalytic activity is proportional to PdO content. Hence, 4% PdO over alumina on 400 cpsi cordierite is employed for all the catalytic oxidation of dichloromethane (DCM) and trichloroethylene (TCE) research reported here.

B. Catalytic oxidation of TCE

1. Temperature and Space Velocity Effect on Reaction

The experiments were run over the temperature range 250-550°C. The initial concentrations of TCE were kept at around

Figure 9 Temperature Programmed Reduction (TPR) on PdO/Al2O3 Powder Catalyst

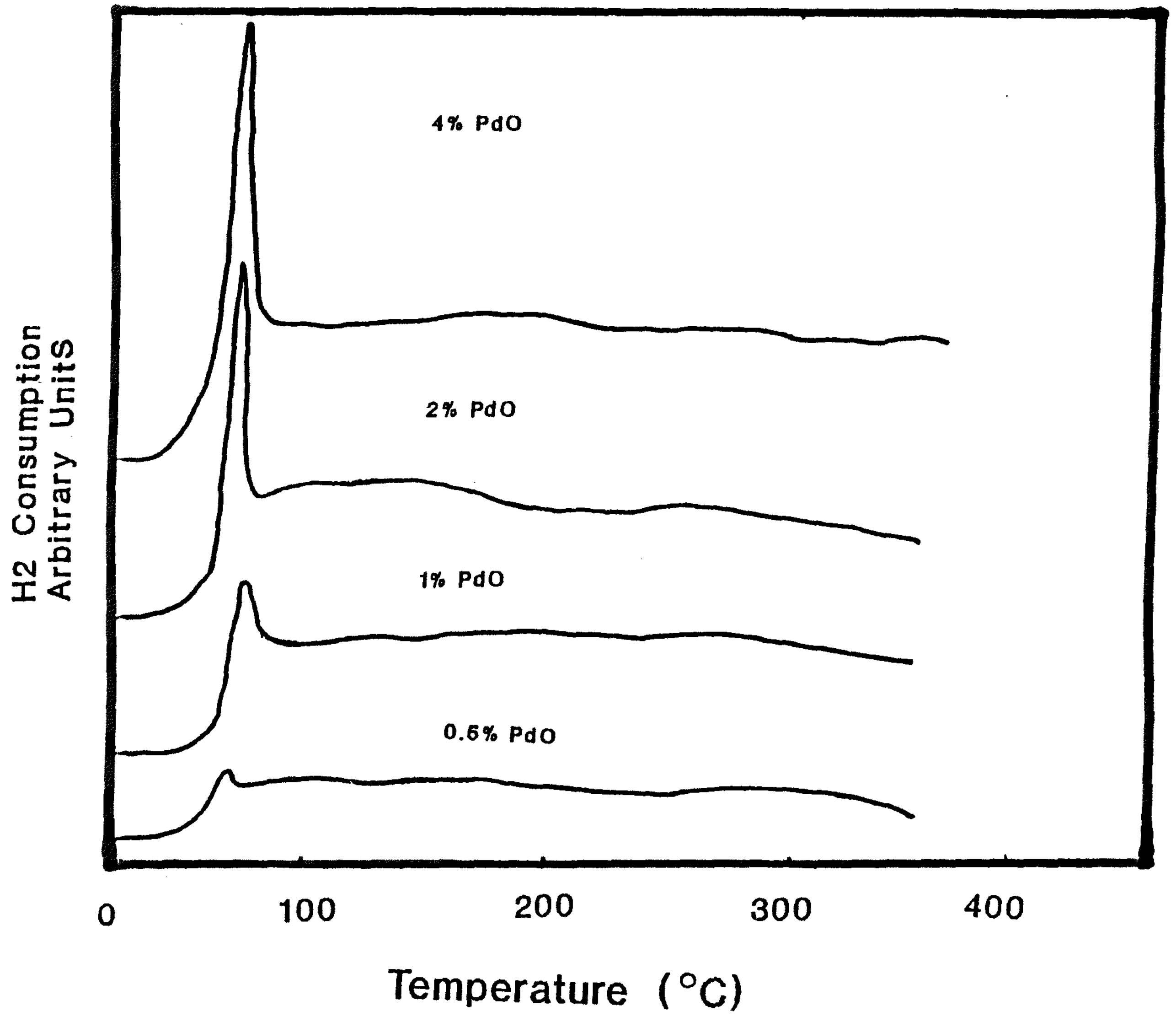


Figure 10 Hydrogen Consumption of TPR
on PdO/Al2O3 Powder Catalyst

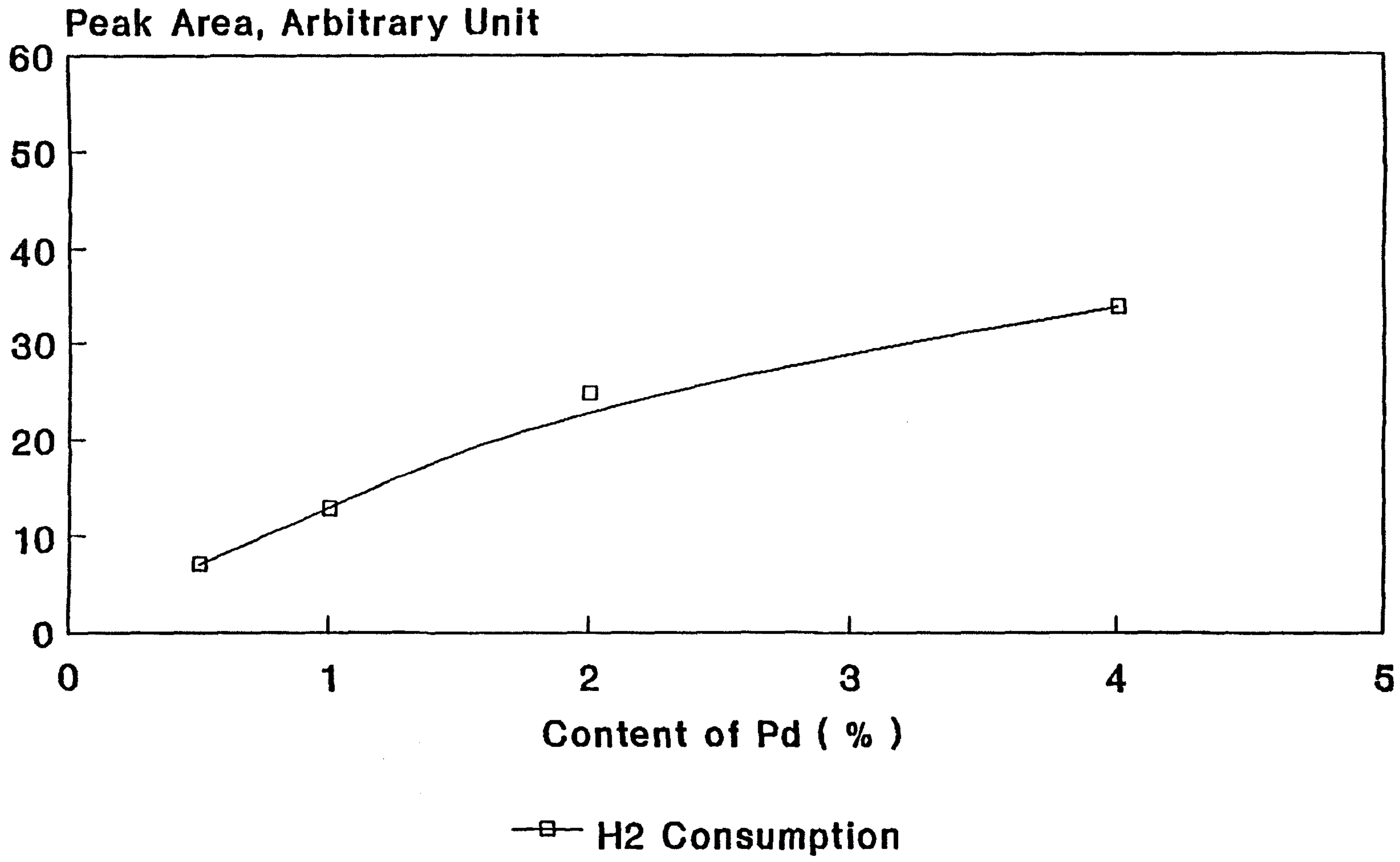
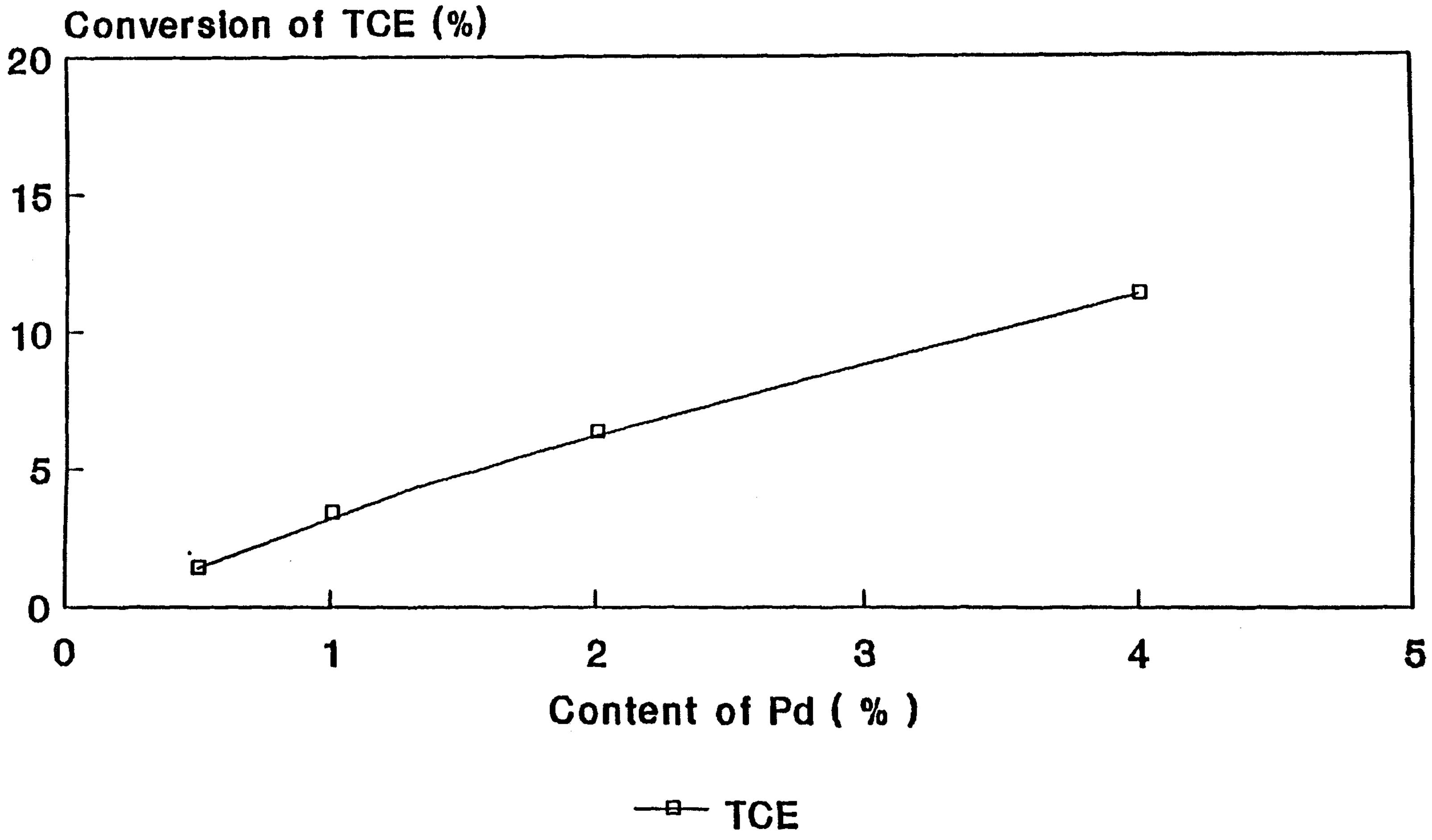


Figure 11 Activity Test on PdO/Al2O3 Powder Catalyst

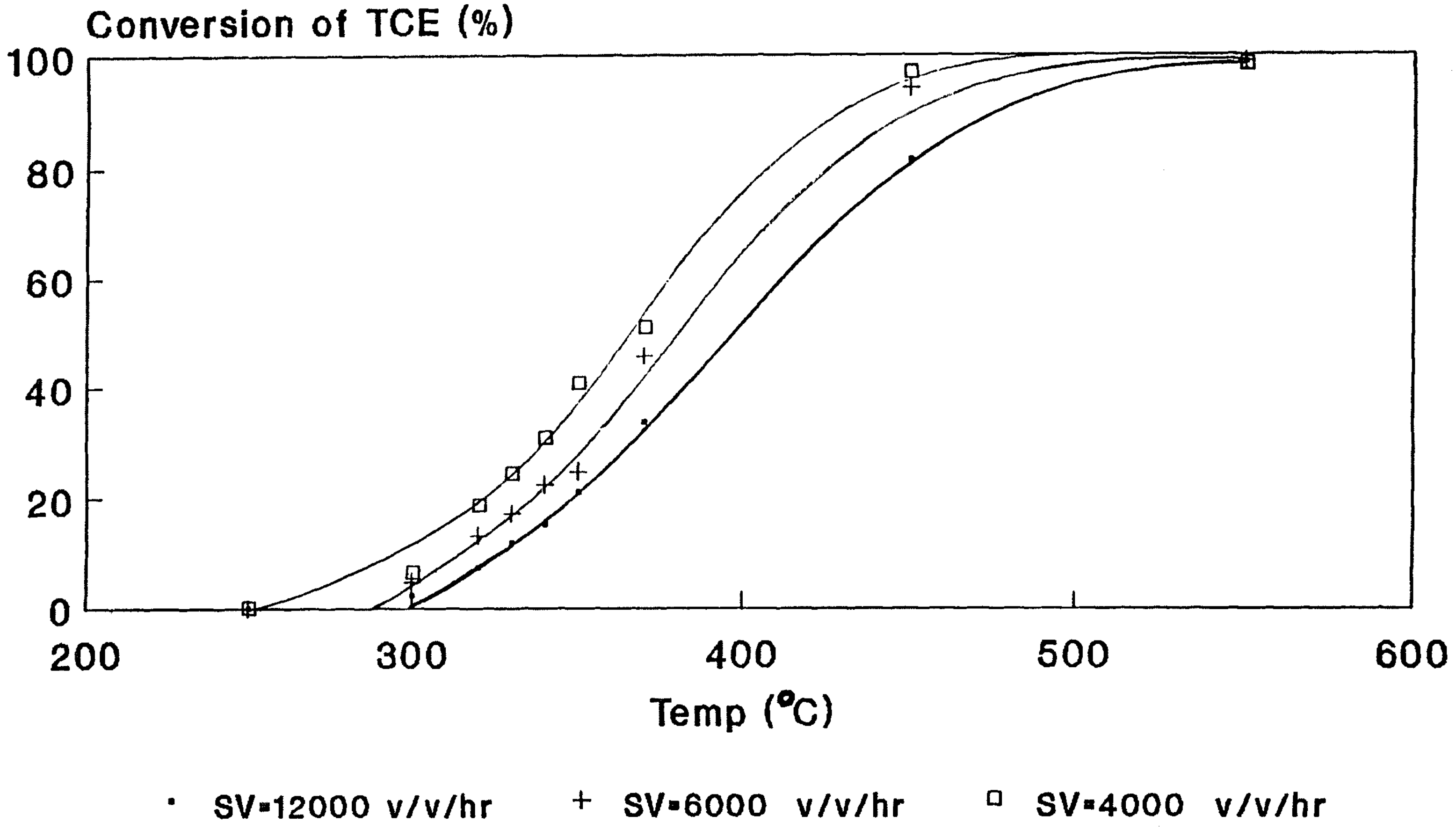


Initial Concentration: 200 ppm TCE
Flow Rate: 960 ml/min

200 ppm in this set of experiments. The conversion of TCE as a function of temperature is shown in Figure 11. As temperature is increased from 250 °C to 550 °C , the rate of conversion of TCE increases exponentially, this is followed by much reduced rate of conversion, and finally the rate of conversion approach zero. Figure 12 shows that conversion of TCE follows the three stages predicted from theory, kinetics control, pore diffusion control, and mass transfer control. Space velocity plays an important role in the reaction. Basically, higher light-off temperatures are measured at higher space velocities.

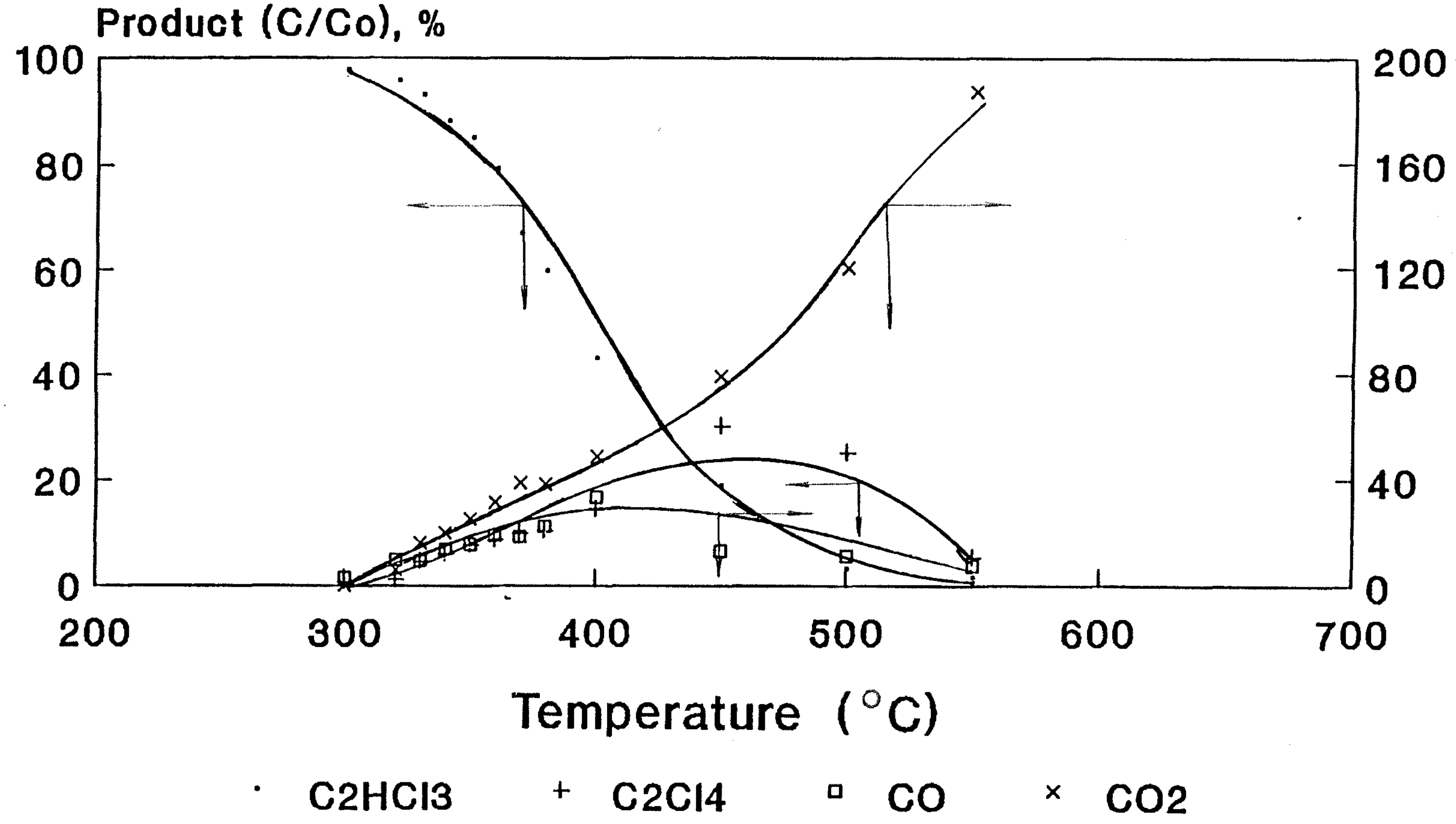
Product distributions for TCE oxidation as a function of space velocities are shown in Figures 13, 14 and 15 and Appendix Tables A.1 and A.2. It is shown that carbon balances (see Table 1) are well satisfied. The only chlorocarbon detected is C_2Cl_4, in addition to unconverted C_2HCl_3, over the space velocities range from 4,000 to 12,000 v/v/hr. Complete oxidation of TCE, i.e., conversion greater than 95 %, occurs at 550 °C. A comparison of TCE oxidized by air and 20% O_2 in Helium is shown in Figures 16 and 17. Tables 2 and 3 show that carbon and chlorine balance are well satisfied in these experimental results. The same product distribution was obtained with these oxidants at SV=6000 v/v/hr. The products at 550 °C are CO_2, C_2Cl_4, HCl, Cl_2 and C_2HCl_3. The total mass of chlorinated hydrocarbons are below 5% of initial concentration of TCE. Chlorine gas was found in comparable concentrations to HCl in these

Figure 12 Conversion of TCE as a Function of Temperature



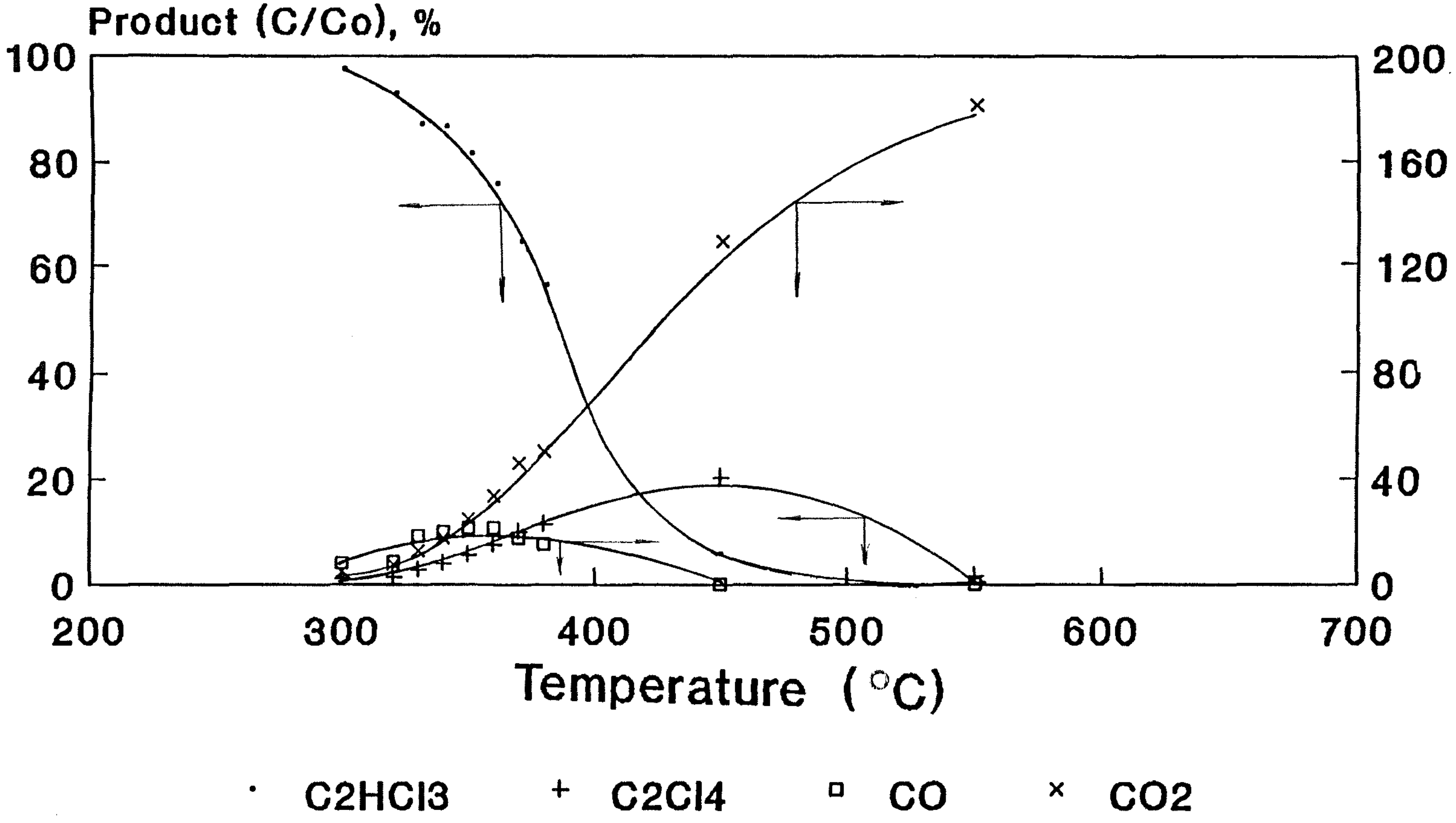
Initial concentration : 200 ppm
Oxidant : 20% O_2 in helium

Figure13 Product Distribution of C2HCl3 Oxidation



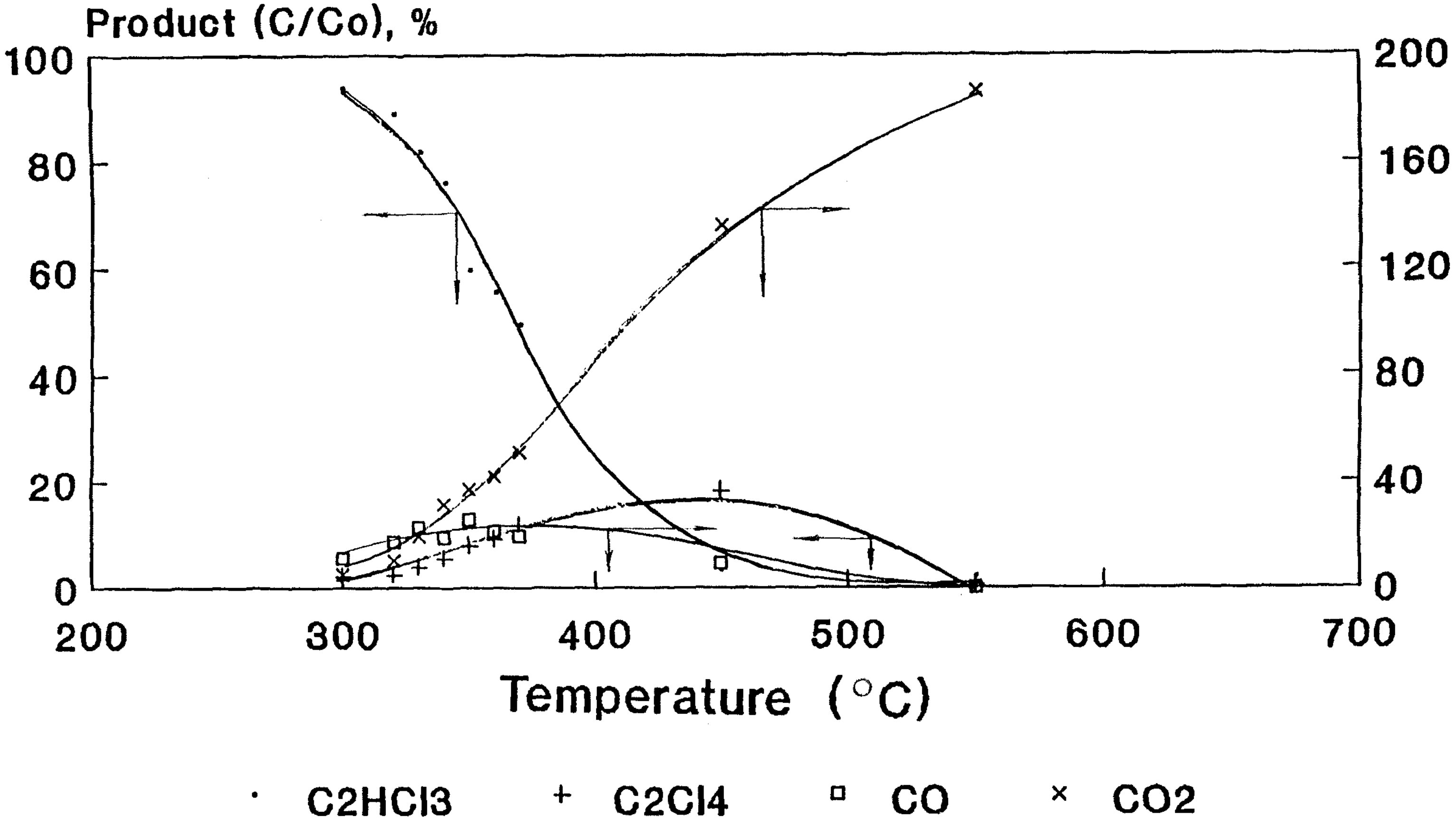
Space Velocity: 12000 v/v/hr
Oxidant: 20% O2 in Helium
Catalyst: 4% PdO/Al2O3/400cpsi monolith

Figure 14 Product Distribution of C2HCl3 Oxidation



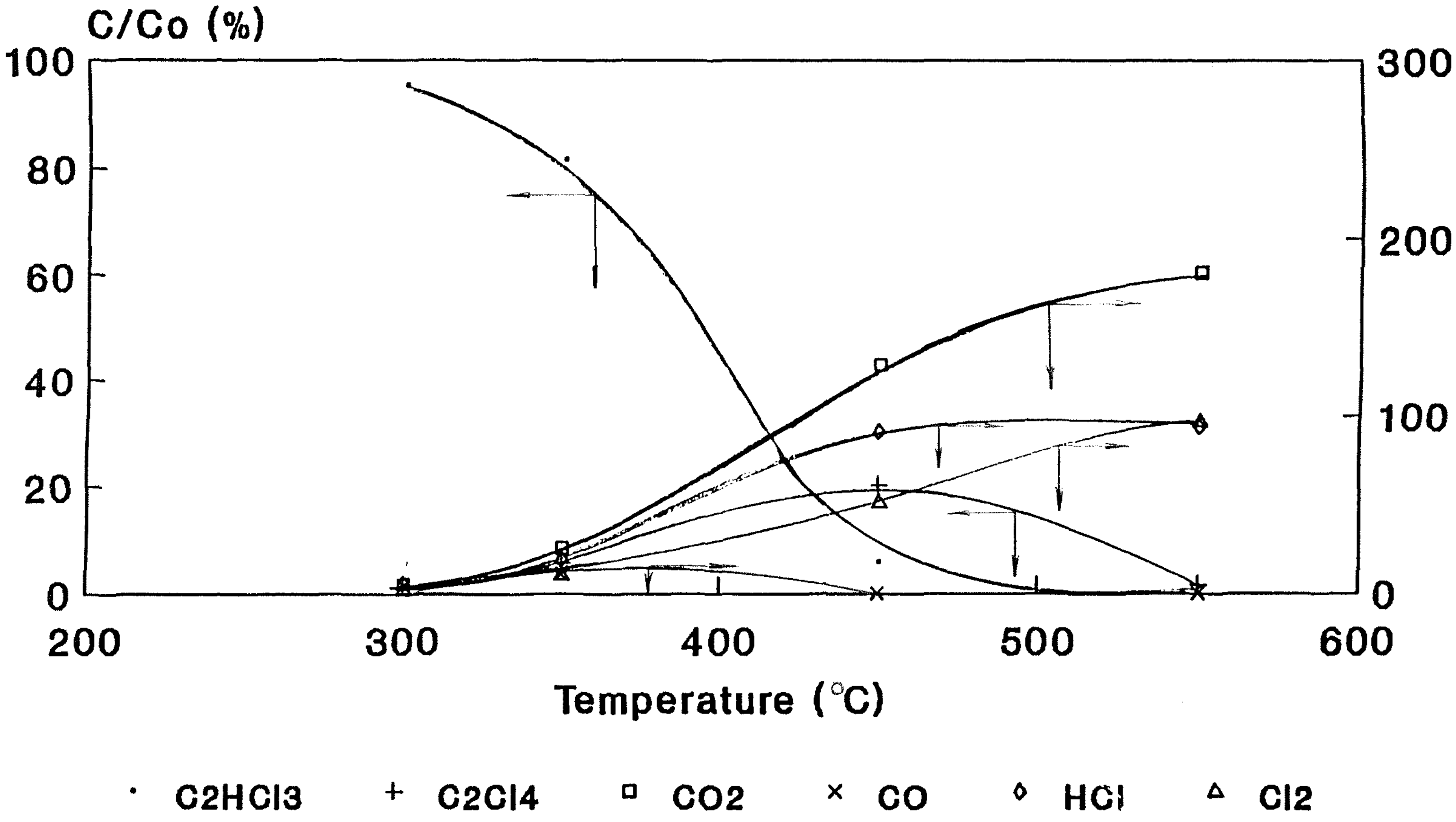
Space Velocity: 6000 v/v/hr
Oxidant: 20% O2 in Helium
Catalyst: 4% PdO/Al2O3/400cpsi monolith

Figure 15 Product Distribution of C_2HCl_3 Oxidation



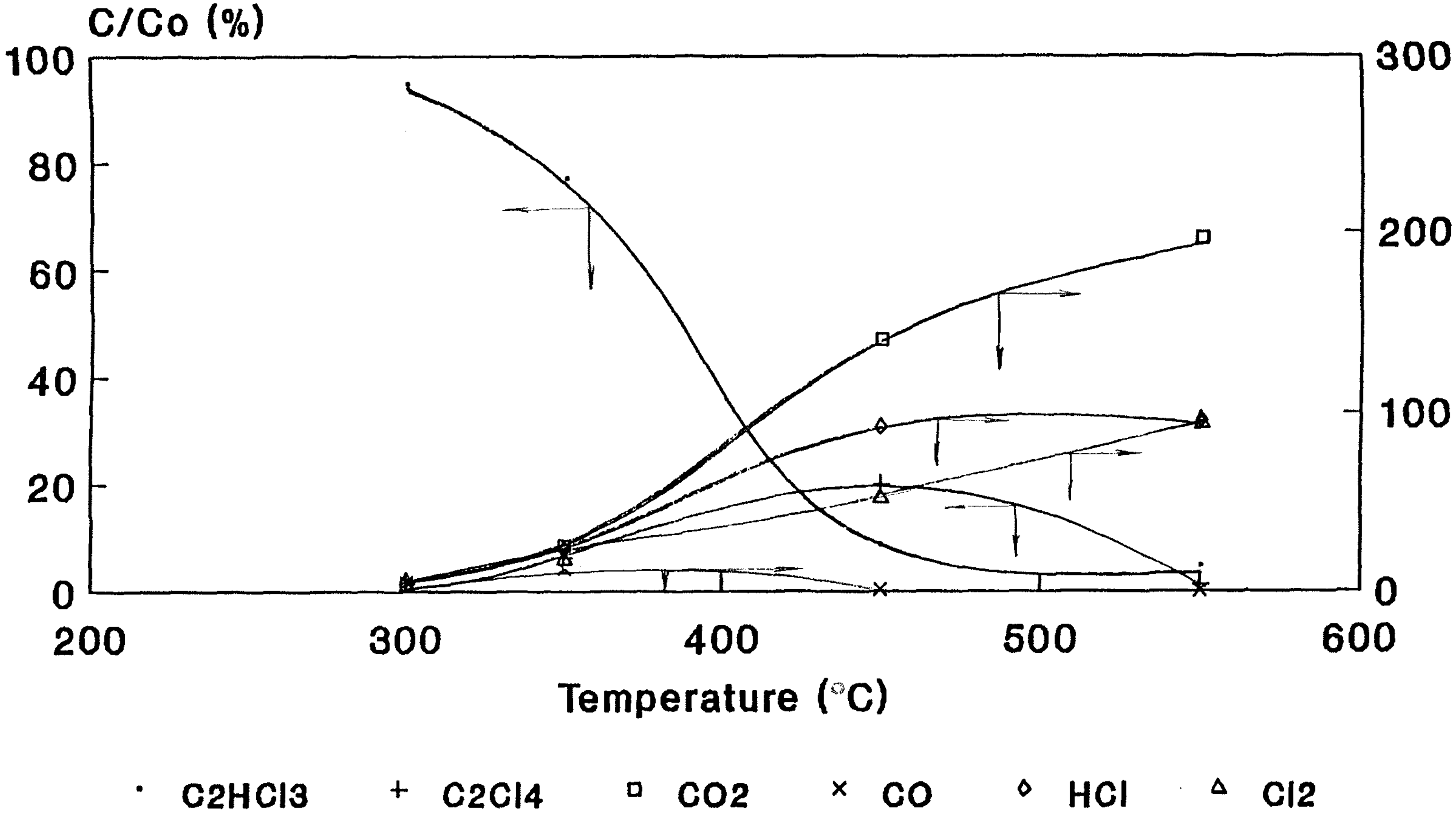
Space Velocity: 4000 v/v/hr
Oxidant: 20% O_2 in Helium
Catalyst: 4% PdO/Al_2O_3/400cpsi monolith

Figure 16 Product Distribution of TCE Oxidation



Space Velocity: 6000 v/v/hr
Oxidant: 20% O2 in Helium
Catalyst: 4% PdO/Al2O3 400 cpsi monolith

Figure 17 Product Distribution of TCE Oxidation



Space Velocity: 6000 v/v/hr
Oxidant: Air.
Catalyst: 4% PdO/Al2O3 400 cpsi monolith

Table 1 Product Distribution of Catalytic Oxidation of TCE over 4% PdO/alumina on Cordierite.

Temp (°C)	TCE, Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	Carbon balance %
300	220	215	1.5	3.1	0.0	99.1
320	222	212	2.4	10.4	12.0	102
330	228	212	10.3	10.0	36.0	107
340	228	201	13.5	15.0	44.7	107
350	228	194	17.6	17.3	57.0	109
360	208	164	18.1	21.4	64.9	104
370	206	137	20.4	18.5	79.1	100
380	228	136	23.3	25.1	86.2	94.3
400	227	97.6	32.9	37.7	110	90.3
450	219	41.0	66.0	14.0	173	91.3
500	219	6.6	55.0	11.8	264	90.9
550	215	3.0	11.2	7.3	403	102

SV = 12,000 v/v/hr
Oxidant : 20% O_2 in helium
Date : 01/08/91

Table 2 Product Distribution of Catalytic Oxidation of TCE over 4% Pdo/alumina on Cordierite

Temp (^oC)	TCE, Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	HCl (ppm)	Cl_2 (ppm)	Carbon balance %	Chlorine balance %
300	222	212	2.2	8.7	9.8	10.4	2.4	103	98.9
350	231	180	13.4	24.7	57.1	43.0	22.6	101	98.1
450	224	13.0	45.5	0.0	289	202	114	90.6	96.9
550	224	2.5	3.4	0.0	405	209	215	92.9	98.2

SV = 6,000 v/v/hr
Oxidant : 20% O_2 in helium
Date : 01/16/91

Table 3 Product Distribution of Catalytic Oxidation of TCE over 4% Pdo/alumina on Cordierite

Temp (^oC)	TCE, Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	HCl (ppm)	Cl_2 (ppm)	Carbon balance %	Chlorine balance %
300	213	202	2.8	9.8	7.5	17.9	10	100	102
350	213	164	13.0	25.8	54.1	50.5	18	102	98.6
450	205	17.0	40.8	1.4	288	185	105	99	99.0
550	203	8.9	2.2	0.0	399	185	189	104	98.0

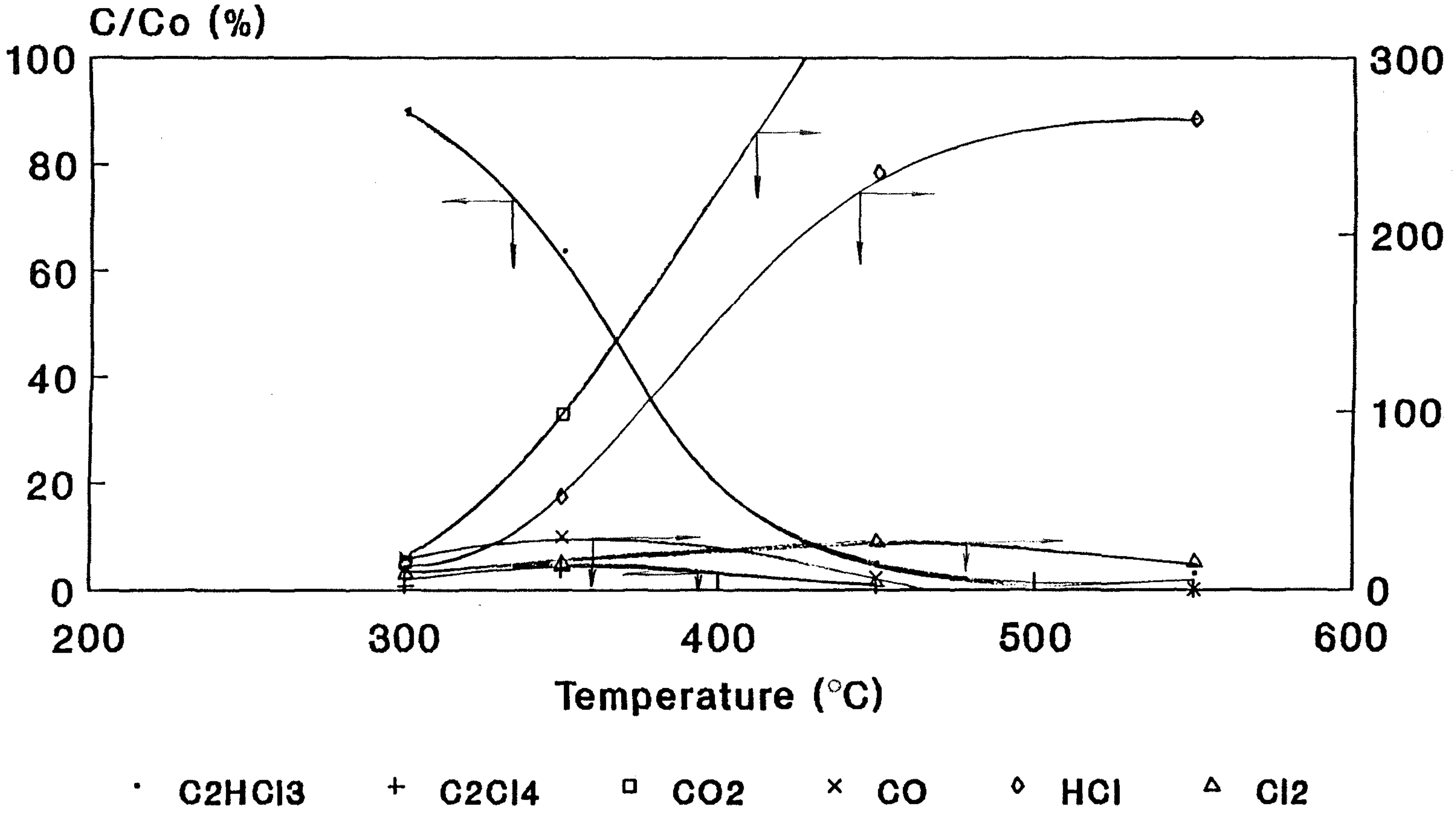
SV = 6,000 v/v/hr
Oxidant : Air
Date : 02/14/91

experiments because TCE contains more chlorine atoms than hydrogen atoms. It is desirable to inhibit the formation of chlorine gas and enhance the selectivity to hydrogen chloride in this system because chlorine is a toxic gas that is not easily collected.

2. Methane Effect on TCE Oxidation

The methane effect on TCE oxidation was investigated in these experiments because it provides not only hydrogen atoms which react with chlorine to produce hydrogen chloride, but it itself oxides to provide heat which increases the rate of TCE oxidation. The product distribution of TCE oxidation in the presence of 0.5% methane in air is shown in Figure 18 and summarized in Table 4. It was found that the concentration of hydrogen chloride was increased and the concentration of chlorine was reduced substantially as temperature increased. Formation of byproduct C_2Cl_4 was also substantially reduced. However, the rate of CO formation at low temperatures increased. Figure 19 shows how conversion of TCE is improved in the presence of CH_4, when compared to the reaction without methane at low temperatures. Clearly methane is oxidized and provides heat to enhance the conversion of TCE. However, the rate of conversion of TCE at high temperatures does not change significantly with the addition of methane. Figure 20 summarizes the comparison of conversion of methane with TCE and without TCE. The results show TCE inhibits methane oxidation.

Figure 18 Product Distribution of TCE Oxidation



Space Velocity: 6000 v/v/hr
Oxidant: Air, added with 0.5% Methane
Catalyst: 4% PdO/Al2O3 400 cpsi monolith

Table 4 Product Distribution of Catalytic Oxidation of TCE over 4 % PdO/alumina on Cordierite

Temp (°C)	TCE Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	HCl (ppm)	Cl_2 (ppm)	CH_4 Co (ppm)	CH_4 (ppm)	H_2O (ppm)	Carbon balance %	Chlorine balance %
300	209	188	1.5	26.0	22.6	29.3	17.0	4935	4925	15.9	100	101
350	231	147	8.2	52.7	150	120	32.8	4911	4832	140	99.5	95.2
450	238	11.3	1.3	8.4	1315	559	63.8	4878	3902	3784	98.1	102
550	226	6.6	0.0	0.0	4728	599	33.9	4901	392	8828	95.9	101

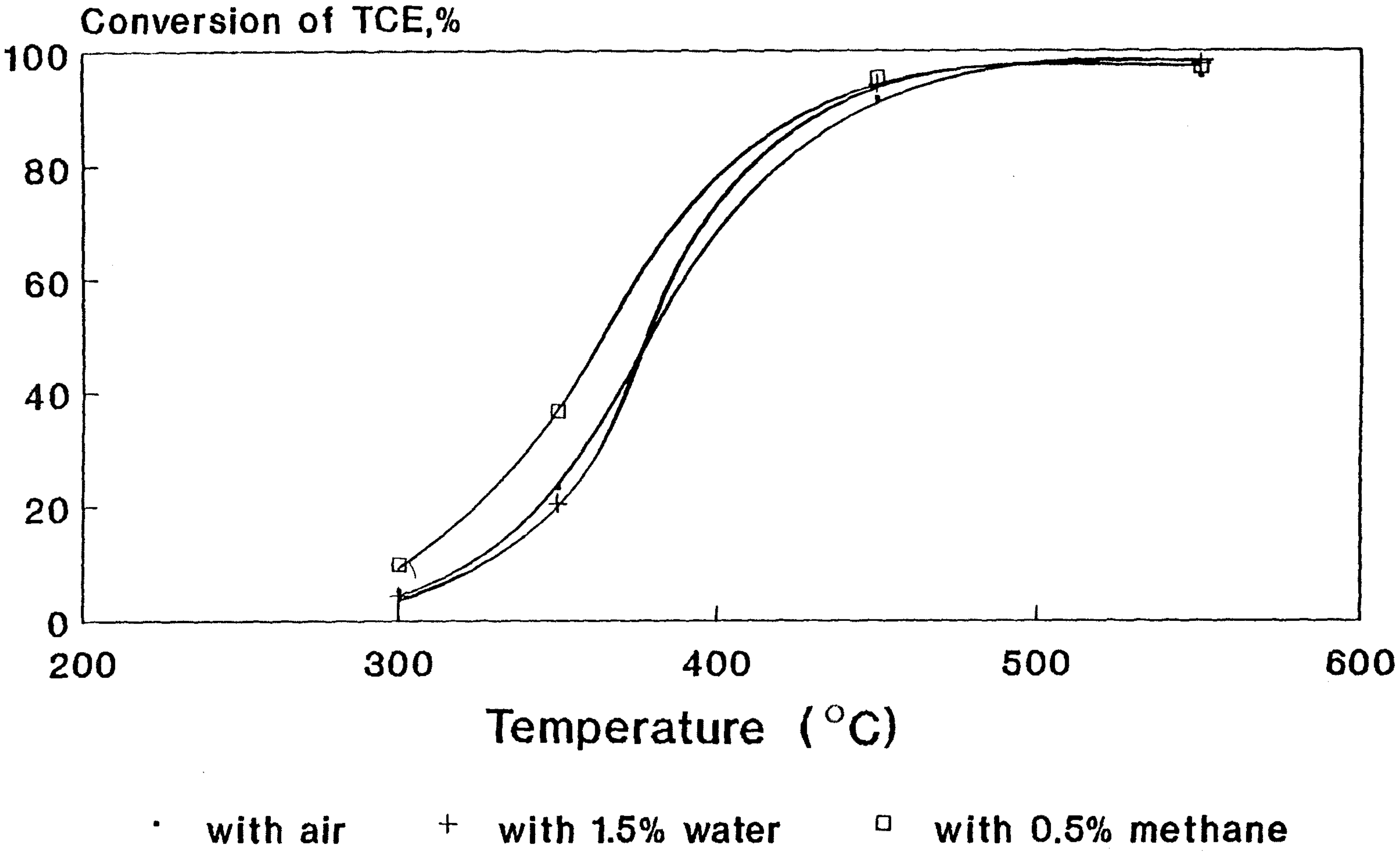
SV = 6,000 v/v/hr
Oxidant : Air
Date : 02/23/91

Table 5 Product Distribution of Catalytic Oxidation of TCE over 4% Pdo/alumina on Cordierite

Temp (°C)	TCE, Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	HCl (ppm)	Cl_2 (ppm)	Carbon balance %	Chlorine balance %
300	214	204	1.0	0.0	47.6	11.1	6.6	107	99.7
350	233	185	1.9	0.0	100	72.5	31.2	102	98.8
450	219	12.5	1.8	4.4	420	512	61.3	103	103
550	195	4.5	1.0	0.0	392	538	25.0	103	104

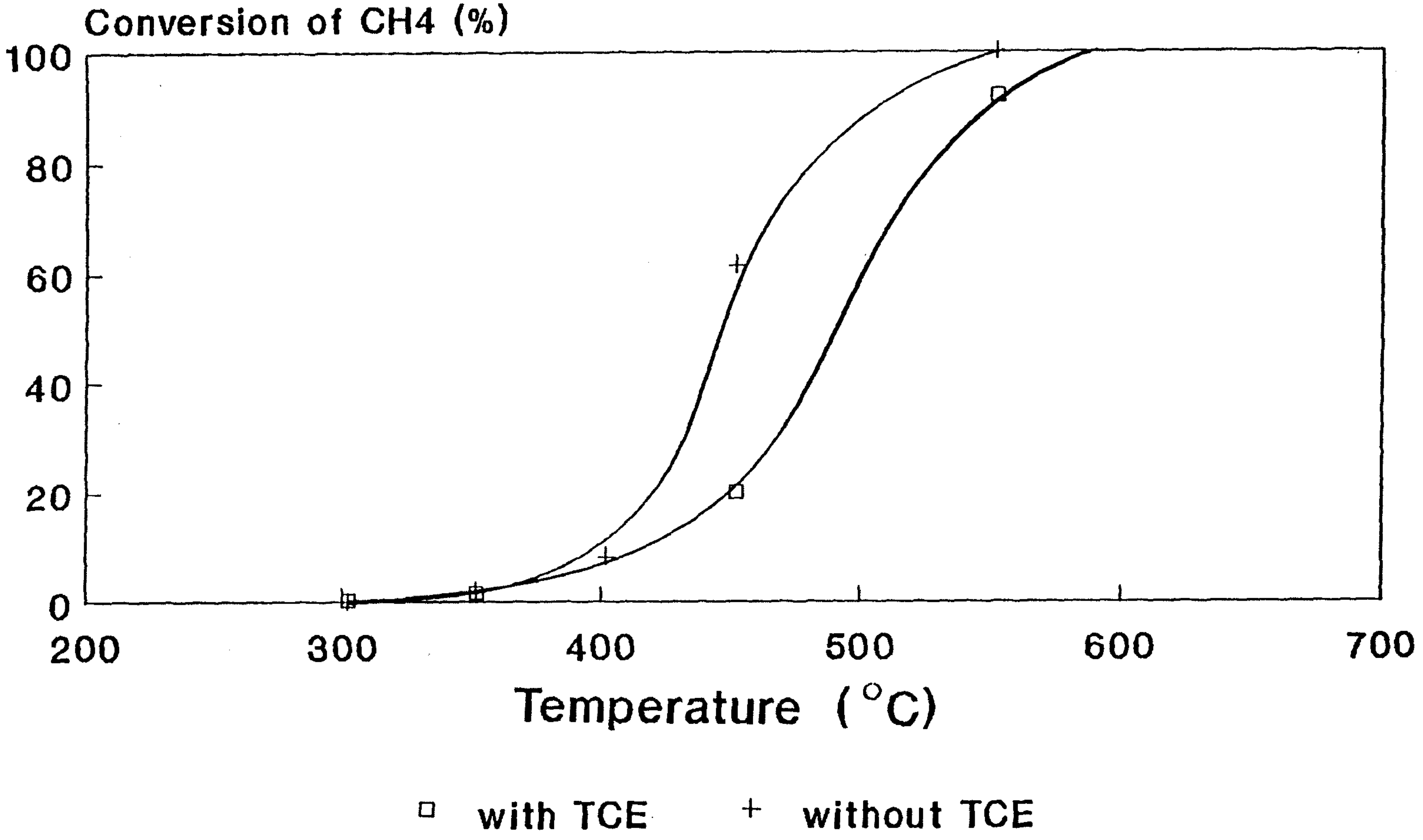
SV = 6,000 v/v/hr
Oxidant : Air, added with 1.5% water
Date : 02/19/91

Figure 19 Conversion of TCE Catalytic Oxidation



SV=6000 v/v/hr
4% PdO on Al2O3/400 cpsi Cordierite

Figure 20 Catalytic Oxidation of CH4 over 4% PdO on Al2O3/monolith



SV = 6000 v/v/hr
Methane Co = 0.5%

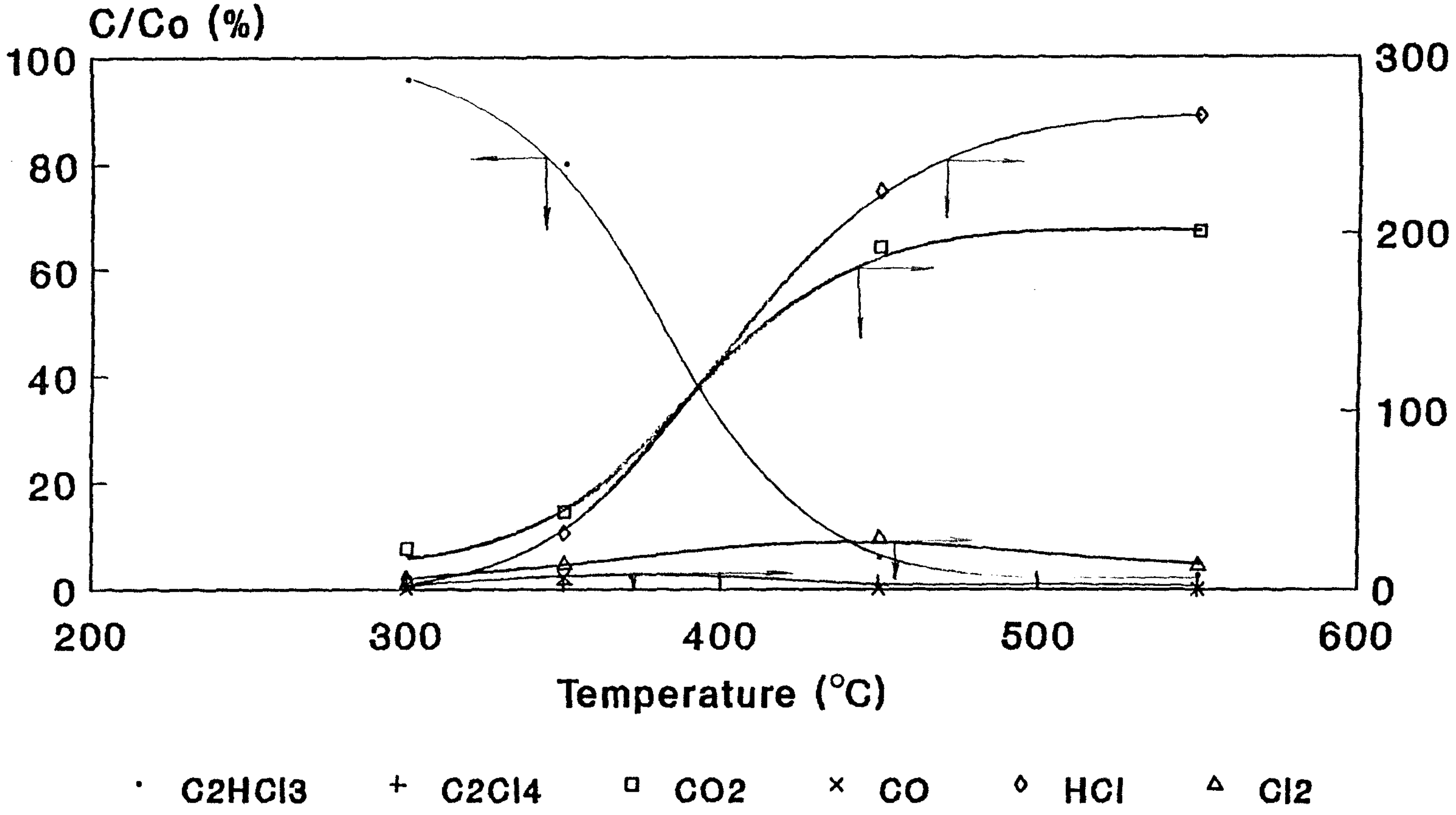
3. Water Effect on TCE Oxidation

In order to convert the Cl_2 normally produced from the oxidation of TCE to HCl, a common hydrogen source, water, was added. It has been suggested that water can easily dissociate on the oxygen-precovered surface of the catalyst which provide hydrogen atoms to react with chlorinated hydrocarbons at low temperatures (Heras and Viscido, 1988). Alternately, mechanism can be written that includes surface gas phase reactions of Cl atoms with water to give HCl and OH (Narayanan et al., 1990). The product distribution from the catalytic oxidation of TCE with the addition of 1.5% water is shown in Figure 21. It is observed that activity is not affected by the addition of water, and the rate of C_2Cl_4 byproduct formation is reduced drastically. No significant amount of CO is detected at low temperatures since water dissociation probably causes the water gas-shift reaction to take place on the surface of PdO catalyst. Material balance for this reaction is summarized in Table 5. The results show selectivity to hydrogen chloride is enhanced with water addition.

4. Oxygen Effect on Mechanism and Kinetic Study

In these experiment, air was employed as an oxidant. However, 20% O_2 in helium was used during initial experiments as simulated air in order to enhance the response of the GC thermal Conductivity detector for CO and CO_2. Later, a nickel catalytic reactor was installed upstream from the FID detector allowing CO and CO_2

Figure 21 Product Distribution of TCE Oxidation



Space velocity: 6000 v/v/hr
Oxidant: air, added with 1.5% water
Catalyst: 4% PdO/Al2O3/400 cpsi monolith

methanation and thus enhanced sensitivity for CO and CO_2. Figures 16 and 17 show product distribution of TCE catalytic oxidation with air or 20% O_2 in helium. The results show no difference between these two oxidants. So, previous experiments run with 20% O_2 in helium are compatible with results of experiment run with air.

In these experiments, O_2 was in large stoichiometric excess over 200 ppm TCE. For kinetics study, the measured rates of oxidation of TCE in air are correlated first using the empirical power law form:

$$-r_{C2HCl3} = k_1 C_{C2HCl3}{}^{a} C_{O2}{}^{b} \text{ , gmole/sec,} \qquad (4\text{-}1)$$

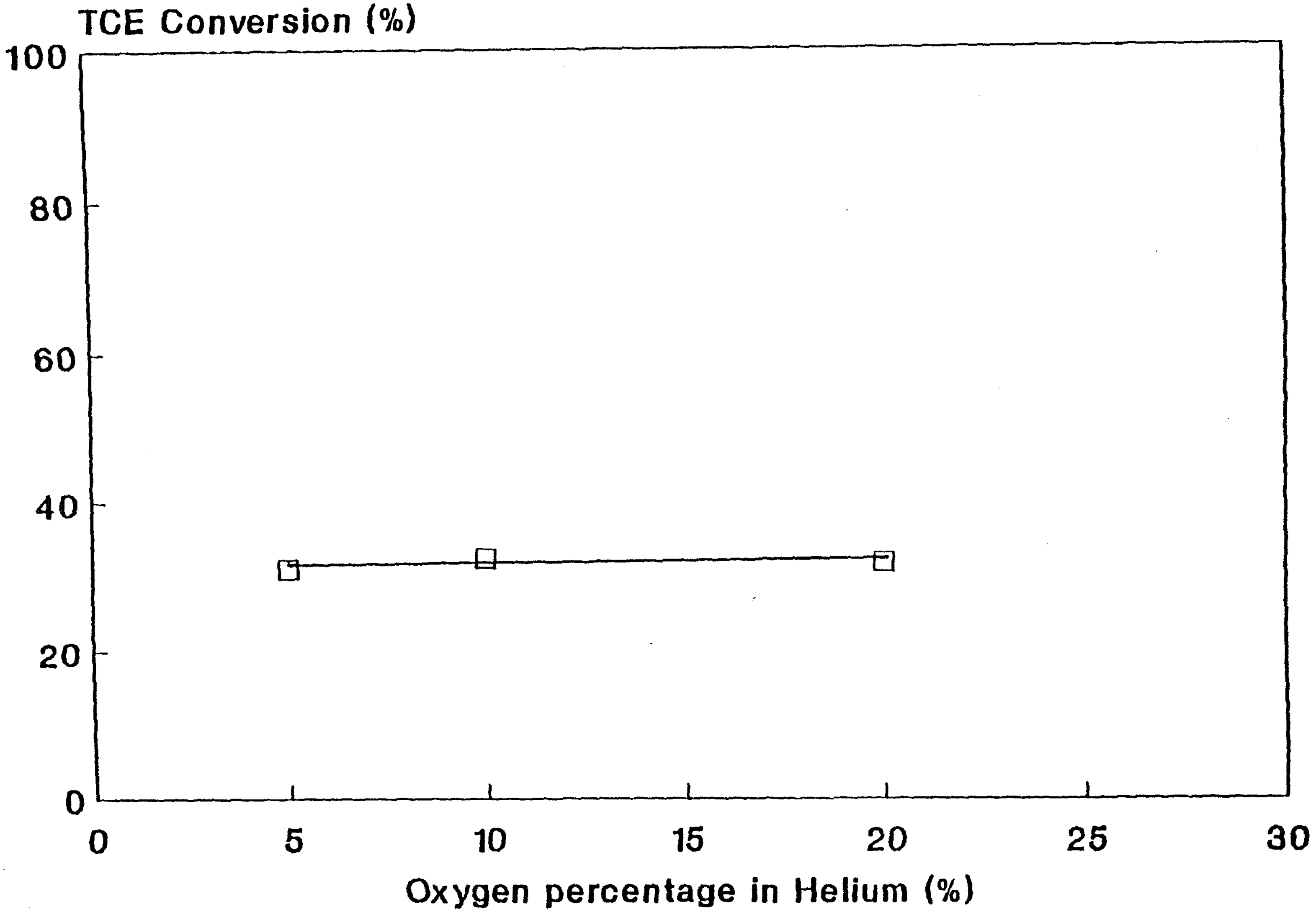
where C_{C2HCl3} and C_{O2} are the concentrations of C_2HCl_3 and O_2, respectively. The reaction order, with respect to O_2, was studied by changing the concentration of oxygen. From Figure 22., the change of concentration of oxygen over the range studied has no marked effect on the rate of oxidation of C_2HCl_3 Therefore, it was concluded that the rate of C_2HCl_3 oxidation was zero order with respect to oxygen within the experimental conditions studied. Therefore, the rate reaction can be written:

$$-r_{C2HCl3} = k_2 C_{C2HCl3}{}^{a}\text{, gmole/sec,} \qquad (4\text{-}2)$$

where $k_2 = k_1 {*} C_{O2}$.

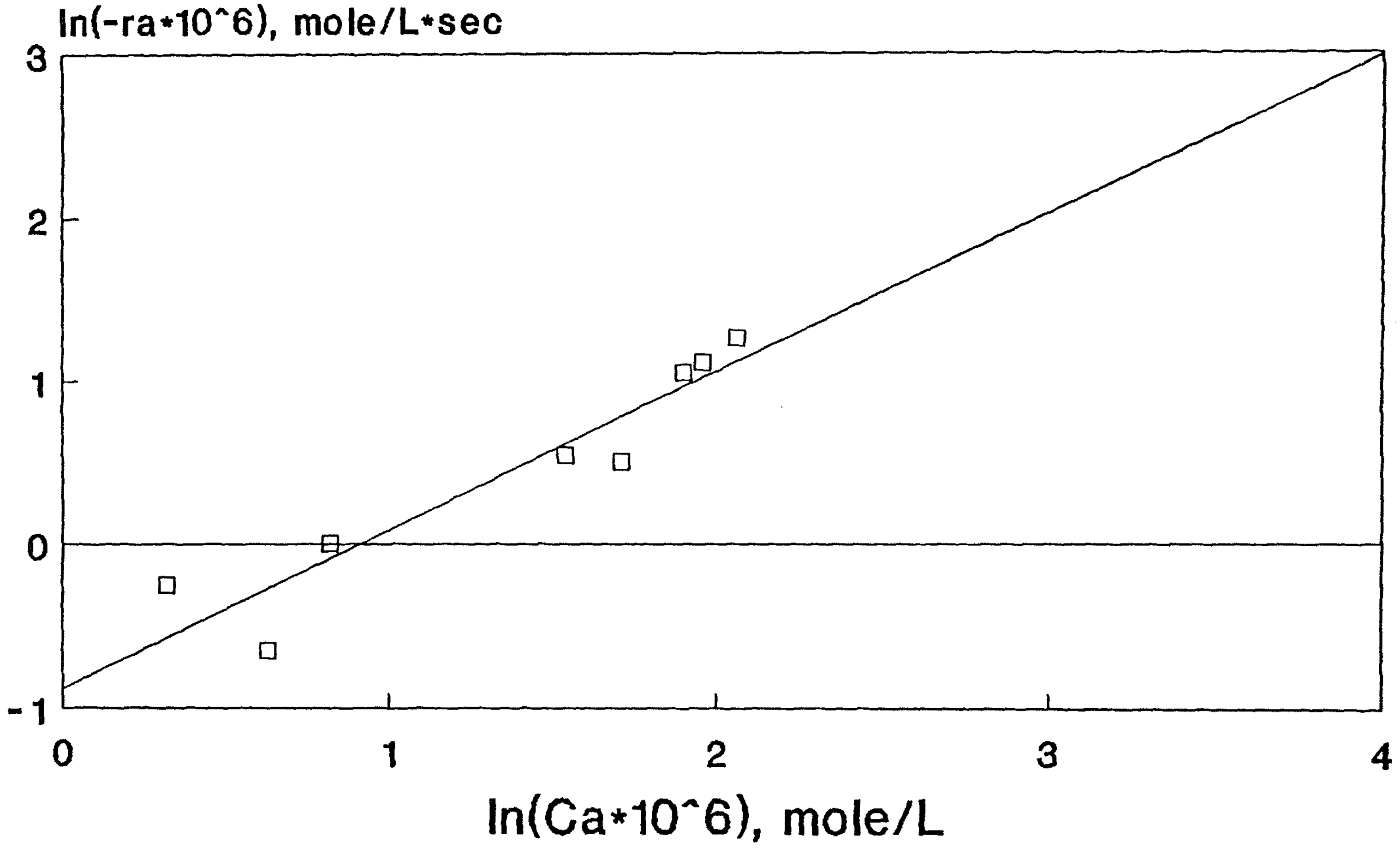
Figure 23 is a plot of the logarithm of the measured reaction rate versus the logarithm of the mean concentration of C_2HCl_3 (see Appendix Table A.3). The order of reaction with respect to C_2HCl_3 was calculated by a least square,

Figure 22 Oxygen Effect on TCE Catalytic Oxidation



SV=4000 v/v/hr

Figure 23 Effect of The Concentration of TCE on Rate



SV=6000 v/v/hr
4% Pdo/Al2O3 on Cordierite

regression and the order was 0.97. Therefore, this reaction was assumed first order.

In order to certify the order of reaction and calculate rate constant, activation energy Ea, preexponetial factor A, an equation was employed to determine the rate of reaction (Levenspiel, 1972 and Fogler, 1986). It is assumed that every channel of honeycomb catalyst is a small plug flow reactor. The equation is written as:

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A} \tag{4-3}$$

where V : bulk volume of honeycomb catalyst, cm^3.

F_{Ao} : molar feed rate, mole/sec

X_A : conversion of C_2HCl_3

$-r_A$: rate of reaction of C_2HCl_3

Substitute eq.(4-2) into eq.(4-3), we obtain

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{k_2C_{Ao}\{ (1-X_A)/(1+e_AX_A) \}} \tag{4-4}$$

where C_{Ao} : initial concentration of C_2HCl_3

e_A : expansion factor

Since the concentration of C_2HCl_3 is very low, the expansion factor can be neglected. Therefore, equation (4-4) can be written(Levenspiel, 1972):

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{k_2C_{Ao}(1-X_A)} \tag{4-5}$$

Rearrange both sides, we obtain

$$\frac{k_2*V*C_{Ao}}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(1-X_A)} \qquad (4-6)$$

where V*CAo/FAo is equal to t, residence time (seconds). Integrating eq.(4-6), we obtain,

$$- k_2t = \text{Ln}\ (1-X_A). \qquad (4-7)$$

where Ln $(1-X_A)$ = ln (C_A/C_{Ao})

Figure 24 shows the plots of the logarithm of the (C_A/C_{Ao}) versus residence time. The data, which are converted for a thermal reaction component (see Appendix Table A.4), are shown to fit the first order equation. The rate constants are obtained from the slope of the lines. The slope were calculated by linear regression.

According to the Arrhenius equation, the rate constant also can be described as follow:

$$k = A \exp(-Ea/RT) \qquad (4-8)$$

where A is the preexponential factor,

Ea is activation energy, kcal/mole,

R is gas constant, kcal/mole-K.

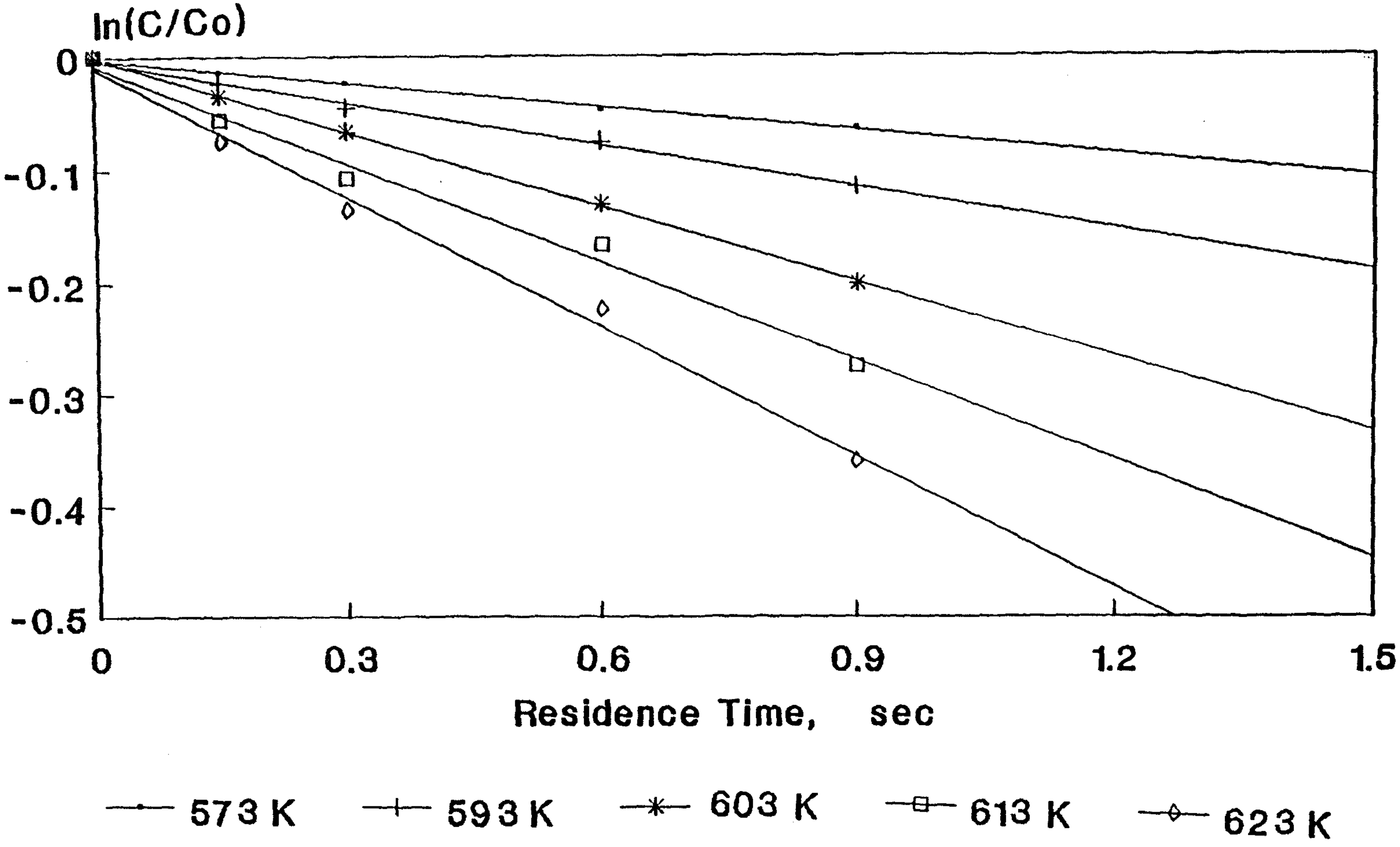
then,

$$\ln k = \ln A + (-Ea/R)\ (1/T) \qquad (4-9)$$

Figure 25 is a plot of the logarithm of the rate constant versus 1/T. The Ea and A were obtained from the slope and intercept. The Arrhenius activation energy, Ea, is estimated as 34 kcal/mole and the pre-exponential factor, A, is $7.2*10^{11}$ sec^{-1}. So, the rate equation can be written:

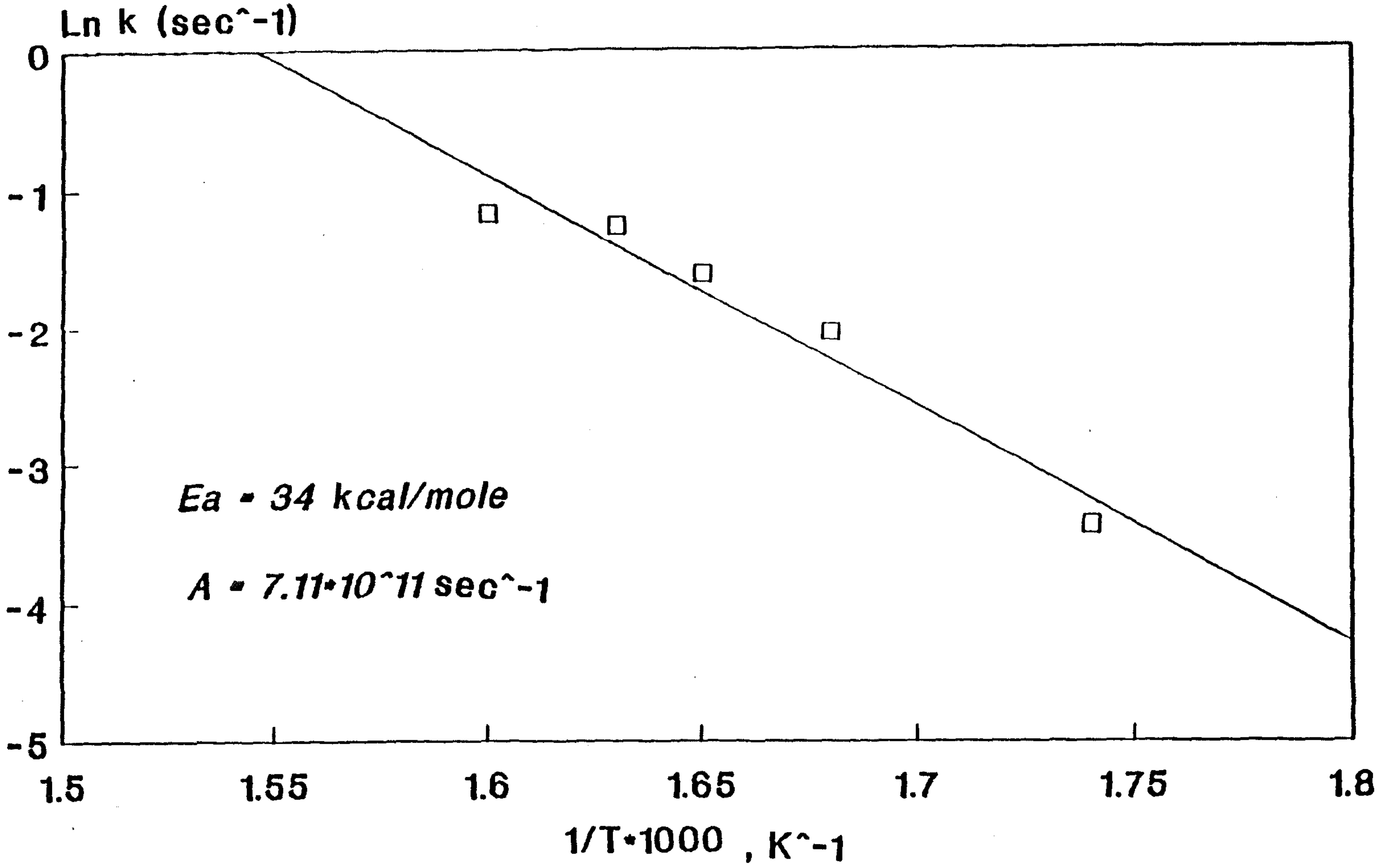
$$-r_{C2HCl3} = 7.2*10^{11}\text{EXP}(34/RT)*C_{C2HCl3} \qquad (4-10)$$

Figure 24 Ln (C/Co) vs. T for TCE Oxidation over 4% PdO on γ-Al2O3/400 cpsi Cordierite



Co : Initial concentration of TCE

Figure 25 Arrhenius Plots for K in the First Order Model



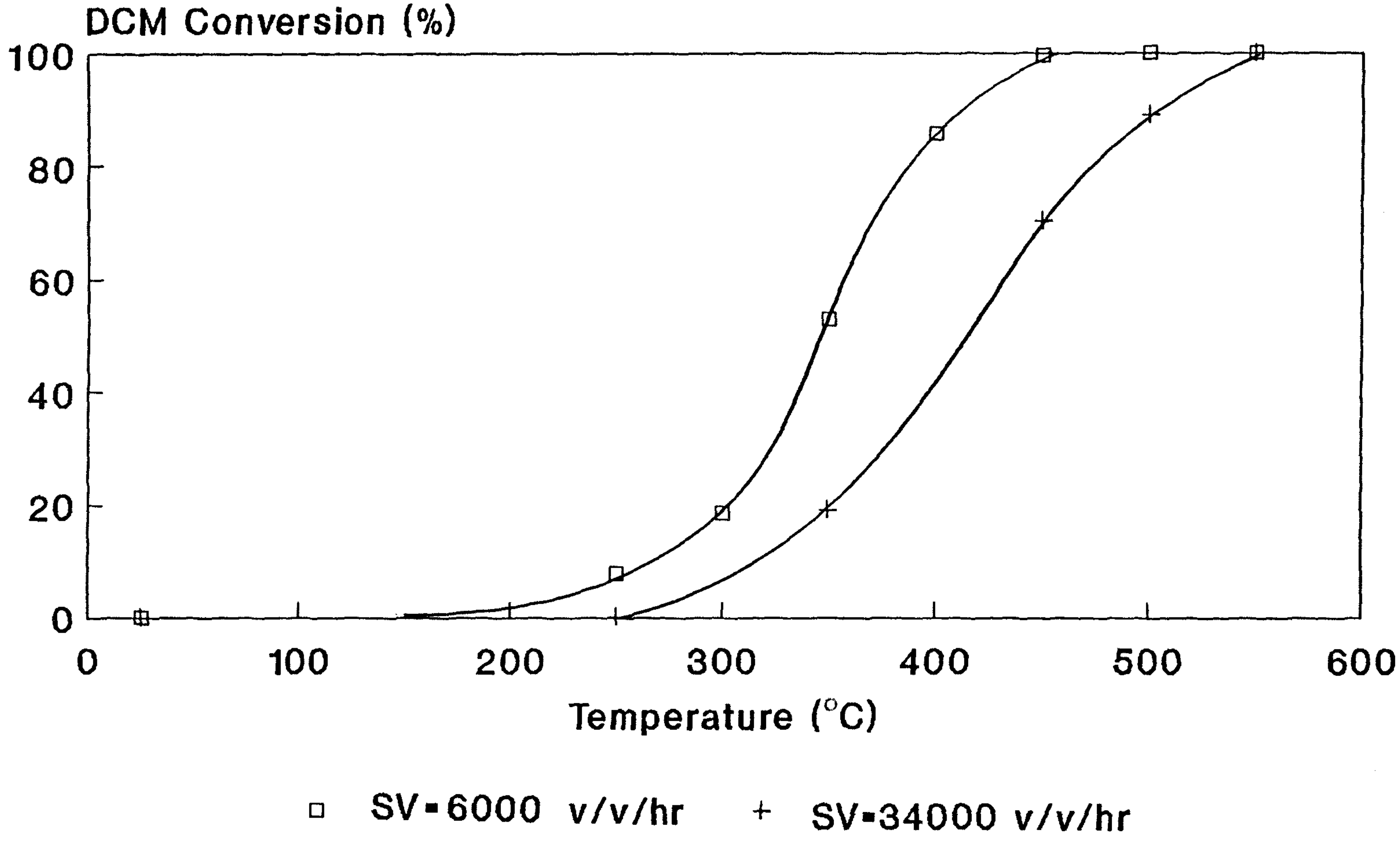
C. Catalytic Oxidation of DCM

1. Temperature and Space Velocity Effect on Reaction

These experiments were run over the temperature range from 250 ^{o}C to 550 ^{o}C. The conversion of DCM versus temperature is shown in Figure 26. Obviously, conversion of DCM is a function of temperatures and it follows the three regions of rate control, kinetics control, pore diffusion control and mass transfer control as mentioned before. These two curves represent two different space velocities. The higher space velocity had poorer conversion of DCM with respect to temperature compared to the lower space velocity. It is observed that at high space velocities poor pore diffusion rate may be occurring due to high linear velocity. Although high linear velocity causes turbulent flow which reduces gas film resistance, it reduces the concentration of DCM in the pore which would slow the reaction rate. From the experimental results, not only temperature but space velocity affect the reaction rate.

Figure 27 shows product distribution of catalytic oxidation of DCM versus to temperature at 6000 v/v/hr space velocity. The undesirable product CH_3Cl is less than 0.5% and complete oxidation occurs at 500 ^{o}C. Table 6 shows the carbon material balances. One can see that essentially all carbon is converted to CO_2. Figure 28 shows the product distribution for the catalytic oxidation of DCM as a function of temperature at 34000 v/v/hr space velocity.

Figure 26 Conversion of DCM as a Function of Temperature



Oxidant: 20% O2 in Helium
Catalyst: 4% PdO/Al2O3 400 cpsi monolith

Figure 27 Product Distribution of DCM Oxidation
SV=6000 v/v/hr
4% PdO Honeycomb Catalyst

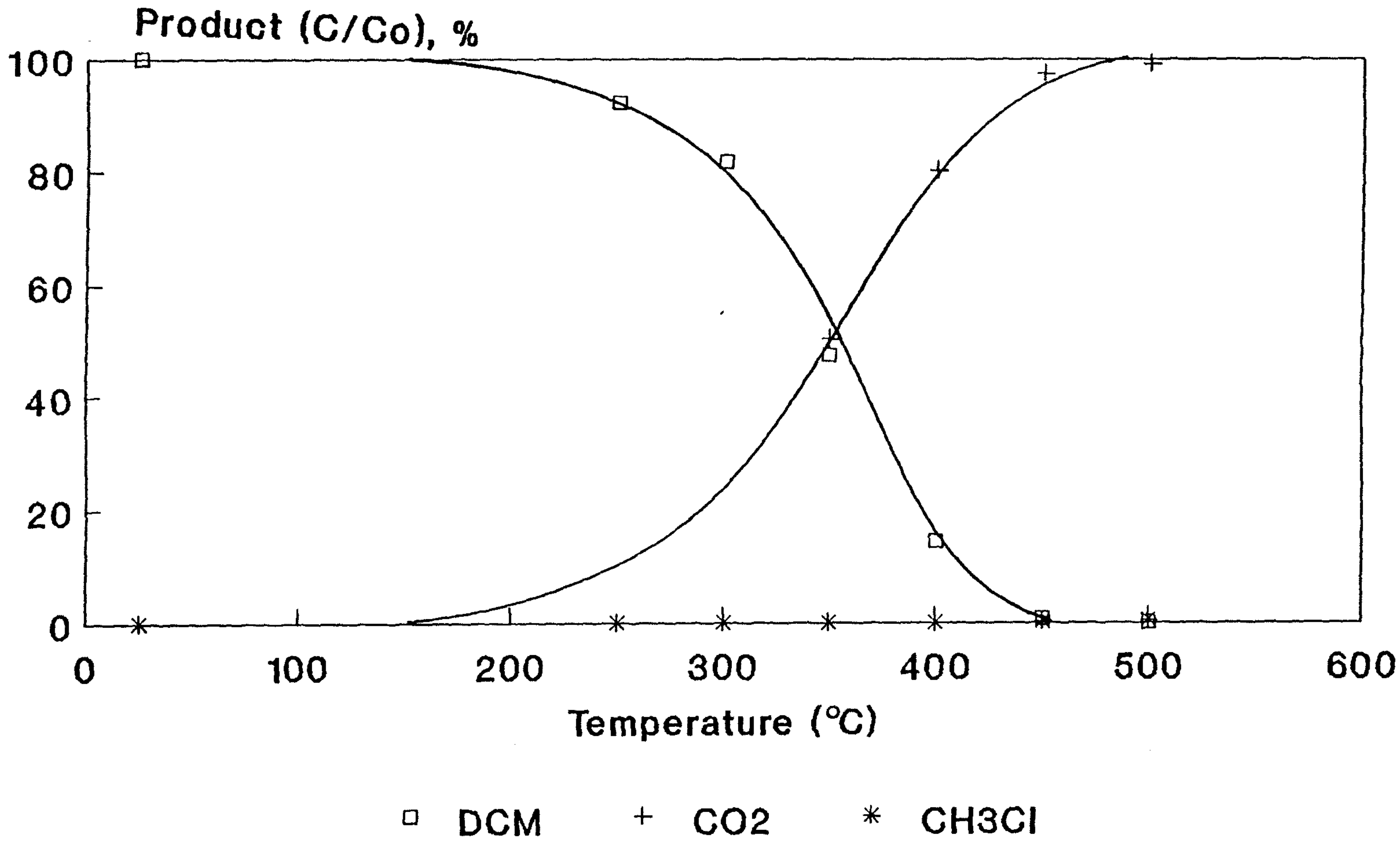


Figure 28 Product Distribution of DCM Oxidation
SV=34000 v/v/hr
4% PdO Honeycomb Catalyst

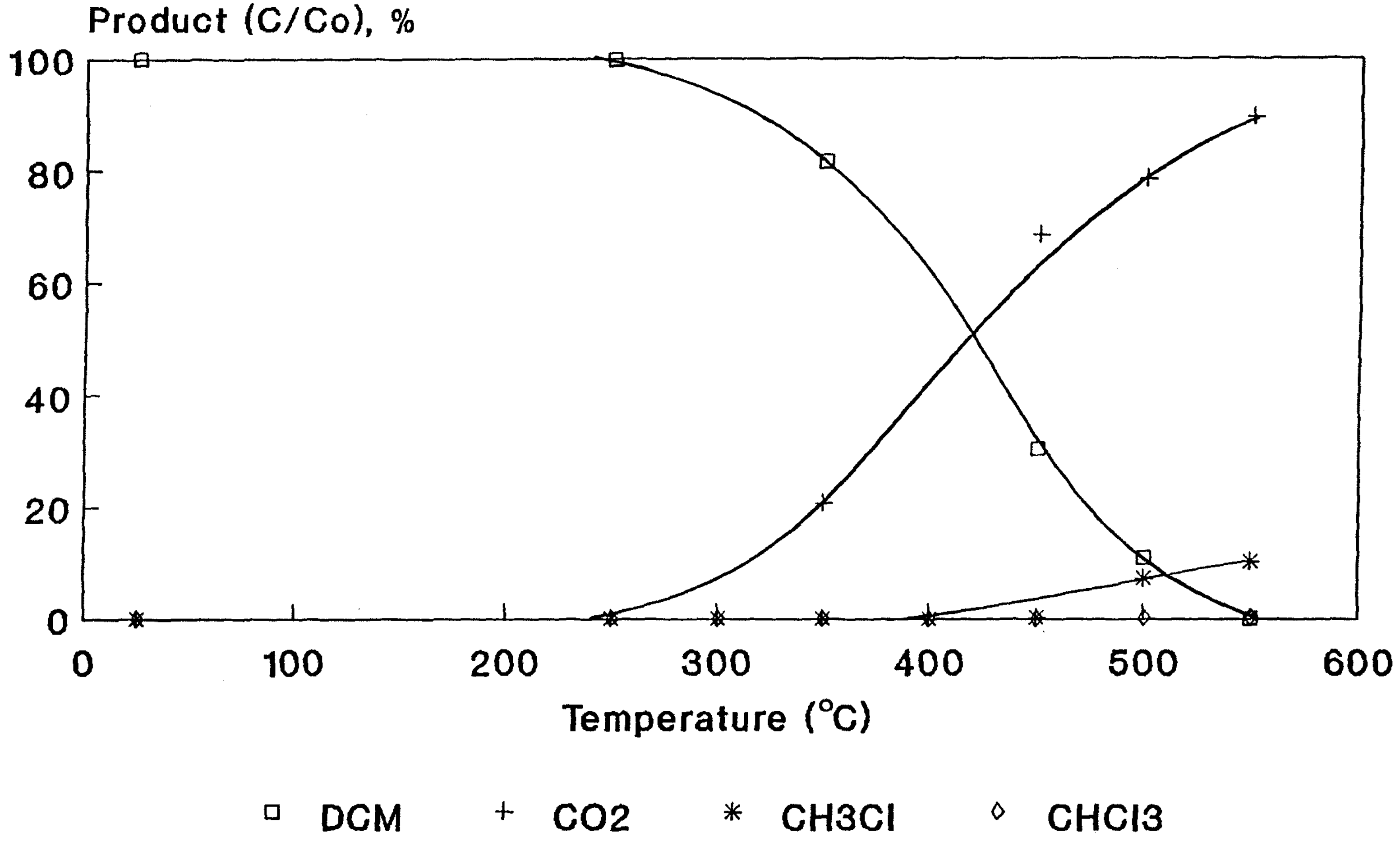


Table 6 Product Distribution of Catalytic Oxidation of DCM over 4% PdO/alumina on Cordierite.

Temp (^oC)	DCM, Co (ppm)	DCM (ppm)	CH_3Cl (ppm)	$CHCl_3$ (ppm)	CO_2 (ppm)	Carbon balance %
250	525	484	-	0.1	0.0	92.2
300	520	424	-	0.3	0.0	81.6
350	510	241	-	0.1	257	97.7
400	513	73.4	-	0.0	410	94.2
450	513	1.5	5.6	0.2	500	98.1
500	515	0.0	2.6	0.0	510	99.5

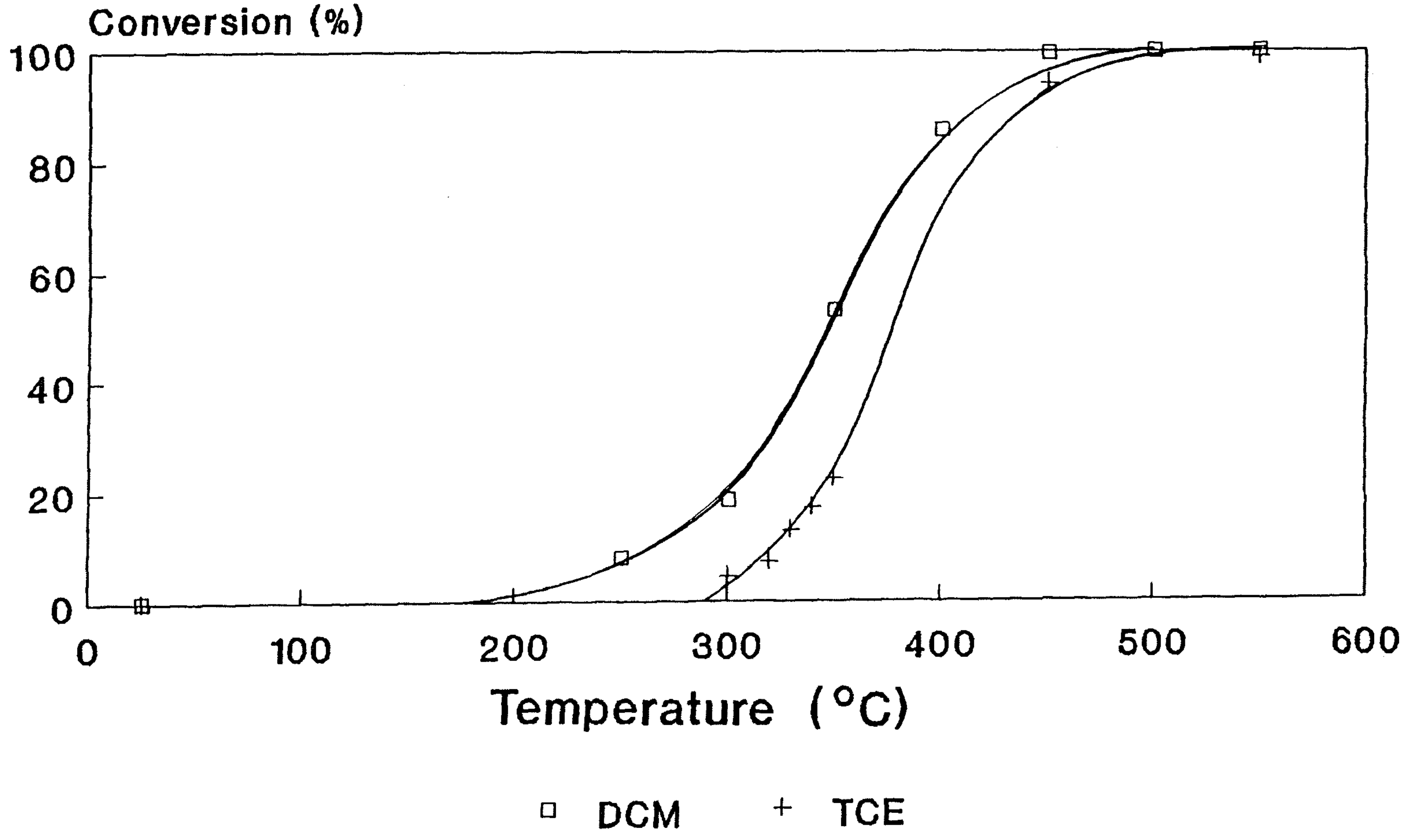
SV = 6,000 v/v/hr
Oxidant : 20% O_2 in helium
Date : 09/27/90

Complete oxidation of DCM occurs at 550 °C. It is found that the undesirable products CH_3Cl and $CHCl_3$ are 10.2 % and 0.27% in the final product distribution (see Appendix Table A.5) and the rest of the feed carbon is converted to CO_2. It is concluded that space velocity has a substantial effect on product distribution and strongly influences on the reaction mechanism.

2. Comparison of Catalytic Oxidation of DCM and TCE

Figure 29 compares conversion of DCM and TCE versus temperature. At 6000 v/v/hr space velocity, the DCM light-off temperature is about 250 °C and TCE light-off temperature is about 310 °C. The difference in these two curves seems to be associated with the kinetics control regime. The results show that the energy barrier for reacting these two compounds on the same catalyst is different. Ramamathan and Spivey (1989) observed that unsaturated two-carbon compounds formed in the initial stages of the reaction are more reactive than single carbon compounds over Cr_2O_3/Al_2O_3 catalyst, leading to complete oxidation to carbon dioxide. Bond (1975) found the conversion of DCM oxidation is slightly higher than TCE oxidation over Pt/Al_2O_3 catalyst at the same temperature. These different results may indicate the importance of catalyst characterization and postulating possible reaction pathways.

Figure 29 Comparison of Activity of DCM and TCE over 4% PdO Al2O3/monolith



SV=6000 v/v/hr

V. DISCUSSION

A. Conventional Combustion of Trichloroethylene (TCE)

Senkan et al., (1986) investigated the homogeneous mechanism of TCE oxidation. Generally, it has the following global two-step oxidation chemistry mechanism:

$$C_2HCl_3 + O_2 \longrightarrow 2CO + HCl + Cl_2 \qquad (5\text{-}1)$$

$$CO + 1/2\ O_2 \longrightarrow CO_2. \qquad (5\text{-}2)$$

The most important initiation reaction for C_2HCl_3 was determined to be the following(Senkan et al., 1986):

$$C_2HCl_3 + M = C_2HCl_2 + Cl + M \qquad (5\text{-}3)$$

In addition, the following HCl elimination reaction

$$C_2HCl_3 + M = C_2Cl_2 + HCl + M \qquad (5\text{-}4)$$

also is important under certain conditions.

Calculations have indicated that Cl is the most important radical intermediate in the combustion of C_2HCl_3. This is because C_2HCl_3 is a hydrogen-lean fuel, and chlorinated species continually scavenge the H atoms from the system by rapid reactions such as:

$$RCl + H = R + HCl, \qquad (5\text{-}5)$$

$$Cl_2 + H = HCl + Cl, \qquad (5\text{-}6)$$

$$HCl + H = H_2 + Cl, \qquad (5\text{-}7)$$

which inhibit the following important chain branching reaction (Senkan et al., 1986):

$$H + O_2 = OH + O. \qquad (5\text{-}8)$$

This in return lowers the concentrations of OH and O radicals as well in the system.

The primary reaction responsible for C_2HCl_3 consumption in flames is that caused by Cl radical attack:

$$C_2HCl_3 + Cl = C_2Cl_3 + HCl$$

$$\text{or} \quad C_2HCl_3 + Cl \longrightarrow C_2HCl_4 \longrightarrow C_2Cl_3 + HCl \qquad (5\text{-}9)$$

Figure 30 shows the schematics of the major reaction pathway in the high-temperature combustion of trichloroethylene.

For conventional combustions of TCE, complete oxidation occurs at 1100 °C. It is observed that concentration of CO is three times CO_2 and Cl_2/HCl ratio is one in the final product distribution. These results, compared to catalytic oxidation show the advantages of the catalytic system which produces, only CO_2 at much lower temperatures.

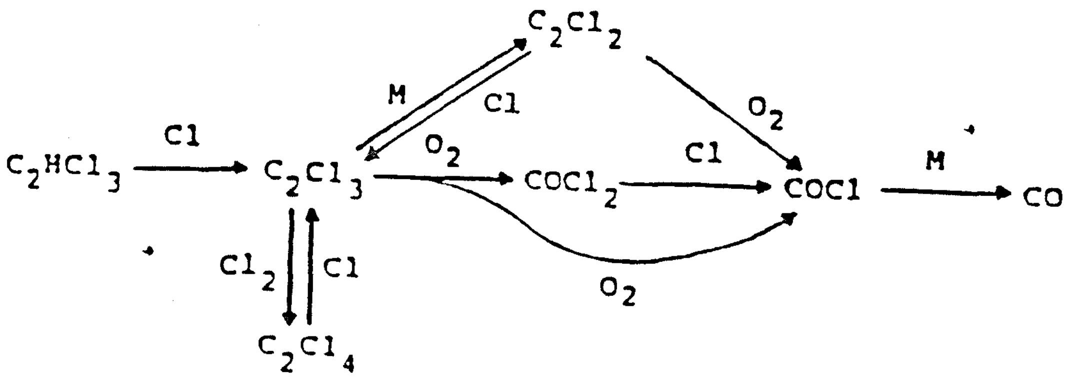


Fig. 30 Schematics of the major reaction pathways in the high-temperature combustion of TCE(Senkan et al.,1986).

B. Catalytic Oxidation of TCE

According to the product distribution for the catalytic oxidation of TCE, a series of reactions may be postulated based on the experimental observations:

$$1/2\ O_2 + * = O* \qquad (5\text{-}10)$$

$$C_2HCl_3 + * = C_2HCl_2* + Cl \qquad (5\text{-}11)$$

$$C_2HCl_3 + * = C_2HCl_3* \qquad (5\text{-}12)$$

$$C_2HCl_3* + Cl = C_2Cl_3* + HCl \qquad (5\text{-}13)$$

$$C_2HCl_2* + O* = CO + CHCl_2* + * \qquad (5\text{-}14)$$

$$CHCl_2* + O* = CO + HCl + Cl* + * \qquad (5\text{-}15)$$

$$C_2Cl_3* + Cl* = C_2Cl_4 + 2* \qquad (5\text{-}16)$$

$$C_2Cl_4 + 2O* = 2CO + Cl_2 + 2* \qquad (5\text{-}17)$$

$$2CO + 2O* = 2CO_2 + 2* \qquad (5\text{-}18)$$

where * indicates active site on the catalyst surface. In these experiments, reaction (5-11) is a primary initiation reaction. Owing to catalytic oxidation, PdO catalyst leads a sequence reaction pathway which is different from conventional incineration. Since C_2Cl_4 is an intermediate product and no other chlorinated hydrocarbons are detected, Reactions (5-14) and (5-15) are fast reaction and reaction (5-16) is a pathway to produce C_2Cl_4. Reactions (5-17) and (5-18) occur spontaneously when temperature is increased above 500^oC. Generally, the overall catalytic reaction is:

$$C_2HCl_3 + 2O_2 = 2CO_2 + HCl + Cl_2 \qquad (5\text{-}19)$$

Figures 31 to 35 show the comparison of product based on catalytic oxidation of TCE with or without the additives of water or methane.

For water addition, the overall reaction is:

$$C_2HCl_3 + H_2O + 3/2O_2 = 2CO_2 + 3HCl \qquad (5\text{-}20)$$

It is observed that selectivity to HCl is increased and to CO and C_2Cl_4 is decreased when temperature is increased. It may be postulated that the following two competing reactions occurred:

$$C_2Cl_4 + 4O^* = 2CO_2 + 2Cl_2 + 4^* \qquad (5\text{-}21)$$

$$C_2Cl_4 + 4OH^* = 2CO_2 + 4HCl + 4^* \qquad (5\text{-}22)$$

The results show reaction (5-22) is more active than reaction (5-21).

For methane addition the overall reaction is:

$$2C_2HCl_3 + CH_4 + 5O_2 = 5CO_2 + 6HCl \qquad (5\text{-}23)$$

It is seen that selectivity to HCl increases and selective to C_2Cl_4 decreases as temperature is increased. Higher concentration of CO is founded in product distribution at low temperature. It may be postulated that methane oxidized incompletely at low temperature:

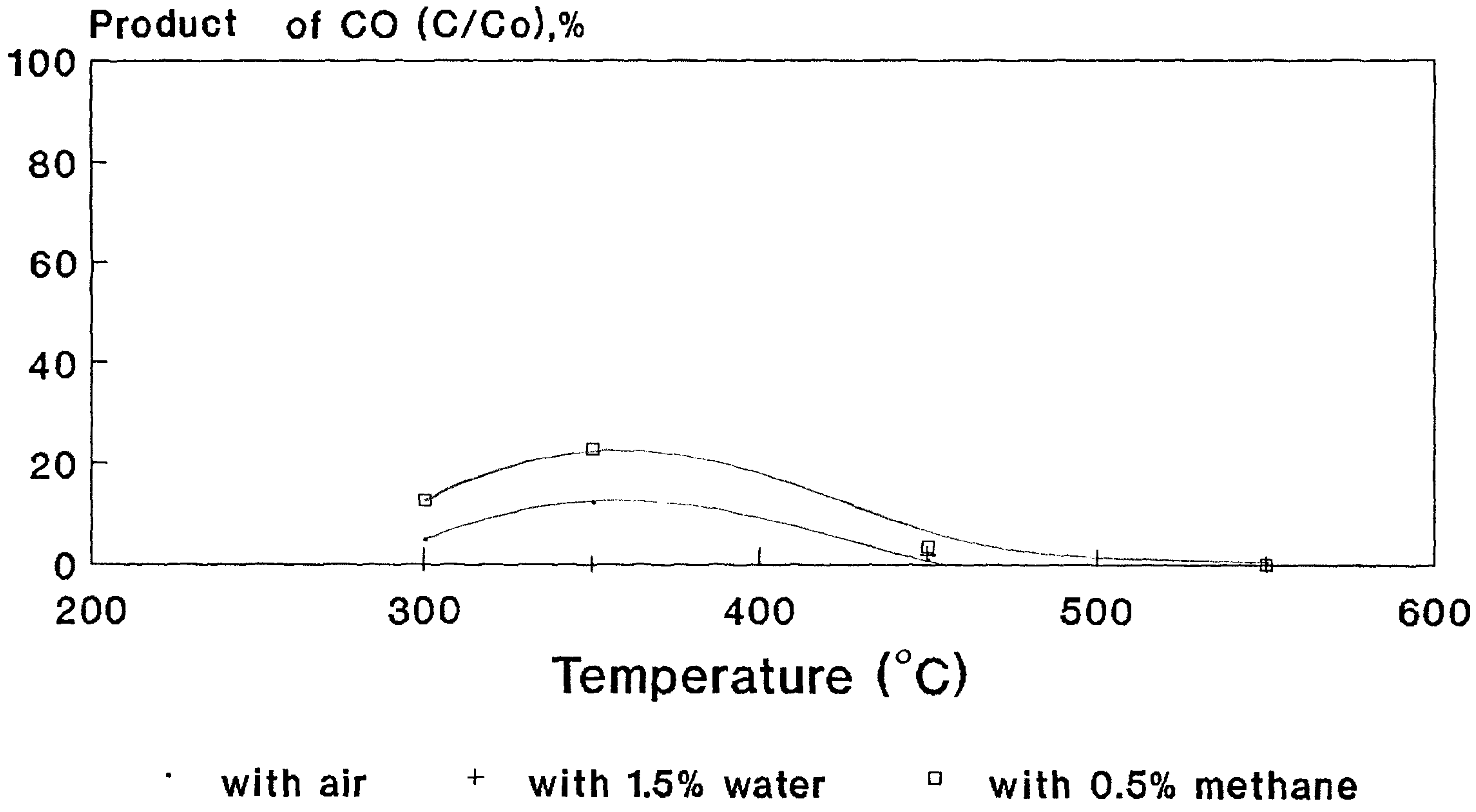
$$CH_4 + 3/2O_2 = CO + H_2O \qquad (5\text{-}24)$$

Due to CH_4 oxidation, a lot of water is produced which enhance the trend of reaction (5-22).

C. Industrial Relevance

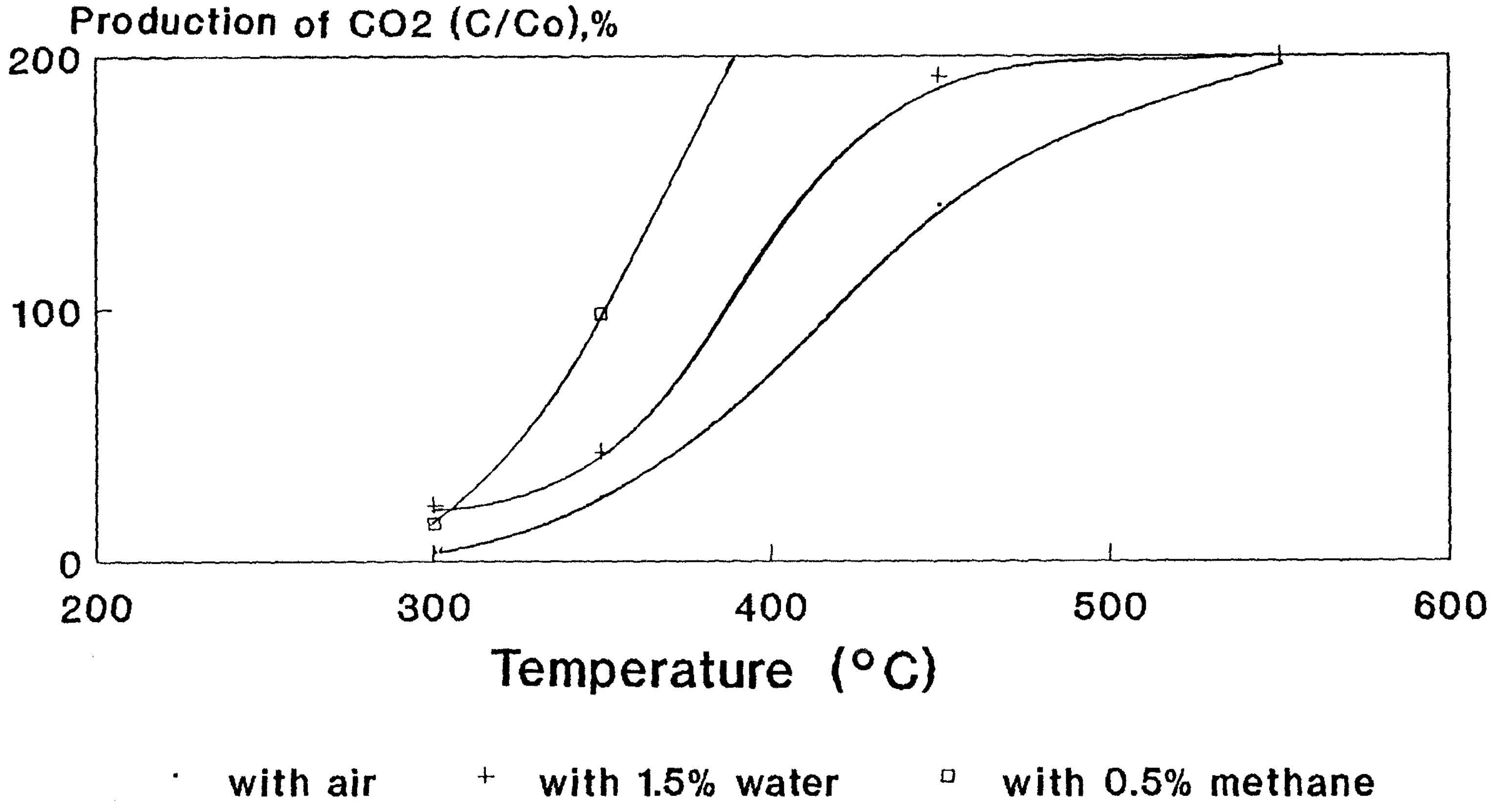
Manufacturers of organic chemicals, automotive painting operations, pharmaceutical industries, etc., generate aromatic and chlorinated compounds as waste streams. These

Figure 31 Comparison of CO Distribution for TCE Oxidation as a Function of Temperature



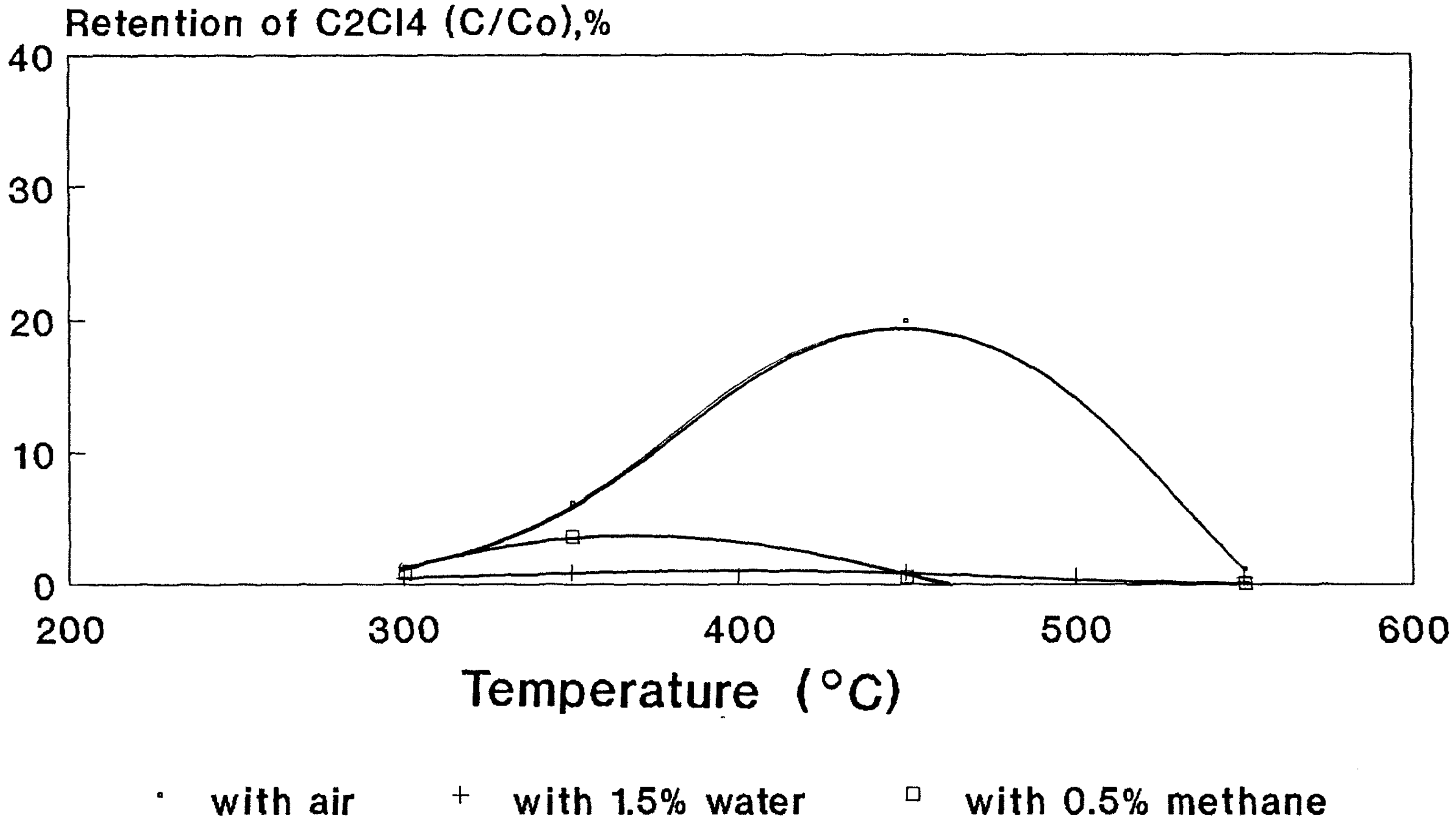
SV=6000 v/v/hr
4% PdO on Al2O3/400 cpsi Cordierite
Co : Initial Concentration of TCE = 200 ppm

Figure 32 Comparison of CO2 Distribution for TCE Oxidation as a Function of Temperature



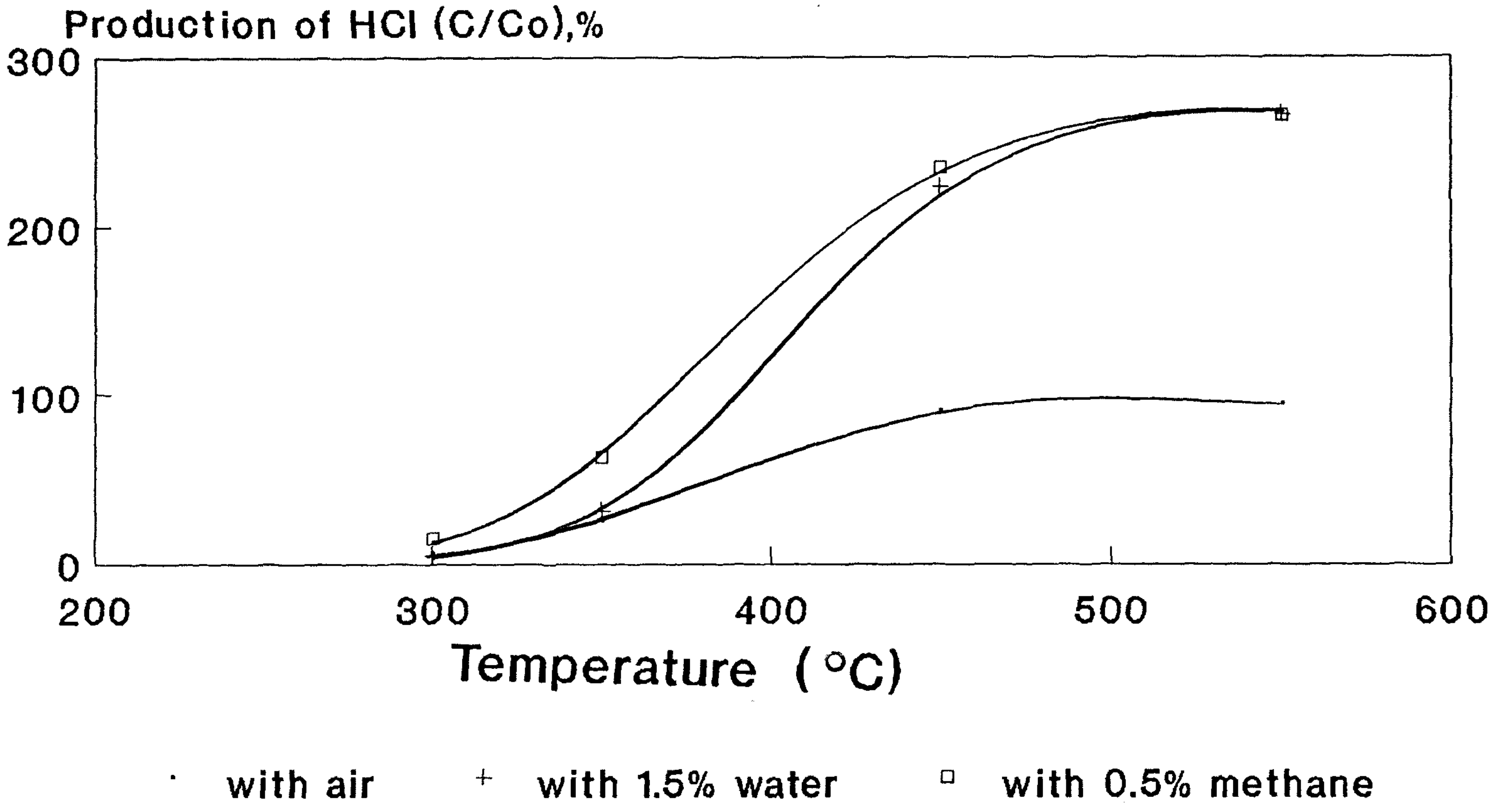
SV=6000 v/v/hr
4% PdO on Al2O3/400 cpsi Cordierite
Co : Initial Concentration of TCE = 200 ppm

Figure 33 Comparison of C2Cl4 Distribution for TCE Oxidation as a Function of Temperature



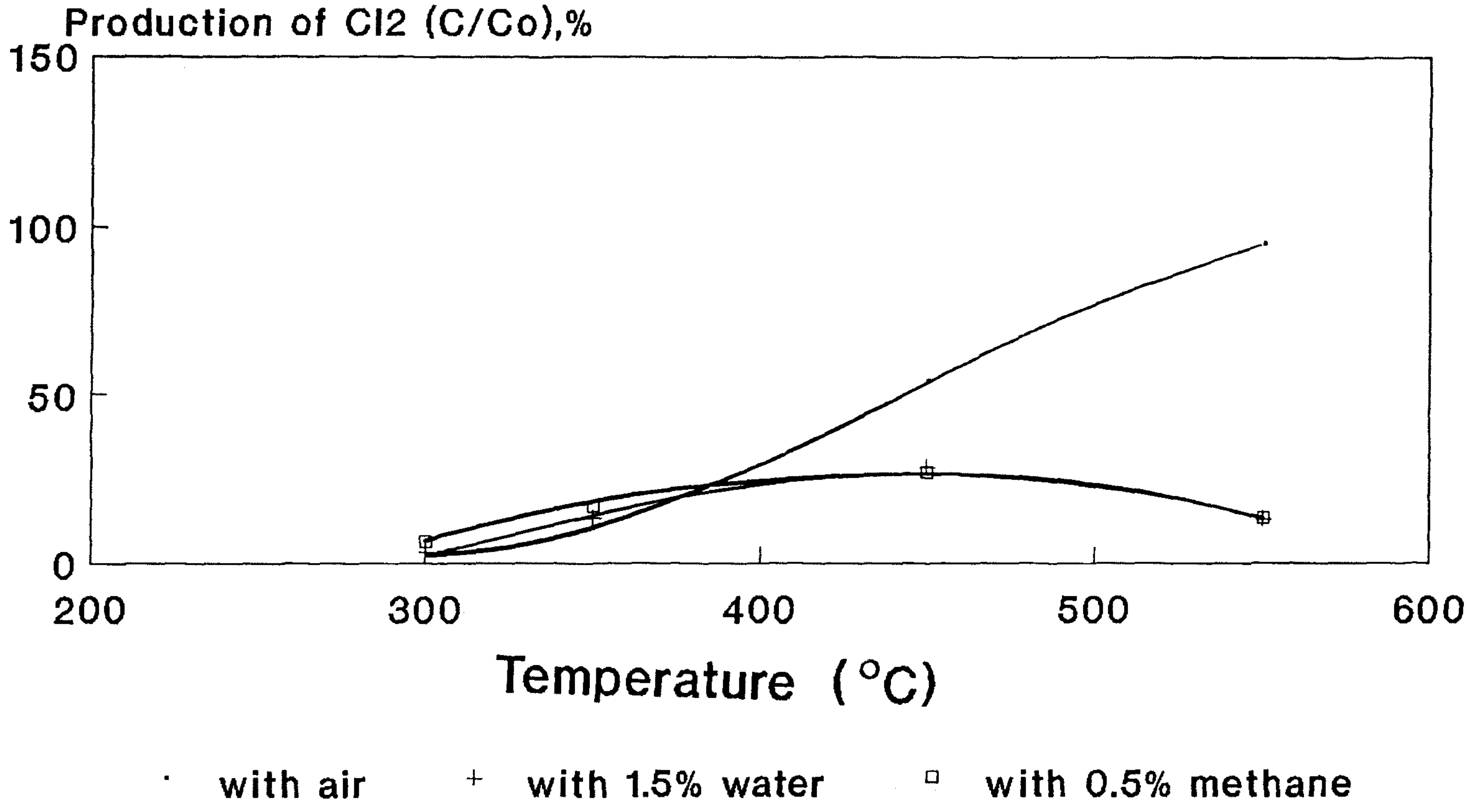
SV=6000 v/v/hr
4% PdO on Al2O3/400 cpsi Cordierite
Co : Initial Concentration of TCE = 200 ppm

Figure 34 Comparison of HCl Distribution for TCE Oxidation as a Function of Temperature



SV=6000 v/v/hr
4% PdO on Al2O3/400 cpsi Cordierite
Co : Initial Concentration of TCE = 200 ppm

Figure 35 Comparison of Cl2 Distribution for TCE Oxidation as a Function of Temperature



SV=6000 v/v/hr
4% PdO on Al2O3/400 cpsi Cordierite
Co : Initial Concentration of TCE = 200 ppm

waste streams may also contain acid gas precursors such as nitrogen, sulfur and phosphorous compounds. Some of the waste types emitted to the atmosphere include benzene, toluene, xylene, methylethyl ketone , carbon tetrachloride, chloroform, formaldehyde, phenols, acid gases, etc. The proper handling and disposal of these toxic organics is one of the primary environmental problems due to their impact on health. Conventional methods for controlling such atmospheric pollutants include condensation, scrubbing, adsorption and incineration with products being disposed of by landfill burial. These methods encounter limitations due to concentration and temperature, they are energy intensive, and the cost of landfill burial is rapidly increasing.

Catalytic incineration represents an alternative which provides for destruction of some contaminant species by providing for oxidation to benign products. Catalytic oxidation can be carried out at temperatures below normal incineration temperatures and is thus less energy intensive. In this work, a halogented compound, TCE, is oxidized over 4% PdO/Al_2O_3 on 400 cells per in^2 cordierite. Compared to conventional combustion at 1000^oC, complete oxidation of TCE with the addition of water or methane occurs at 550 ^oC and the primary products are HCl and CO_2. These two effluents are easily controlled. HCl is removed in a safe neutralization process, and CO_2 is emitted to the atmosphere directly. By way of comparison, the thermal incineration of TCE occurs at 1100^oC and the primary products are Cl_2, HCl, CO, CO_2 and trace chlorinated compounds. These products can be more toxic than the original compound. Dealing with these two processes, we anticipate that the catalytic oxidation route can be a more benign technology.

In recent years, TCE was found as a contaminant of groundwater. A new approach to treat contaminated of groundwater is air stripping, followed with catalytic incineration. The air stream which is rich in moisture after stripping, is then passed into the catalytic converter. In this approach, moisture enhances selectivity of HCl and reduce Cl_2 emissions. This process will undergo a full scale test in the near future. However, a negative result was found is that TCE inhibited methane oxidation over PdO/Al_2O_3 catalyst. This result which is in agreement with data presented by Simone et al.,(1991) who observed chloride , from the precursor salts and other impurities from the alumina, deactivate palladium on alumina for the oxidation of methane. The same situation was found for CH_2Cl_2 which might deactivate platinum on alumina for the complete oxidation of propane in combustion applications (Huang et al., 1990).

VI. CONCLUSIONS

In this study, catalytic oxidation of trichloroethylene and dichloromethane over 4% PdO/alumina on 400 cells per in^2 cordierite were investigated. It is concluded that:

- PdO is the only oxidation state of this catalyst. Higher content of PdO leads to the higher activity, albeit at lower efficiency.
- The light-off temperature for catalytic oxidation of dichloromethane (DCM) is 250 ^{o}C and complete oxidation occurs at 550 ^{o}C. In addition, the light-off temperature for catalytic oxidation of trichloroethylene (TCE) is 310 ^{o}C. and complete oxidation occurs at 550 ^{o}C at the same space velocity of 6000 v/v/hr.
- Temperature and space velocity are the key parameters for catalytic oxidation of DCM and TCE. The former affects destruction efficiency, and the later affects product distribution.
- In the case of catalytic oxidation of TCE, the temperature for complete oxidation of TCE is much lower than normal operating temperatures in conventional incineration processes. Chlorine gas is produced in both case since TCE has insufficient hydrogen to tie up all the chlorine.
- On the assumption that TCE oxidation obeys a first order catalytic rate law, kinetics shows that the oxidation of TCE occurs with an activation energy of 34 kcal/mole and preexponential factor is $7.1*10^{11}$ sec^{-1}.

- When methane fuel is added to the feed stream, it enhances reaction activity at lower temperatures, improves selectivity to HCl, and reduces production of C_2Cl_4. However, TCE may inhibit methane oxidation on PdO catalyst at higher temperatures.
- When water is added to feed stream, it does not affect the rate of TCE destruction, improves selectivity to HCl, and reduces production of C_2Cl_4.

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APPENDIX

Table A.1 Product Distribution of Catalytic Oxidation of TCE over 4% PdO/alumina on Cordierite

Temp (^{o}C)	TCE, Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	Carbon balance %
300	222	212	2.2	8.7	9.8	103
320	222	206	3.1	9.3	16.2	100
330	226	197	6.6	11.8	28.5	98.7
340	230	188	11.3	19.8	44.9	101
350	231	179	13.4	24.7	57.1	101
360	230	174	17.5	24.8	77.5	106
370	230	148	23.0	20.5	105	102
380	224	126	26.0	16.8	112	96.4
450	224	13.0	45.5	0.0	289	90.6
550	224	2.5	3.4	0.0	405	92.9

SV = 6,000 v/v/hr
Oxidant : 20% O_2 in helium
Date : 01/16/91

Table A.2 Product Distribution of Catalytic Oxidation of TCE over 4% PdO/alumina on Cordierite

Temp (^{o}C)	TCE, Co (ppm)	TCE (ppm)	C_2Cl_4 (ppm)	CO (ppm)	CO_2 (ppm)	Carbon balance %
300	212	199	3.2	11.4	9.3	101
320	219	195	5.3	19.1	16.0	99.5
330	219	179	8.3	24.5	27.6	97.3
340	220	167	7.7	20.2	42.9	93.7
350	215	152	14.6	27.1	53.1	96.3
360	215	128	19.4	22.6	72.5	90.7
370	214	105	25.3	20.5	119	93.5
450	212	6.6	38.6	0.0	288	89.2
550	204	3.7	0.6	0.0	379	95.1

SV = 4,000 v/v/hr
Oxidant : 20% O_2 in helium
Date : 01/29/91

Table A. 3

Effect of The Concentration of TCE on Rate

TCE Co (ppm)	TCE C (ppm)	$Ln(-r_{TCE})$ ($*10^6$ mole/sec*l)	$Ln(C_{TCE})$ ($*10^6$ mole/l)
33.7	22.3	-0.25	0.32
45.8	38.2	-0.65	0.63
55.4	40.7	0.0	0.82
113.7	88.6	0.54	1.54
135.1	111.0	0.50	1.71
162.4	120.8	1.04	1.90
173.1	128.5	1.11	1.96
191.5	139.9	1.26	2.06

Space Velocity : 6000 (v/v/hr)
Residence Time : 0.6 sec
Reaction Temp. : 350 °C
Catalyst : 4% PdO / Alumina on Cordierite
Date : March 4, 1991

Table A.4

Conversion of TCE in Kinetic Region

Residence Time (sec) Temp. (°C) / Conv. of TCE (%)	Blank	0.15	0.3	0.6	0.9
300	0.0	1.4	2.3	4.7	6.2
320	0.0	2.3	4.4	7.3	11.0
330	0.6	4.0	7.7	13.0	18.4
340	1.6	7.0	13.4	17.1	24.2
350	2.2	9.4	17.2	22.4	30.4

Feed Concentration : 200 ppm TCE
Catalyst : 4% PdO / Alumina on Cordierite
Date : Feb. 9, 1991

Table A. 5

Product Distribution of Catalytic Oxidation of DCM over 4% PdO/alumina on Cordierite.

Temp (^{o}C)	DCM Co (ppm)	DCM (ppm)	CH_3Cl (ppm)	$CHCl_3$ (ppm)	CO_2 (ppm)	CCl_4 (ppm)	Carbon balance %
250	520	519	0.0	0.0	0.0	0.0	99.8
350	520	421	0.0	0.2	0.0	107	102
450	515	155	1.0	0.2	0.0	351	98.5
500	513	55.9	37.4	1.5	0.0	400	96.5
550	510	0.0	52.0	1.5	1.3	455	100

SV = 34,000 v/v/hr
Oxidant : 20% O_2 in helium
Date : 10/04/90