

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

*Catalytic Oxidation of Trace Concentrations
of Chlorinated Hydrocarbons Over 1.5%
Platinum on Alumina/Monolith*

By Yi Wang

*Thesis submitted to the Faculty of the Graduate School of the New
Jersey Institute of Technology in the partial fulfillment of the re-
quirements for the degree of Master of science in Environmental
Science*

1991

ABSTRACT

Catalytic Oxidation of Trace Concentrations of Chlorinated Hydrocarbons Over 1.5% Platinum on Alumina/Monolith

by

Yi Wang

The catalytic oxidation of chlorinated hydrocarbons CH_2Cl_2 (DCM) and C_2HCl_3 (TCE) was investigated over a 1.5% Pt on Al_2O_3 /monolith at 150 to 450°C. The studies were conducted at space velocities from 1,000 v/v/hr to 30,000 v/v/hr. Chemical equilibrium calculations showed the potential conversion and products distribution. The reactivity and selectivity for destruction of these compounds with air over Pt catalyst were evaluated experimentally. This research was conducted in a tubular reactor system with associated feed and product flow measuring equipment. Feed and product streams were analyzed using gas chromatography (GC) with ECD, FID and TCD detectors. The conclusions from the studies are:

- o The light off temperature is 200°C for CH_2Cl_2 at 1020 v/v/hr space velocity and 325°C for C_2HCl_3 at 30,000 v/v/hr space velocity.
- o Over 99% conversion of DCM is achieved at 400°C and 1020 v/v/hr, and 95% conversion of TCE is achieved at 450°C and 30,000 v/v/hr.
- o Temperature and space velocity are the key parameters for oxidation of chlorinated hydrocarbons.

- o The statistics activation energy for oxidizing C_2HCl_3 is 20 + kcal/mol.
- o Both water and methane strongly influence the selectivity of TCE oxidation to HCl.
- o Carbon and chlorine balances for oxidation of C_2HCl_3 are within 100+10%.
- o No significant CO formation is observed.

ACKNOWLEDGMENTS

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

Special thanks are given to Dr. R. J. Farrauto for his significant guidance and help in developing the experimental approach and for his advise on catalysis. Dr. R. Trattner for serving as member of the committee and Dr. A. E. Cerkanowicz significantly help me understand the physical process occurring on the catalyst by modeling the results of this research. Special thanks are also given to Mr. C. Brockway and Ms. G. San Agustin for their advise and help in instrumental application and in developing experimental methods. The author also acknowledges support form NJIT / Hazardous waste Management Research Center and Engelhard Corporation for this study.

VITA

Name: Yi Wang

Permanent Address:

Degree and Data to be Conferred : M.S. in Environ. Sci. 1991

Data of Birth :

Place of Birth :

Secondary Education :

Collegiate Institutions	Dates	Degree	Date of Degree
NJIT	Sept. 1989	M.S.	May 1991
Tsinghua University	Sept. 1979	B.S.	July 1984

Major: Environment Science

APPROVAL SHEET

Title of Thesis: Catalytic Oxidation of Trace Concentration of
Chlorinated Hydrocarbon over 1.5% Platinum on
Alumina/Monolith

Name of Candidate : Yi Wang

Master Science of Environment Science, 1991

Thesis and Abstract Approved: Date

Henry Shaw , Ph.D.
Professor

Thesis and Abstract Approved: Date

R. J. Farrauto, Ph.D.
Adjunct Professor

Thesis and Abstract Approved: Data

R. Trattner, Ph.D.
Professor

TABLE OF CONTENTS

ABSTRACT.....	i
ACKNOWLEDGEMENTS.....	iii
VITA.....	iv
APPROVAL SHEET.....	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES.....	viii
LIST OF TABLES.....	xi
I. INTRODUCTION.....	1
II. BACKGROUND.....	4
A. Review of Literature.....	4
B. Basic Principles of Catalysis.....	9
1. General Description of a Catalyst.....	9
2. Catalytic Processes and Kinetics Characterization.....	10
3. Catalyst Deactivation.....	13
III. EXPERIMENTAL.....	14
1. Catalyst Material.....	14
2. Materials and Equipments.....	14
3. Analytical Instruments.....	17
4. Experimental Procedures.....	24
IV. EXPERIMENTAL RESULTS.....	26
A. Catalytic Oxidation of Dichloromethane.....	26
1. Catalyst and Space Velocity.....	26
2. Chlorocarbon Feed Concentration Estimates.....	26

B. Catalytic Oxidation of Trichloroethylene.....	34
1. Catalyst and Space Velocity.....	34
2. Determination of Feed Concentration.....	34
3. Results.....	35
a. Aging Experiments.....	35
(1). General Description.....	35
(2). The Effect of Temperature on Reaction.....	36
(3). The Effect of Aging Time on Reaction.....	39
(4). The Effect of Aging Time on Reaction Kinetics.....	39
C. The Effect of Additives on C ₂ HCl ₃ Oxidation.....	54
V. DISCUSSION.....	67
1. Reactants.....	67
2. Catalytic Oxidation of Trichloroethylene.....	70
A. Explanation on Products Distribution.....	70
B. Effect of Aging Time on Reaction.....	72
C. Kinetics Study with Oxidation of Trichloroethylene.....	73
D. The Effect of Additives on Oxidation of Trichloroethylene.....	76
VI. CONCLUSIONS.....	82
VII. FUTURE WORKS.....	84
VIII. REFERENCES.....	85
APPENDIX	
Repeat Experiment : Oxidation of DCM at 1020v/v/hr.....	89
Repeat Experiment : Oxidation of DCM at 2040v/v/hr.....	90
Repeat Experiment : Methane Effect.....	91
Repeat Experiment : Water Effect.....	92
Calculated Rate Constants k at Different Aging Time.....	92

LIST OF FIGURES

Figure 1	Arrhenius Equation.....	12
Figure 2	Conversion of reactant as a function of temperature showing rate controlling regions.....	12
Figure 3	Flow Schematic of Catalytic Oxidation Unit.....	15
Figure 4	Design for quartz tubular reactor.....	16
Figure 5	Design for Ni-catalyst system.....	19
Figure 6	Peak resolution and retention time for chlorocarbon products from TCE oxidation.....	20
Figure 7	Peak resolution and retention time for chlorocarbon products from DCM oxidation.....	21
Figure 8	Peak resolution and retention time of CO ₂ , CO and CH ₄ on FID.....	22
Figure 9	Product distribution of CH ₂ Cl ₂ at 1020v/v/hr.....	28
Figure 10	Effect of space velocity on oxidation of DCM.....	31
Figure 11	Product distribution of CH ₂ Cl ₂ at 2040v/v/hr.....	33
Figure 12	Product distribution of C ₂ HCl ₃ fresh catalyst.....	37
Figure 13	Product distribution of C ₂ HCl ₃ 25 hours aged catalyst.....	40
Figure 14	Product distribution of C ₂ HCl ₃ 50 hours aged catalyst.....	42

Figure 15	Product distribution of C_2HCl_3	
	75 hours aged catalyst.....	44
Figure 16	Product distribution of C_2HCl_3	
	100 hour aged catalyst.....	46
Figure 17	Aging experiments with C_2HCl_3 at $450^\circ C$	48
Figure 18	Determination of rate constant k	
	fresh catalyst.....	49
Figure 19	Determination of rate constant k	
	25 hours aged catalyst.....	50
Figure 20	Determination of rate constant k	
	50 hours aged catalyst.....	51
Figure 21	Determination of rate constant k	
	75 hours aged catalyst.....	52
Figure 22	Determination of rate constant k	
	100 hours aged catalyst.....	53
Figure 23	Arrhenius plot for k in the first order	
	fresh catalyst.....	55
Figure 24	Arrhenius plot for k in the first order	
	25 hours aged catalyst.....	56
Figure 25	Arrhenius plot for k in the first order	
	50 hours aged catalyst.....	57
Figure 26	Arrhenius plot for k in the first order	
	75 hours aged catalyst.....	58
Figure 27	Arrhenius plot for k in the first order	
	100 hours aged catalyst.....	59

Figure 28	Water effect on products distribution.....	61
Figure 29	Methane effect on products distribution.....	63
Figure 30	Effect of additive on oxidation of C_2HCl_3	66
Figure 31	Comparison of CH_2Cl_2 vs C_2HCl_3 conversion.....	68
Figure 32	Structure of CH_2Cl_2 and C_2HCl_3	69
Figure 33	The weaker bond in DCM and TCE after adsorption.....	69
Figure 34	Effect of oxygen on oxidation of C_2HCl_3	75
Figure 35	Variation of pre-exponential with aging time.....	77
Figure 36	Comparison of HCl selectivity.....	79
Figure 37	Comparison of C_2Cl_4	80

LIST OF TABLES

Table 1 GC operating condition.....23

Table 2 Product distribution for oxidation of
CH₂Cl₂ at 1020v/v/hr.....30

Table 3 Product distribution for oxidation of
CH₂Cl₂ at 2040v/v/hr.....32

Table 4 Product distribution of aging experiment
fresh.....38

Table 5 Product distribution of aging experiment
25 hours aged.....41

Table 6 Product distribution of aging experiment
50 hour aged.....43

Table 7 Product distribution of aging experiment
75 hours aged.....45

Table 8 Product distribution of aging experiment
100 hours aged.....47

Table 9 Arrhenius Activation energies and pre-exponential
factors at different aging times.....60

Table 10 Catalytic oxidation of C₂HCl₃ with
1.5% water.....62

Table 11 Catalytic oxidation of C₂HCl₃ with
0.6% methane.....64

INTRODUCTION

Chlorinated compounds present environmental hazards in a number of different ways. Chlorinated hydrocarbons are widely used in dry cleaning and degreasing operations, organic chemicals manufacturing, automotive painting operations, etc. Chlorinated compounds can be found as air pollutants which affect stratosphere ozone and water pollutants which affect human health because of their carcinogenicity. Some chlorocarbons found in potable water are known to be toxic to humans through the damage they cause to the liver. Chlorocarbons are very stable and are often recycled when economically feasible. However, there are times when their concentration is very low, then it is most economical to destroy them by high temperature incineration. This procedure may produce harmful effluents that need to be removed with post-combustion treatment such as scrubbing. The purpose of our work is to devise a simpler, safer and hopefully less expensive procedure by which trace chlorinated compounds could be destroyed. Catalytic oxidation is such an option for the control of these emissions, albeit, wet scrubbing will still be required.

The objective of this research is to understand the fundamentals of catalytic oxidation processes for chlorinated hydrocarbons. This includes kinetic studies for catalytic destruction of low concentrations of chlorinated hydrocarbons, the effect of

catalyst type and support, the effect of space velocities, feed concentrations, the catalytic reaction temperature, and catalyst deactivation.

Since some chlorinated hydrocarbon molecules contain more chlorine atoms than hydrogen atoms, they produce Cl_2 in addition to the more desirable HCl . HCl is easily scrubbed in an alkaline medium. A desirable research 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 sufficient 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 decomposition into hydrogen chloride. The carbon atoms of the chlorinated molecule are essentially converted to carbon dioxide.

There are considerable advantages in using catalytic 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 (Bonacei et al., 1988). It should be noted that conventional combustion systems require back mixing (swirling) auxiliary fuel, staged burning, high operating temperatures (producing NO_x), and long average residence times (requiring large reactor volumes and consequently 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 could also be brought down and on site or mobile incineration made more economical. It has been estimated that the additional capital cost, even when using a noble metal, can be offset by lower fuel charges provided the catalyst lasts for more than three months.

BACKGROUND

A. Review of the literature

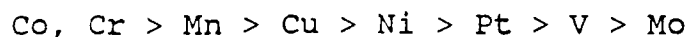
Chlorinated hydrocarbons (CHCl_s) are widely used in dry-cleaning and in degreasing operations, and as solvents in the pharmaceutical industry, but their vapors are toxic to human beings because of damage they cause to the liver (Bond, 1973). Dichloromethane (DCM) and trichloroethylene (TCE) are typical of the solvents described above.

In the recent years , TCE has been discovered in groundwater and in aquifers 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 a 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 hydrocarbon vapor (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 °C. Chlorinated hydrocarbons are

usually destroyed by thermal incineration at temperature of at least 1100 °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 it.

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 catalysts. The activity of metal oxide catalysts for the complete oxidation of chlorinated compounds was summarized by Ramanathan et al., (1989) as follows:



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 Al₂O₃ catalysts are effective in treating a number of chlorinated compounds, such as CH₂Cl₂, CCl₄, C₂H₂Cl₂, C₂HCl₃, C₂Cl₄, 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.

Platinum metal deposited on various supports, e.g., aero-foilsection ceramic rods, or metallic ribbons have been used for many years as combustion catalysts. These supported platinum catalysts have high activity toward hydrocarbon oxidation. Processes such as wire enamelling or paint drying involve the evaporation of solvents which can be oxidized over platinum to avoid explosive concentrations and permit air recycle (Ramanathan, 1989).

Ceramic honeycomb supports with a porous alumina washcoat on which platinum is deposited have a high geometric area to volume ratio and the open structure minimises the pressure drop through the oxidizer. By concentrating the small platinum content at the outer surface of the alumina washcoat, it is used to best advantage under diffusion-limited reaction condition.

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 a Co_3O_4 catalyst with a Pt catalyst. The Co_3O_4 catalyst was observed to be the more effective in the presence of chlorinated fuels. Hung et al., (1989) showed that a $\text{Cr}_2\text{O}_3/\text{Co}_3\text{O}_4$ binary catalyst performed better than a Pt catalyst in the catalytic oxidation of CH_3Cl and CH_2Cl_2 in the presence of propane. The product distribution as a

function of temperature was not determined.

Some investigators evaluated transition metal oxides catalysts on support. A catalyst containing impregnated chromium oxide on a support was used in the oxidation of chlorinated compounds to treat CH_3Cl (Senkan et al., 1986), 1,1-dichloroethane (Ramanathan et al., 1989), hexachlorobezene and hexachlorobutadiene (Johnston, 1976) and PCB's (Novinson, 1989). Cr_2O_3 catalysts were shown to have good activity for chlorinated compounds destruction. However, the undesirable by-product Cl_2 can not be easily scrubbed. In the study by K. Ramanathan et al., (1989), the selectivity to chlorine is 66.7%. Apparently, catalytic oxidation does not completely convert these compounds to CO_2 , H_2O , HCl or Cl_2 .

Hydrated nickel oxides, manganese oxides, cobalt oxides (Lavanish et al., 1976, and Sare et al., 1977) and titania catalysts (Tanguay, 1989) were evaluated for the catalytic oxidation of $\text{C}_2\text{-C}_4$ halogenated hydrocarbons and dichloromethane. Conversions of 45 to 90 percent were obtained for vinyl chloride (VCM), vinylidene chloride (VDCM) and trichloroethane over the nickel oxides (II) and (II, III). At temperatures over 450°C , nickel oxide catalysts started to deactivate by thermal sintering. For an

initial concentration of 46.5 ppm VCM or VDCM at 107 °C, 99 percent conversions were measured for cobalt oxides (II) catalyst. Cobalt oxides (II) catalysts deactivated by reacting with Al₂O₃ support to form CoAl₂O₄ at temperatures over 850 °C, which is an inactive composition. Titania catalyst showed a poor activity for the destruction of CH₂Cl₂.

A catalyst's overall effectiveness depends on the selectivity of products from any practical detoxication. Previous research in the heterogeneous catalytic oxidation of low concentrations of chlorinated hydrocarbons in air has focused on identifying highly active catalysts and final reaction products at temperatures high enough for essentially complete oxidation. In general, reaction conditions chosen that result in complete oxidation to H₂O, CO₂ and HCl.

Catalytic process are being developed for destroying hazardous organics in aqueous waste stream. E. G. Baker et al., (1989) develop a catalytic process which can treat waste that are too dilute in organic material to incinerate and are too toxic for biotreatment. The aqueous stream are treated with a reduced nickel catalyst at 350 °C to 400 °C and 3000 to 4000 psig, which converts the organics to innocuous gases.

Bob Olfenbutte (Olfenbuttel) 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 supported-catalyst, in which active catalytic components are supported on inert or ceramic substrate. Since molecules vary in size and chemical structure, so, different catalysts are necessary to promote their reaction. The optimization of a catalyst is specific for each reaction and operating condition. Therefore, determination of performance of a catalyst is dependent on practical reaction considerations.

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 transports through pore structure to active sites.

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

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

5. Desorption: a product desorbs from the active sites.

6. Product diffusion: a product diffuses through pores from the sites.

7. Product diffusion: a product diffuses 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 need to be carefully chosen to obtain the desired reaction.

Much research is required to optimize the properties of a catalyst and the conditions for its 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:

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

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

where,

k = rate constant,

A = Pre-exponential constant,

E = activation energy (kcal/mole),

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

T = absolute temperature (K).

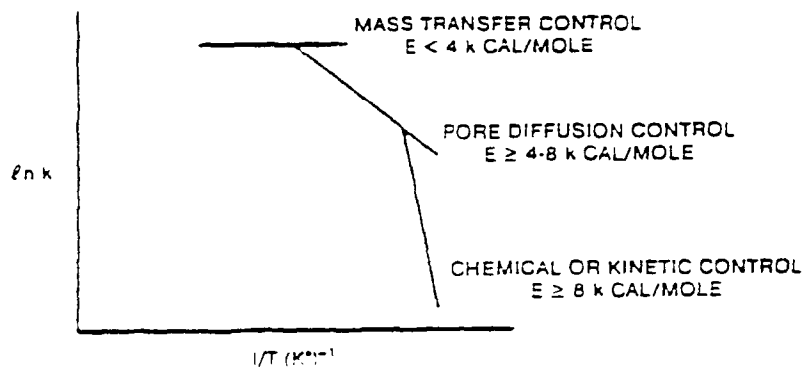


Figure 1 Arrhenius Equation

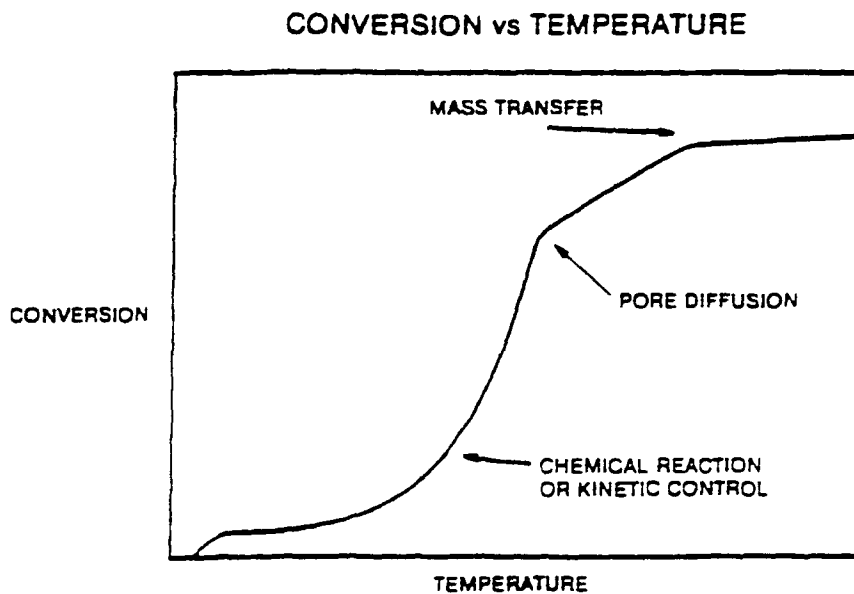


Figure 2 Conversion of reactant as a function of temperature showing rate controlling regions

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 reactions are less sensitive to temperature.

3. Catalyst Deactivation

A catalyst may lose 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 species.

A catalyst poison is an impurity present in the feed stream that reduces catalyst activity. In the oxidation of chlorinated hydrocarbons, a catalyst can easily 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 chlorides (Satterfield, 1980). Therefore, a chloride tolerant catalyst or an additive can avoid catalyst poisoning is a task for studying the process of catalytic oxidation of chlorinated hydrocarbons.

EXPERIMENTAL

1. Catalysts

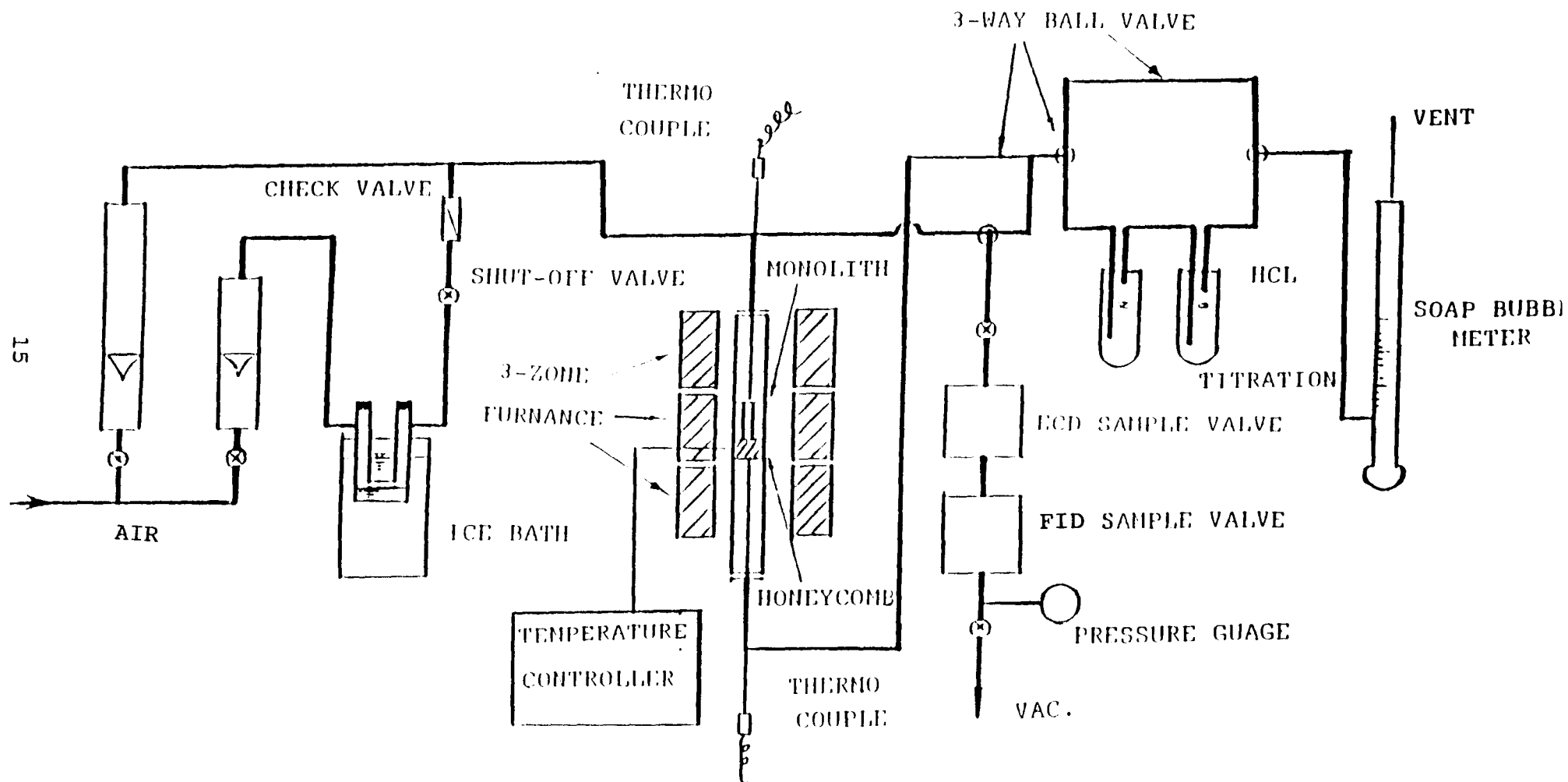
The catalysts used in this research were provided by Engelhard Corporation. The catalysts were 1.5% platinum deposited on an alumina washcoat and carried on a 400 (or 200) cells per square inch cordierite honeycomb.

2. Materials and Equipment

The experiments are based on a laboratory-scale tubular reactor system as shown in Figure 3. This system consists of a 2.5 cm inside diameter quartz tube reactor residing in a vertical three zone controlled furnace containing known volume of platinum monolith catalyst, the middle zone was designed to maintain a flat temperature profile over the length of the catalyst monolith. Catalyst lengths of 2.5, 5.0 and 7.5 cm were used. The design of quartz tube reactor is shown in Figure 4.

A glass U-tube containing either C_2HCl_3 or CH_2Cl_2 feed in liquid form was placed in a ice-bath and part of the air feed was bubbled through the U-tube, becoming saturated with the chlorocarbons at $0^\circ C$. The chlorocarbon containing air stream is mixed with the rest of the air before entering the reactor. The flow rates of inlet gases were measured with four calibrated Cole Parmer rotameters.

Figure 3 FLOW SCHEMATIC OF CATALYTIC OXIDATION UNIT



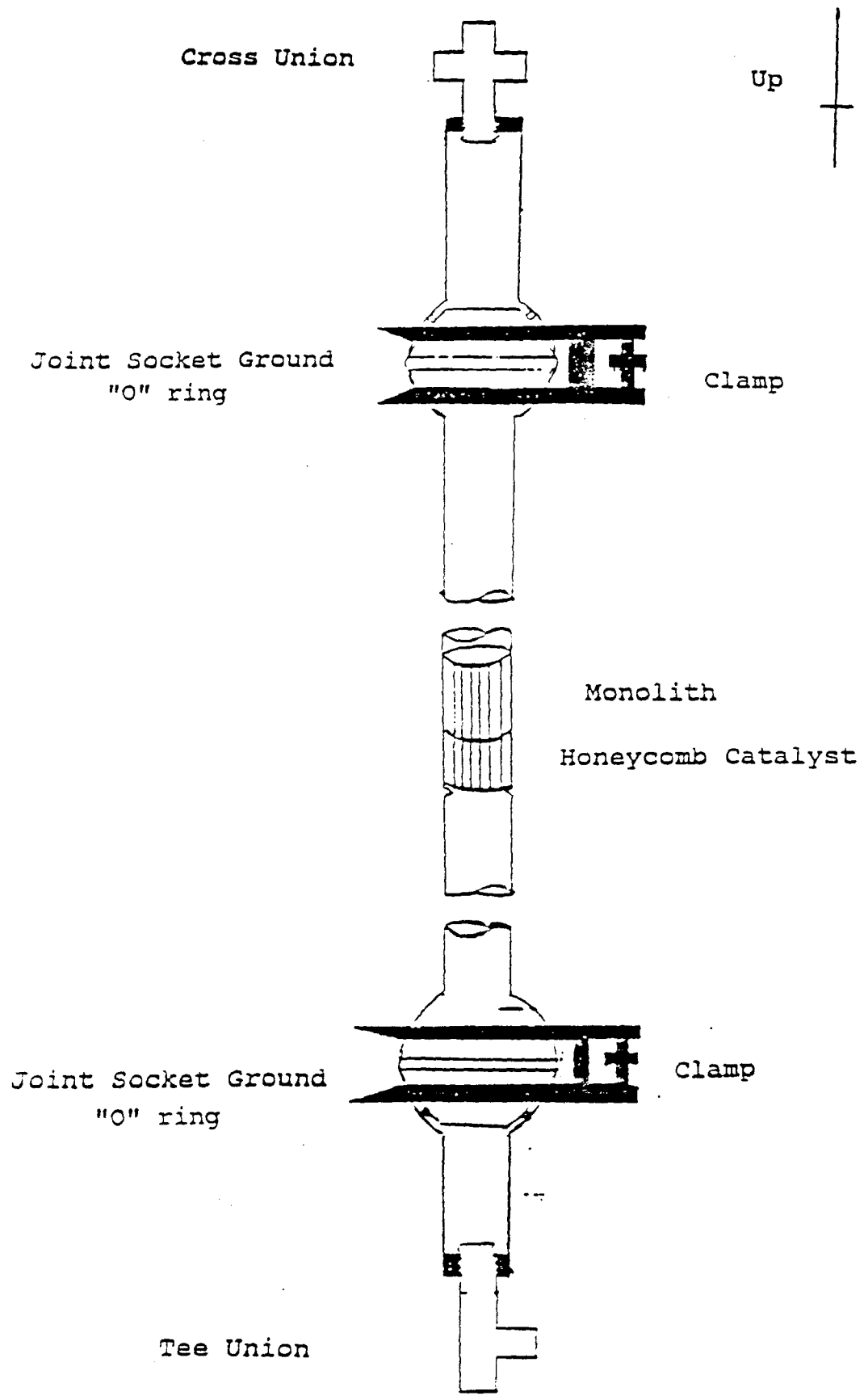


Fig. 4 Design for quartz tube reactor.

The reactor temperature was monitored by two 0.16 cm chromel-alumel (K-type) thermocouples which were inserted in both sides of quartz tube reactor and placed in the center line immediately before and after the catalyst. Since the measured temperatures were kept below 500°C, no corrections were made for radiation.

The HCl concentrations were determined by absorbing it in a bottle of distilled water followed by a bottle of NaOH solution with phenolphthalein as the indicator. After the indicator turned colorless, the solution was removed from the flow path and the concentration of the chloride ion in the aqueous solution measured by NaOH titration. The concentrations of Cl₂ were determined using commercially available Draeger Gas Detector Tubes. This method of analysis was reported to be accurate within 10 percent according to the manufacturer.

The gases were purchased from the Liquid Carbonic Co. and they were used directly from cylinders in the experiments. Air was of research grade purity zero air, with less than 5 ppm H₂O and less than 1 ppm hydrocarbons. Both C₂HCl₃ and CH₂Cl₂ purities were reported to be 99+ percents as liquids.

3. Analytical Instruments

The concentrations of feed and product compounds were measured using Hewlett Packard 5890 gas chromatographs. One has flame ionization (FID) and thermal conductivity (TCD) and the other

has electron capture (ECD) and flame photometric (FPD) detectors.

The CO, CH₄ and CO₂ were separated on a 1/8 inch in diameter by 6 feet long stain-less steel column packed with 80/100 mesh Poropak Q and hydrogenated over Ni-catalyst system to CH₄ before detection by flame ionization. The operating method for the nickel hydrogenation catalyst system is shown in Figure 5. When the ten-point sampling valve is at the off position, the product effluents pass through the sampling loop and discharge to the hood. Once the valve is switched over to the on position, the effluents are carried out by Helium from the sampling loop in to the Poropak Q column. The individual peaks are then hydrogenated with hydrogen to CH₄ using the Ni-catalyst at 350°C. Thus, the CO, CH₄ and CO₂ peaks are detected as CH₄ but recognized based on retention time.

The chlorinated hydrocarbons were separated on a 1/8 inch 10 feet stainless steel column packed with 80/100 mesh Chromosorb GAW and detected by electron capture.

Both carbon dioxide and carbon monoxide concentrations were calibrated with purchased standard gas mixtures. The chlorinated hydrocarbon concentrations were calibrated with the pure compounds by liquid injection. Hewlett Packard 3396A integrators were used as both recorders and integrators.

Figure 6, 7 and 8 show the typical peak resolution and

Figure 5 Nickle Hydrogenation Catalyst System

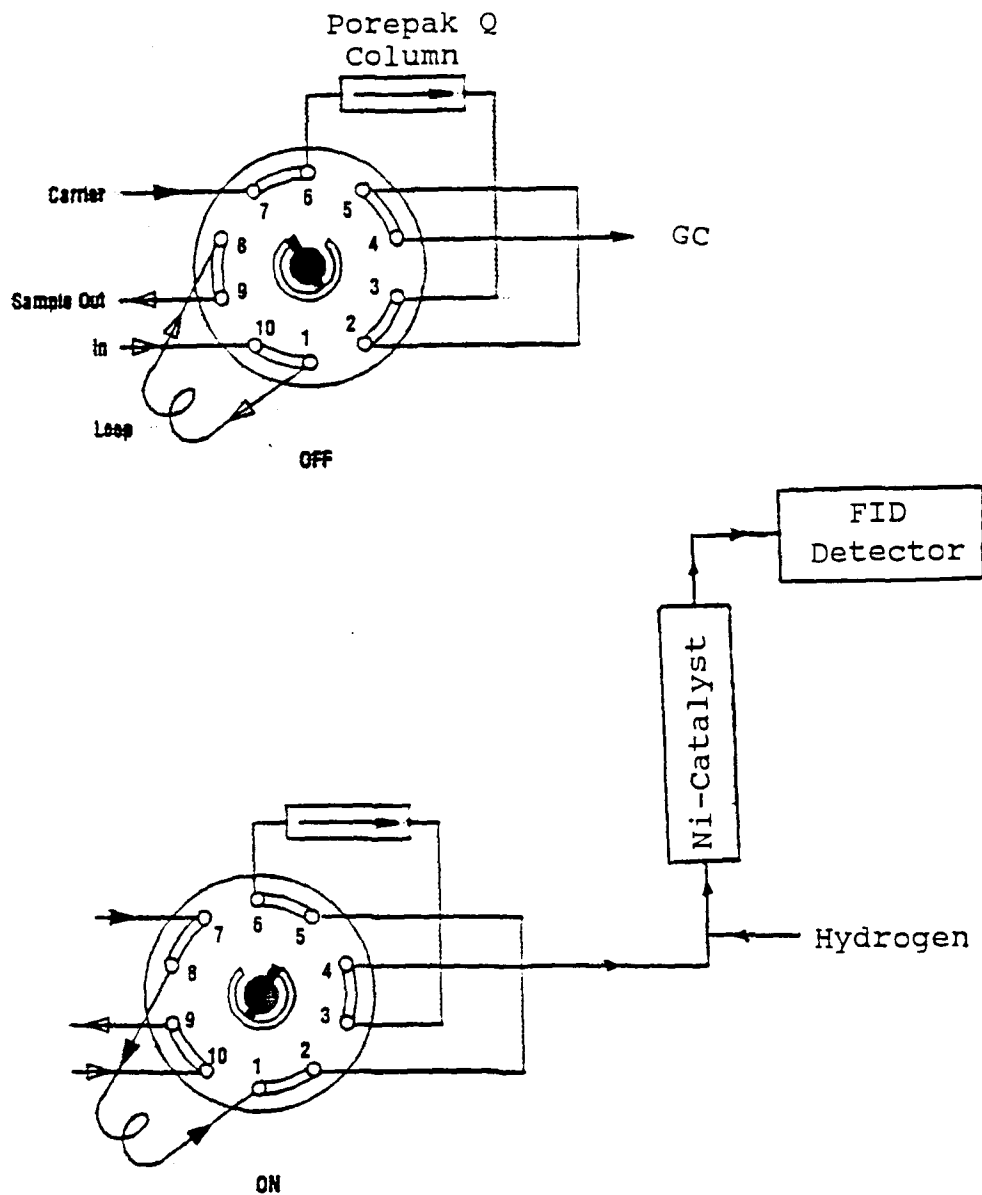
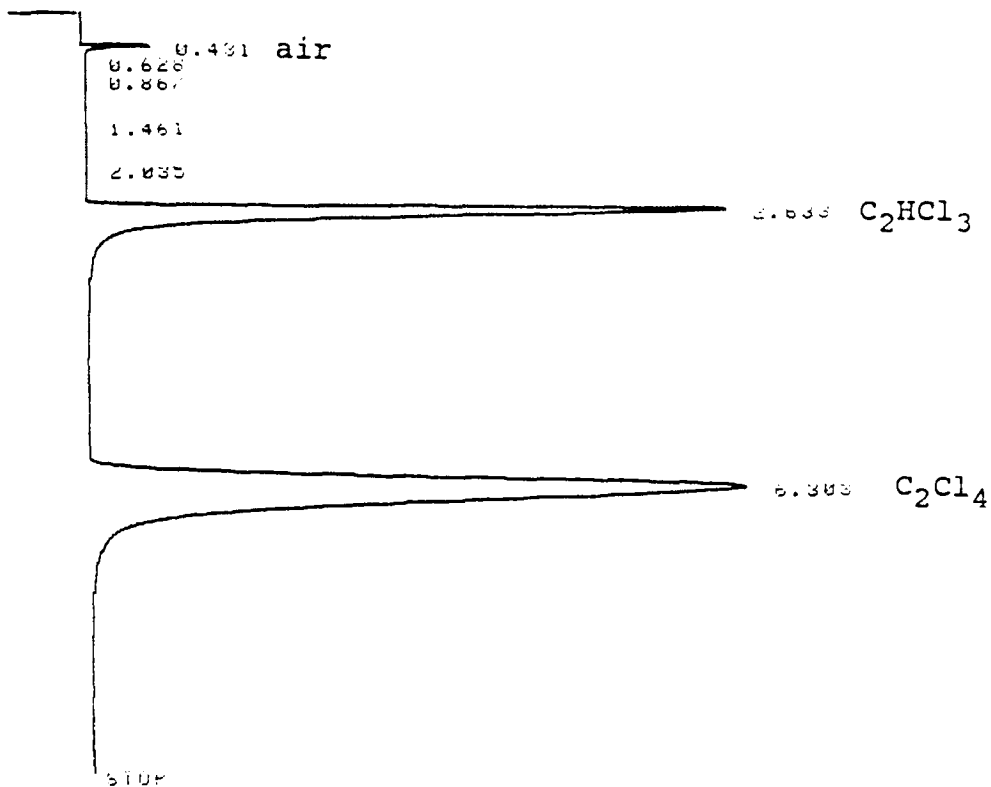


Figure 6 Peak resolution and retention time for chlorocarbon products from TCE oxidation.

* RUN # 955 MAY 8, 1981 11:37:50

START: not ready



RUN# 955 MAY 8, 1981 11:37:50

AREA%

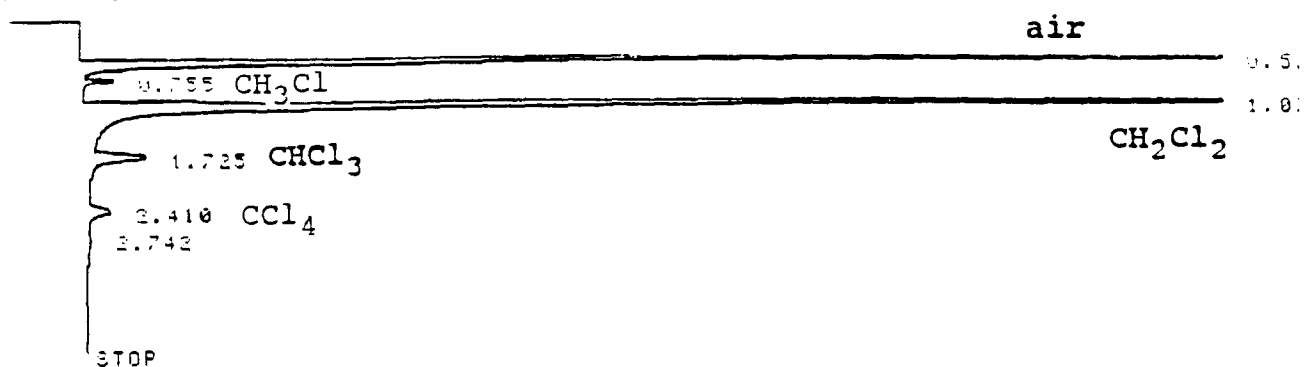
RT	AREA	TYPE	WIDTH	AREA%
0.431	507952	PF	.034	.54986
0.628	995	BF	.026	.00127
0.867	1292	PM	.061	.00165
1.461	3366	BF	.091	.00431
2.035	5402	PF	.125	.00691
2.633	22898672	PF	.164	29.29571
6.303	54746240	PF	.383	70.04032

TOTAL AREA=7.6164E+07

MUL FACTOR=1.0000E+00

Figure 7 Peak resolution and retention time for chlorocarbon products from DCM oxidation.

RUN # 134 JUL 10, 1990 14:12:51
 START: not ready

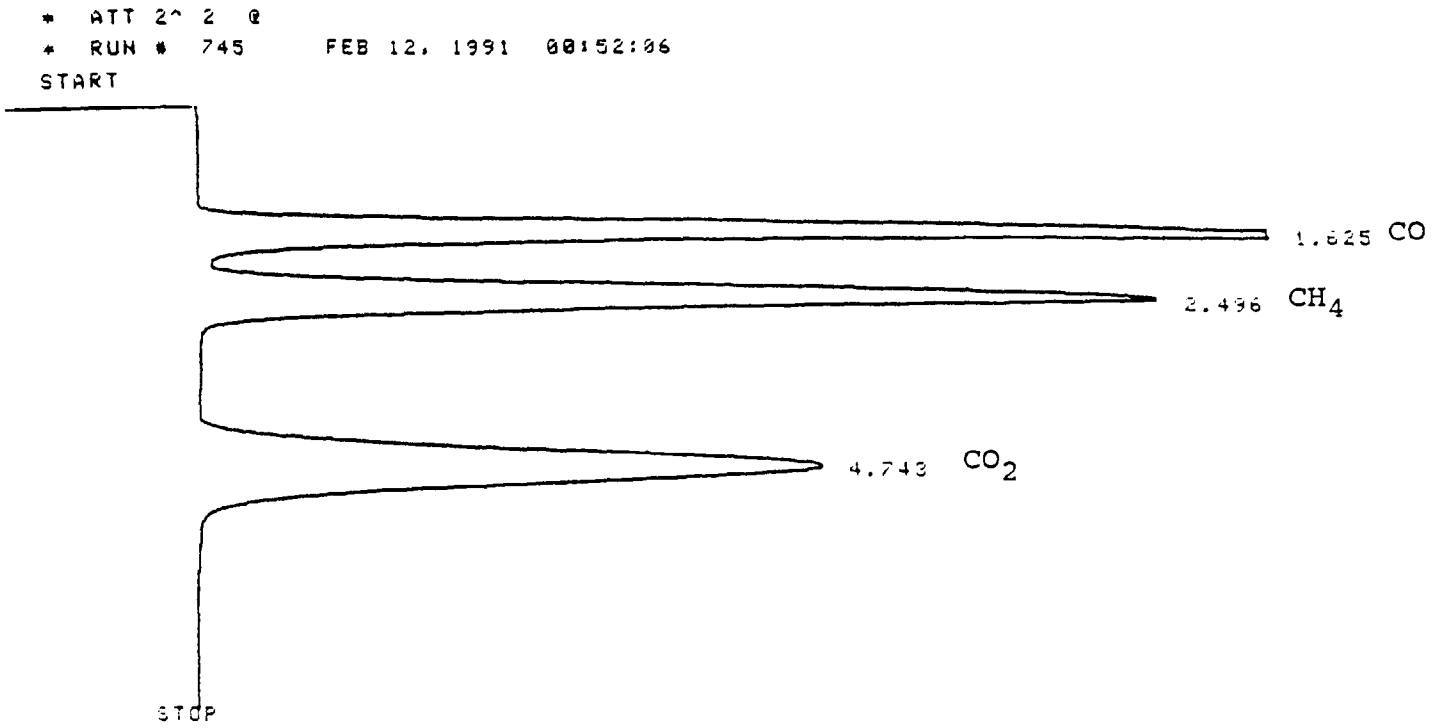


RUN# 134 JUL 10, 1990 14:12:51

RT	AREA	TYPE	WIDTH	AREA%
0.520	4248739	FB	0.336	45.49955
0.755	71691	FB	0.042	0.76977
1.071	4548787	FB	0.065	48.71278
1.725	309727	FB	0.106	3.31685
2.410	155338	SP	0.126	1.66351
2.742	3506	FB	0.014	0.3755

TOTAL AREA=9.3380E+06
 MUL FACTOR=1.0000E+00

Figure 8 Peak resolution and retention time of CO₂, CO and CH₄ on FID.



RUN# 745 FEB 12, 1991 00:52:06

AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.625	512793	PV	.248	31.86755
2.496	534768	VV	.327	33.23320
4.743	561577	VP	.522	34.89925

TOTAL AREA=1609138
 MUL FACTOR=1.0000E+00

retention time for the reactants and products. Table 1 presents GC conditions for both FID and ECD.

The hydrogen chloride was collected in an impinger with pure distilled water and the effluent was then bubbled through a bottle of NaOH solution with phenolphthalein as the indicator. When the second bottle become colorless, then the first bottle was titrated using standard NaOH solutions with methyl orange as the indicator.

4. Experimental Procedure

The flow schematic for this study is provided in Figure 3. A glass bubbler U- tube containing the desired chlorinated hydrocarbon reactant as a liquid was connected between the dry zero air feed line and reactor. A fixed concentration of reactant was picked up from the saturation bubbler maintained at 0°C using an ice-bath, mixed with an additional amount of zero air, and swept into the reactor. A fixed bed of platinum- alumina monolith catalyst rested in a vertical cylindrical (2.5 cm) quartz tube. The air and reactant stream was preheated in the quartz tube and introduced into the catalyst bed downflow. After steady flow conditions were obtained, flow was directed to the HCl collecting bubblers. The temperature profile through the bed could be measured by moving the two thermocouple on each side of the monolith. Most of the effluent products stream was directed to the HCl

Table 1. GC operating conditions

ECD : For chlorinated hydrocarbon

Detector Temperature : 250°C

Injection Temperature : 200°C

Oven Temperature : 40°C

Carrier Gas : Nitrogen, 30ml/min

Intergrator
Attenuation : 9

FID : For CO₂, CO and CH₄

Detector Temperature : 200°C

Injection Temperature : 150°C

Oven Temperature : 40°C

Carrier Gas : Helium, 5ml/min

Aux Carrier Gas : Helium, 30ml/min

Air : 400ml/min

Hydrogen : 35ml/min

Nickle Catalyst System Temperature : 350°C

Intergrator
Attenuation : 3

collecting impinger and a very small fraction of the gas stream, pulled by a vacuum pump, flowed through the ten points gas sampling valve, into a 32 ul loop from which the product samples were picked up by the carrier gas helium to the on-line gas chromatographs. The part of the effluents that flowed through the sampling loop/gas sampling valve and the gases exiting the gas chromatographs were discharged to a hood.

Experimental Results

A. Catalytic Oxidation of Dichloromethane

1. Catalyst and Space Velocity

The catalytic oxidation of dichloromethane was conducted over 1.5% platinum- alumina /monolith/200cpsi, (i.e., honeycomb has 200 cells per square inch). The two catalyst lengths used were 7.62 cm and 3.81 cm and each had 69 cells. The actual catalyst volume for the longer catalyst was:

$$\begin{aligned}V_C &= 7.62 * (69/200) * 2.54^2 \\ &= 16.96 \text{ cm}^3\end{aligned}$$

Using total flow rate of 300 cm³/min, a space velocity for the 7.62 catalyst can be calculated as follow:

$$\begin{aligned}SV &= \text{total flow rate/catalyst volume} \\ &= (300 \text{ cm}^3/\text{min} * 60 \text{ min/hr}) / 16.96 \text{ cm}^3 \\ &= 1020 \text{ v/v/hr}\end{aligned}$$

The corresponding space velocity for the 3.81 cm catalyst was 2040 v/v/hr.

2. Chlorocarbon Feed Concentration Estimates

The vapor pressure of different organic compounds can be calculated using the following equation (Reid, 1987):

$$\ln P = A - B/(T+C)$$

in which: P = vapor pressure at temperature T in mmHg

A, B and C = empirical constants

T = temperature in K

The parameters of dichloromethane are:

A = 16.3029

B = 2622.44

C = -41.70

At T = 273 K ; P = 144.4 mmHg

In order to obtain 600 ppm feed concentration, dichloromethane in liquid form in a ice bath were carried out by 1 ml/min air, and then diluted with 300 ml/min air. The feed concentration was estimated as follows :

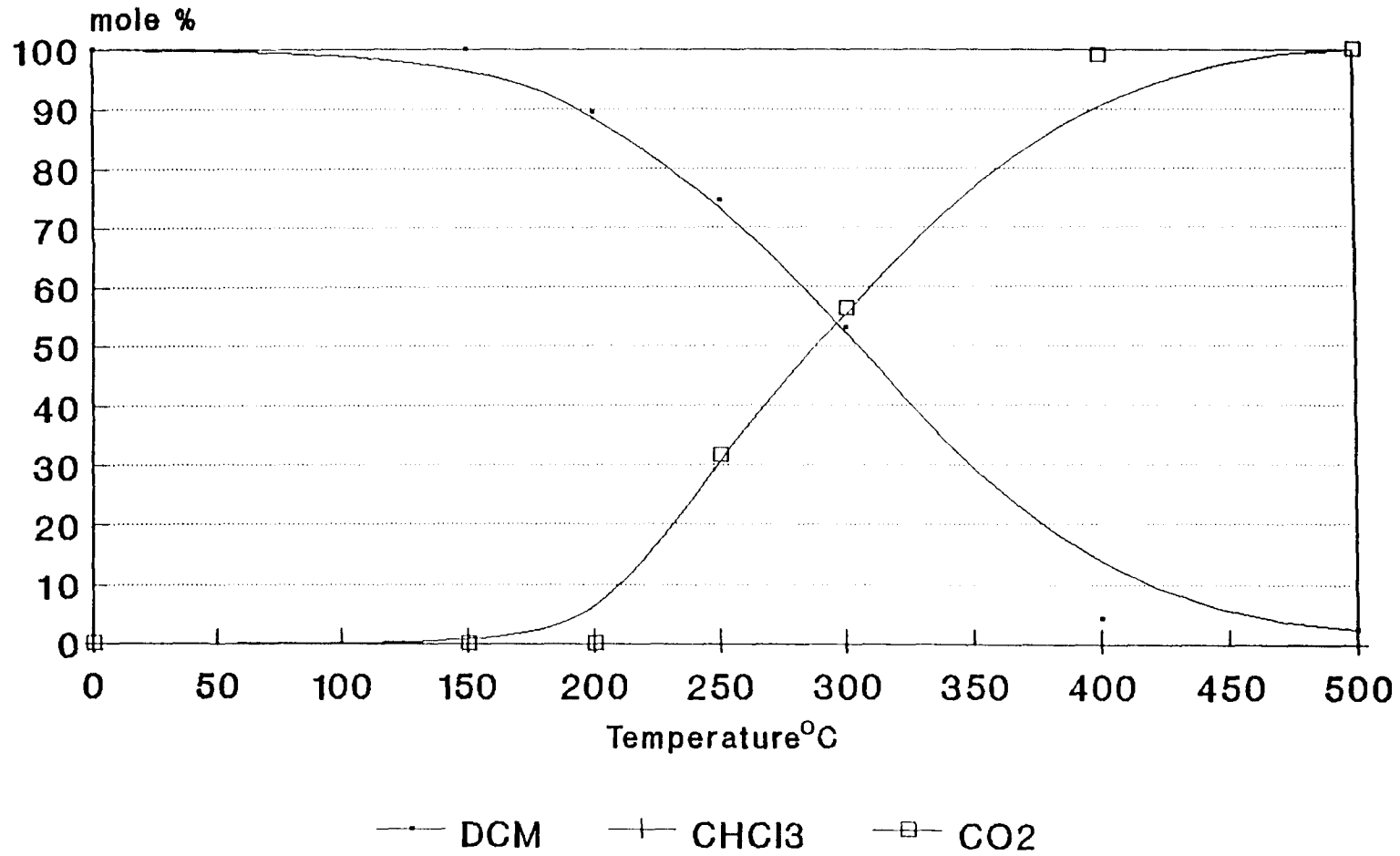
$$\begin{aligned} C &= (\text{carrier flow rate}) * (P/760) / \text{total flow rate} \\ &= (1 \text{ ml/min}) * (144.4 \text{ mmHg} / 760 \text{ mmHg}) / 301 \text{ ml/min} \\ &= 630 \text{ ppm} \end{aligned}$$

The actual feed concentration was measured by gas chromatography at various intervals through each experiment.

3. Results

The catalytic oxidation of dichloromethane was conducted in the temperature range of 100 to 450°C, and at the indicated space velocities of 1020 v/v/hr and 2040 v/v/hr. The dependence of conversion of dichloromethane on temperature at space velocity 1020 v/v/hr is shown in Figure 9. This results are summarized in

Figure 9. product distribution of CH₂Cl₂
1.5%Pt-rAl₂O₃/monolith/200cpsi



Feed = 492 ppm
SV = 1020v/v/hr

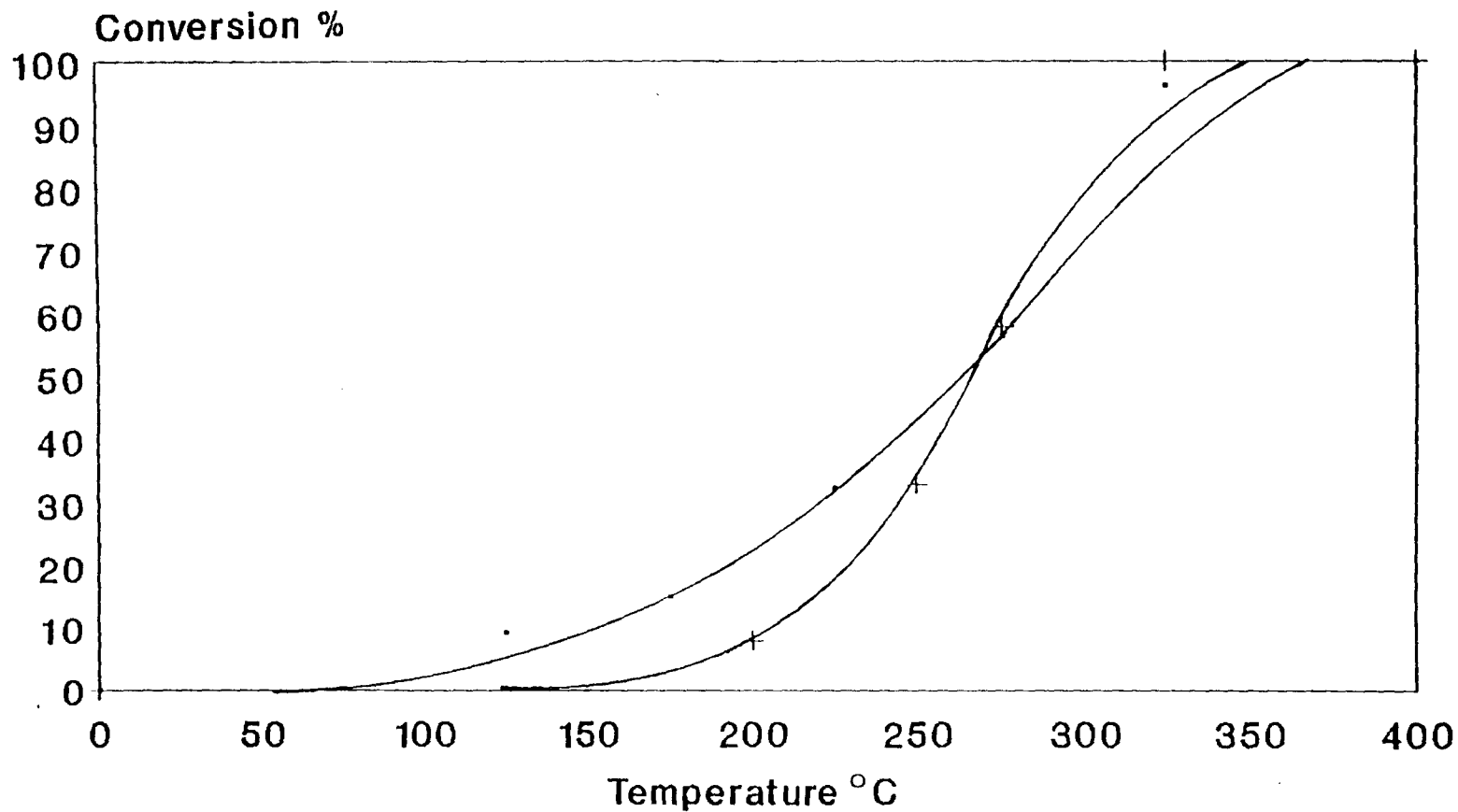
Table 2. It was found that at temperatures between 100°C and 200°C, there was only a very slight increase in conversion with increasing temperature. The catalytic light-off temperature was achieved at 200°C, as temperature was increased over 225°C, conversion increase rapidly. At 400°C, 100% conversion was reached. Table 2 also shows the excellent carbon balances that were determined between 225 and 400°C. It should also be noted that a comparison of DCM conversion using FID and ECD detection were in good agreement only above 30% conversion. In another series of experiments, the temperature dependence of the conversion of dichloromethane at different space velocities was examined. The comparison of conversion over two space velocities is shown in Figure 10. At temperature below 275°C, the conversion at low space velocity increase faster with temperature, but the change of conversion with temperature was similar for the two space velocities at temperatures higher than 275°C. Most of the reactant was converted to carbon dioxide and hydrogen chloride. Very low concentrations of chloroform, an intermediate product, was detected. These results are shown in Figure 11. The DCM conversion measurements in Table 3 show better agreement between the two chromatographic detectors (ECD and FID). Carbon balances were very good even at higher space velocities. The intermediate product chloroform was initially

Table 2. *Product Distribution for Oxidation of CH₂Cl₂ At 1020v/v/hr*

<i>Temp.(°C)</i>	<i>Concentration (ppm)</i>				<i>Conversion (%)</i>	
	<i>CH₂CL₂</i>	<i>CHCL₃</i>	<i>CO₂</i>	<i>C balance</i>	<i>FID</i>	<i>ECD</i>
20	492	0	0	0	0	0
125	480	0	0	0	9.35	2.43
175	451	0.01	0	0	15	8.28
225	362	0.73	0	96.3	32.2	26.3
275	270	2.35	183	92.1	56.1	45
325	51	0.88	461	104	96.3	89.7
400	4	0	520	107	100	99

HCl titration result: 1026ppm HCl was obtained at 400°C

Figure 10. Effect of Space Velocity on Oxidation of DCM



• 1020v/v/hr + 2040v/v/hr

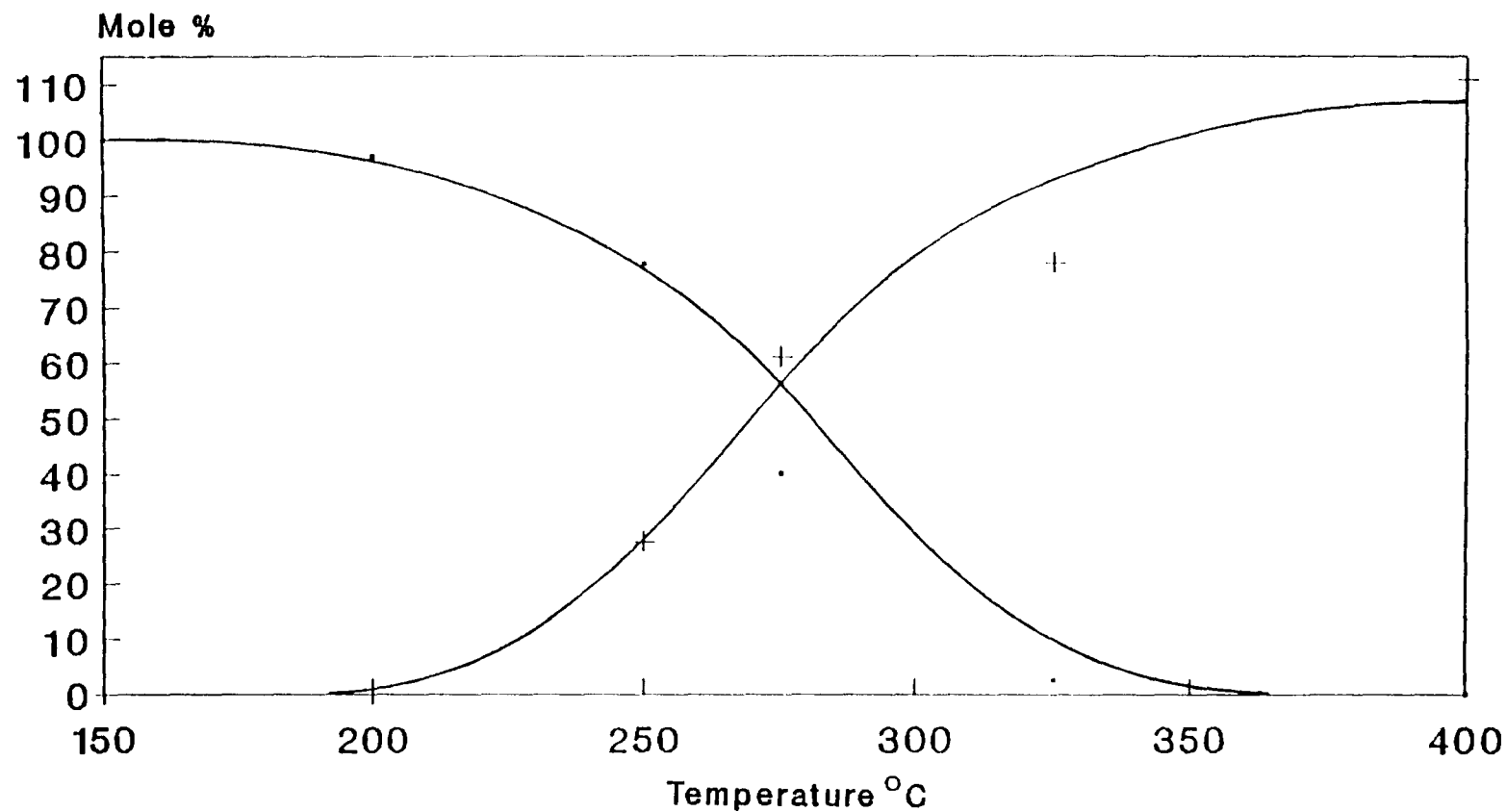
1.5%Pt-rAl₂O₃/monolith/200cpsl
Feed = 490ppm

Table 3. Product Distribution for Oxidation of CH₂Cl₂ At 2040v/v/hr
Temp.(°C) **Concentration (ppm)** **Conversion (%)**

	CH ₂ CL ₂	CHCL ₃	CO ₂	C balance	FID	ECD
20	481	0	0	0	0	0
200	467	1.15	0	0	8	3
250	372	5.01	132	105	32.8	22.8
275	191	3.69	292	100	57.6	60.3
325	11	0.31	372	80	100	97.7
400	0	0	532	110	100	100

HCl titration result: 997ppm HCl was obtained at 400°C

Figure 11. Product Distribution of CH₂Cl₂
1.5%Pt-rAl₂O₃/monolith/200cpsi



· CH₂Cl₂ + CO₂

Feed = 480ppm
SV = 2040v/v/hr

formed at 200°C, and increased to a maximum at 250°C before decreasing at higher temperatures.

B. Catalytic Oxidation of Trichloroethylene

1. Catalyst and Space Velocity

Those experiments were based on a 1.5% platinum-alumina/monolith/400cpsi (i.e., the monolith contains 400 cells per square inch). To obtain high space velocities, high temperature resistant cement was used to block a number of cells, thus reducing catalyst volume. Only 25 cells were allowed to remain. The length of catalyst monolith was 7.62 cm, therefore, the actual volume of modified catalyst was:

$$\begin{aligned}V_c &= 7.62 * (25/400) * 2.54^2 \\ &= 3.0726 \text{ cm}^3\end{aligned}$$

Different space velocities were obtained during the experiments by using different flow rates:

$$\text{Space Velocity} = \text{flow rate/catalyst volume}$$

2. Determination of Feed Concentration

As described above, the following equation was used for calculating vapor pressure:

$$\ln P = A - B/(T+C)$$

For trichloroethylene (TCE), the empirical constants are:

$$A = 16.1827$$

$$B = 3028.13$$

$$C = -43.15$$

At $T = 298 \text{ K}$ (room temperature) the vapor pressure of TCE is:

$$P = 74.3 \text{ mmHg}$$

The initial feed concentration can be calculated as:

$$C_i = (\text{carrier flow rate}) * (P/760) / \text{total flow rate}$$

3. Results

a. Aging Experiments

(1). General Description

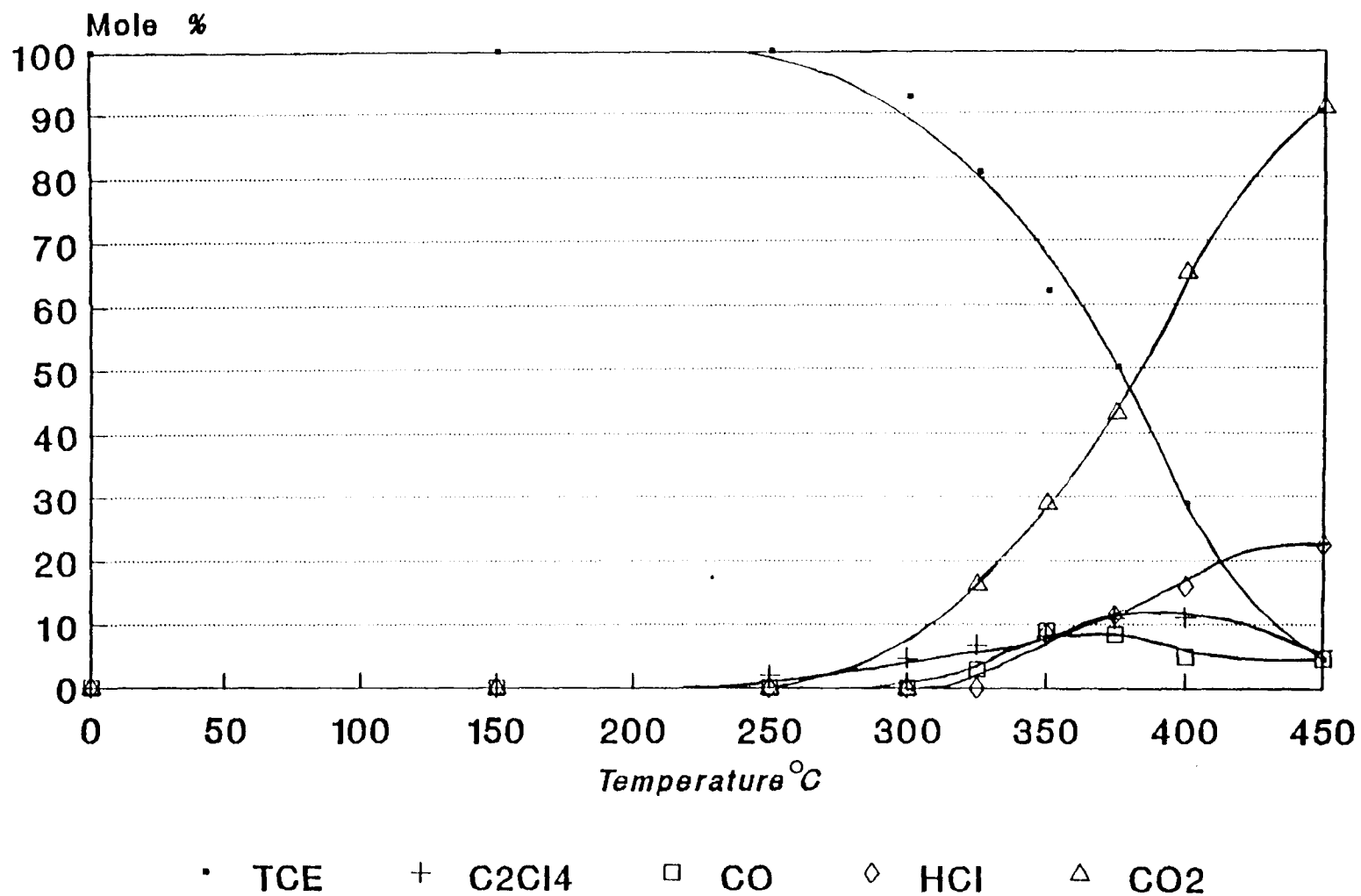
The aging experiments were run to determine catalyst deactivation over 100 hours. To avoid losing platinum sites because of vaporization, the maximum temperature was limited to 450°C , at which 95% conversion of TCE can be achieved. A fresh catalyst was used to catalytically oxidize 50 ppm trichloroethylene at 30,000 v/v/hr space velocity over the temperature range 150 to 450°C . After this run, the catalyst bed was cooled down to room temperature. Then the furnace was heated directly to 450°C , and 50 ppm C_2HCl_3 was fed at 30,000 v/v/hr space velocity and this condition was maintained for 25 hours, followed then by a cool-down again to room temperature. The 25 hours aging experiment was repeated 3 more times with the same catalyst at the same operating conditions as the 25 hours run. Interspersed between the 25 hours runs were 150 to 450°C characterization runs to compare the

degree of catalyst deactivation with the fresh catalyst.

(2). The Effect of Temperature on Reaction

The results from the aging experiments are presented in this section. The dependence of conversion as well as product distribution on temperature for fresh catalyst is plotted in Figure 12, the product distributions, material balances for carbon and chlorine, and selectivities to CO_2 and HCl are summarized in Table 4. Since the experiment was conducted at high space velocity 30,000 v/v/hr, the light-off temperature of 300°C is significantly higher than that for dichloromethane oxidation. Figure 12 shows that in the temperature range 250 to 330°C , conversion increases slowly with increasing temperature. As temperature is increased further, then conversion increase rapidly, such that at 450°C , about 95% conversion is obtained. The main products are carbon dioxide and hydrogen chloride. Trace amount of carbon monoxide and perchloroethylene are also produced. The selectivities to CO_2 and HCl at different temperature were calculated and are given in Table 4. Almost 90% selectivity to CO_2 is obtained, but only 22% selectivity to HCl is achieved. As temperature increases, very low concentrations of CO are produced. At 350°C , the amount of CO reaches a maximum and then decrease with increasing temperature. The distribution of C_2Cl_4 follow a similar trend to that of CO . At 400°C , the amount of C_2Cl_4

Figure 12. Products Distribution : Fresh Catalyst
 1.5%Pt- γ Al₂O₃/400cpsi SV=30,000/hr



Products are represented by mole%

Table 4. Product Distribution of Aging Experiment : Fresh

Temp. (°C)	TCE*	C ₂ Cl ₄ *	CO ₂	CO*	HCl*	Conv. (%)	C Bal (%)#	Cl Bal (%)#	CO ₂ Sel (%)@	HCl Sel (%)@
150	41	0	0	0	0	0	100	100	0	0
250	41	0.8	0	0	0	0	100	102	0	0
300	38	1.98	0	0	0	7.2	97	99	0	0
325	33.1	2.8	13.8	2.4	0	19.2	104	90	84.8	0
350	25.4	3.34	23.7	7.3	10.6	38.1	108	81.4	76	22.6
375	20.5	4.53	35.3	6.9	14.3	49.9	112	76.5	86.3	23.3
400	11.8	4.55	53.2	4.1	19.7	71.3	110	55.8	91	22.5
450	1.8	2.51	74.5	3.7	27.6	95.7	106	34.9	95	23.4

38

Note:

1. * ppm(v).
2. # material balance.
3. @ selectivity.

reaches a maximum and then decreases.

(3). The Effect of Aging Time on Reaction

Dependence of conversion on temperature for different aging times were investigated systematically. All results are shown in Figures 13, 14, 15 and 16 and Tables 5, 6, 7 and 8.

As described above, after 25, 50, 75 and 100 hours of operation at 450°C, experiments were conducted at the same operating conditions that were used with the fresh catalyst. The results show that in all cases, there was only a very slight change in conversion versus temperature curves, and the catalyst was not obviously deactivated. Similar products distribution trends were obtained for all cases. The comparison of conversion versus temperature curves at different aging time is shown in Figure 17.

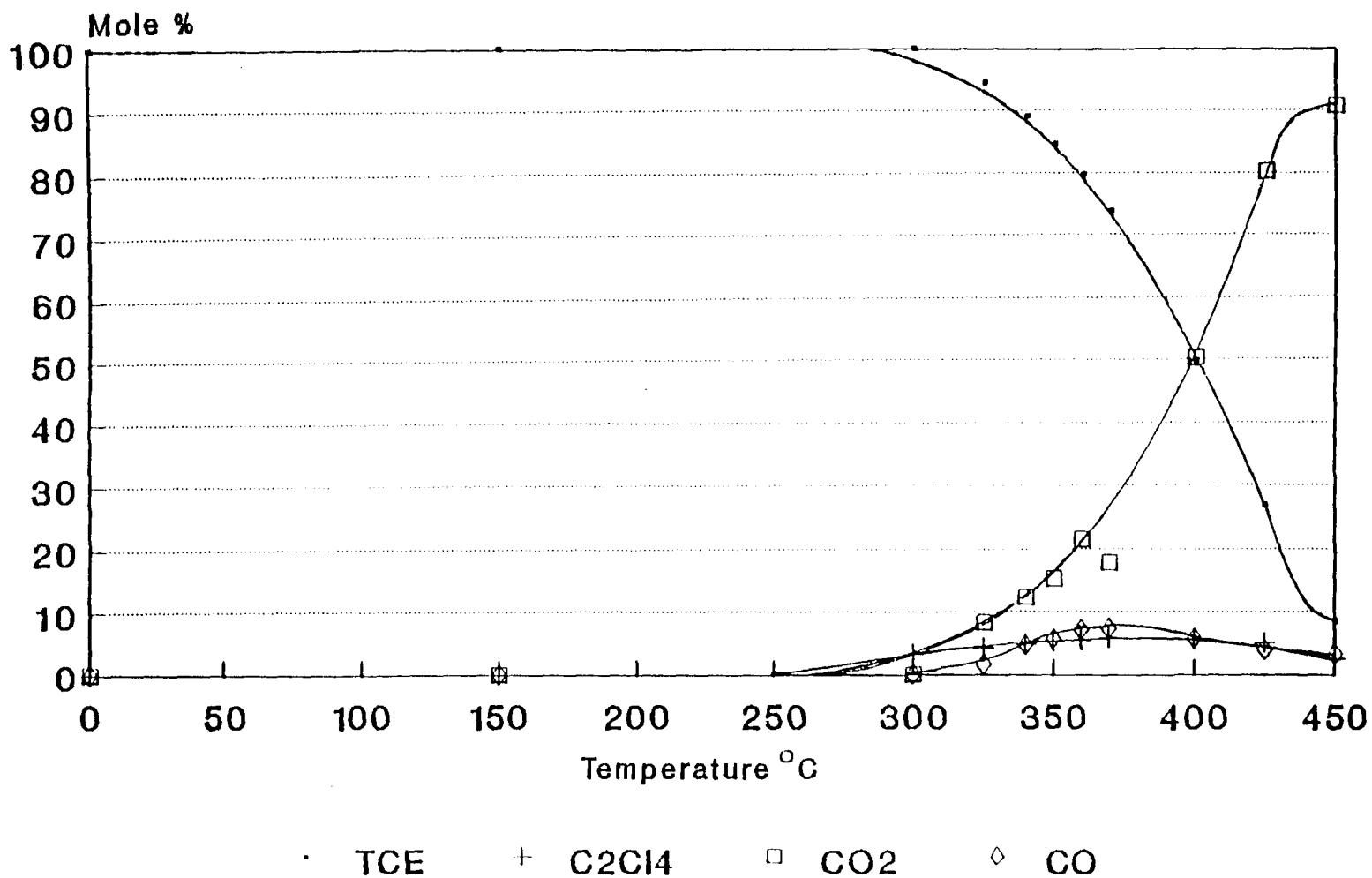
(4). The Effect of Aging Time on Reaction Kinetics

To study the chemical kinetics of catalytic oxidation of trichloroethylene, all data were collected at conversions less than 30% (i.e., in the chemical kinetics control region). For each case, different space velocities were used to calculate the rate constant k at same temperatures. Figures 18, 19, 20, 21 and 22 show Arrhenius plots for the first order rate constant k for each set of runs between the 25 hours aging tests.

According to Arrhenius equation:

$$k = A \cdot \exp(-E_a/RT)$$

Figure 13. Products Distribution : 25 hours Aged
 1.5%Pt- γ Al₂O₃/400cpsi SV=30,000/hr



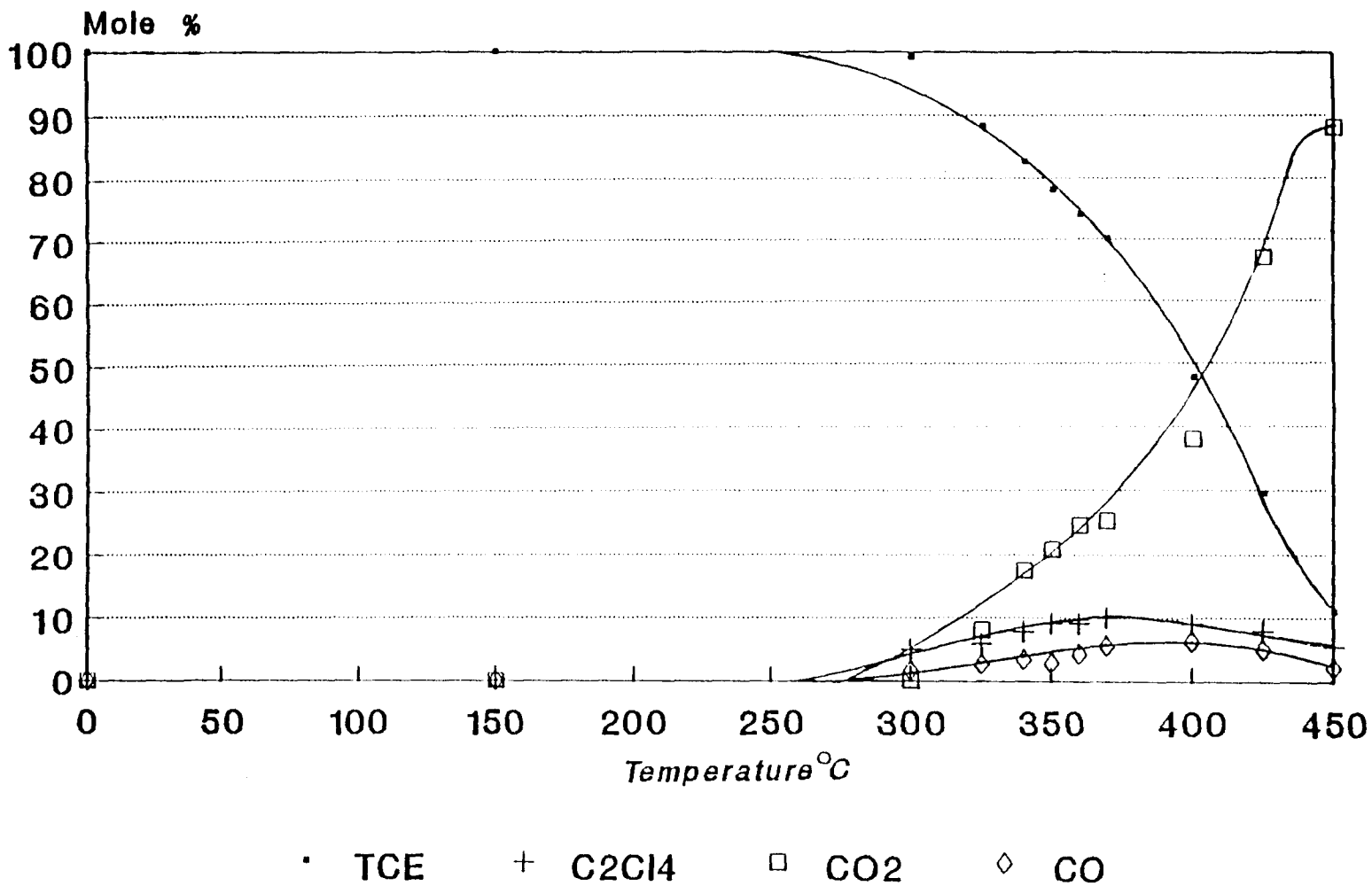
Products are represented by mole%
 Feed Conc. of TCE = 50ppm

Table 5.

Product distribution after 25 hours of operation at 450°C.

Temp. (°C)	TCE	C ₂ Cl ₄	CO ₂	CO	Conv. (%)	C Bal (%)
150	50	0	0	0	0	100
300	50	1.65	0	0	0	102
325	47.2	2.12	8.3	1.7	5.5	107
340	44.5	2.47	12.2	4.8	11	107
350	42.3	2.63	15.3	5.7	15.5	106
360	39.8	2.79	21.5	7.2	20.4	108
370	36.9	2.89	17.7	7.3	26.2	98
400	24.9	2.80	37.2	5.8	50.3	94
425	13.4	2.61	80.1	4.1	73.2	113
450	4.2	1.30	90.6	3.3	91.6	102

Figure 14. Products Distribution : 50 hours Aged
 1.5%Pt- γ Al₂O₃/400cpsi SV=30,000/hr



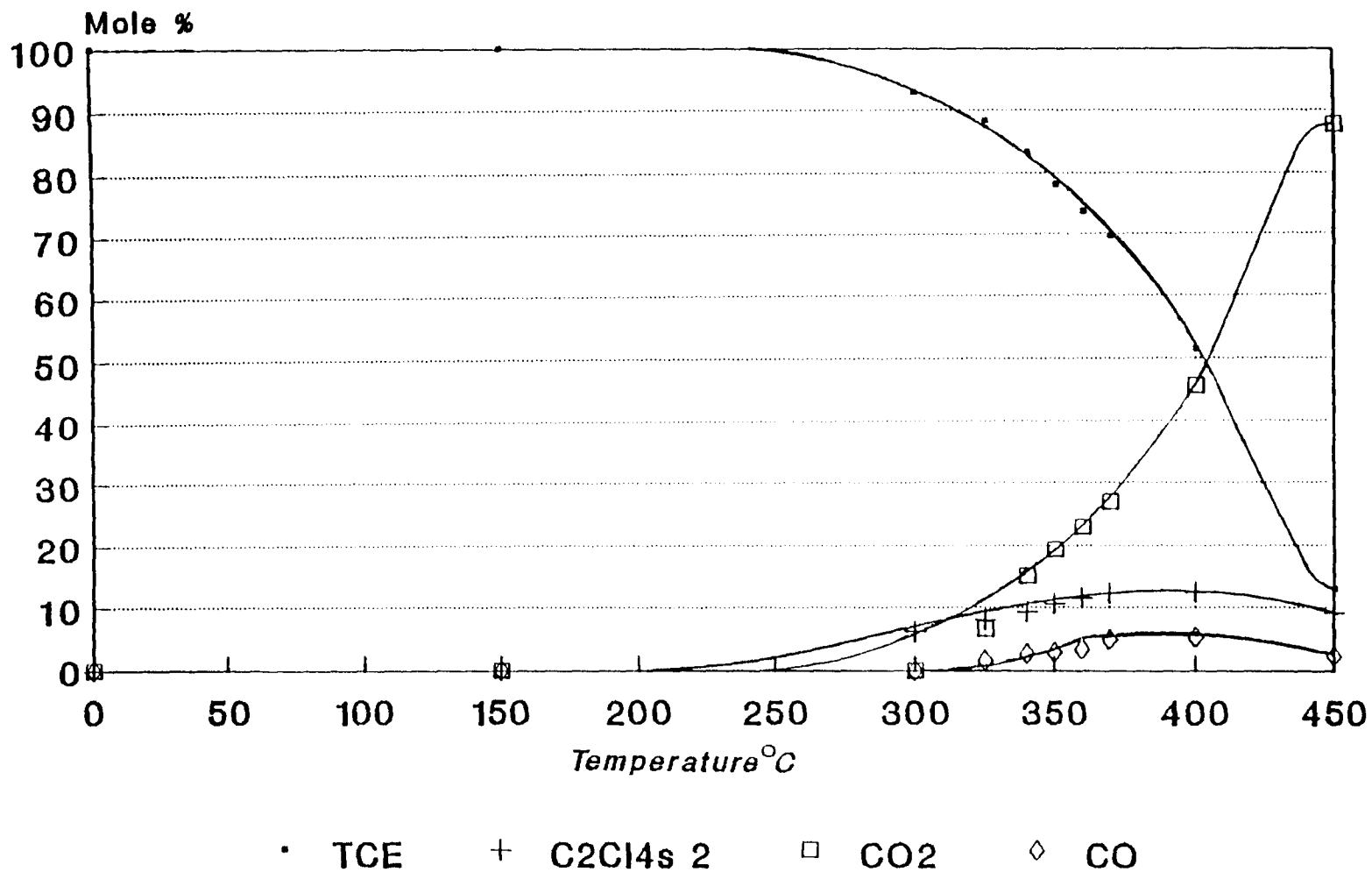
Products are represented by mole%

Table 6.

Product distribution after 50 hours of operation at 450°C.

Temp. (°C)	TCE	C ₂ Cl ₄	CO ₂	CO	Conv. (%)	C Bal (%)
150	53	0	0	0	0	100
250	53	0	0	0	0	100
300	52.9	2.73	0	1.7	5.2	105
325	46.8	3.2	8.5	3.0	11.8	103
340	43.7	4.13	18.4	3.7	17.5	108
350	41.3	4.82	22	3.2	22	108
360	39.2	4.87	26.1	4.75	26	110
370	37.0	5.32	26.8	6.1	30.2	106
400	25.3	4.81	40.2	6.7	52.2	97
425	15.7	4.3	71.0	5.5	70.4	106
450	5.8	3.03	93.4	2.2	89.0	107

Figure 15. Products Distribution : 75 hours Aged
 1.5%Pt- γ Al₂O₃/400cpsi SV=30,000/hr



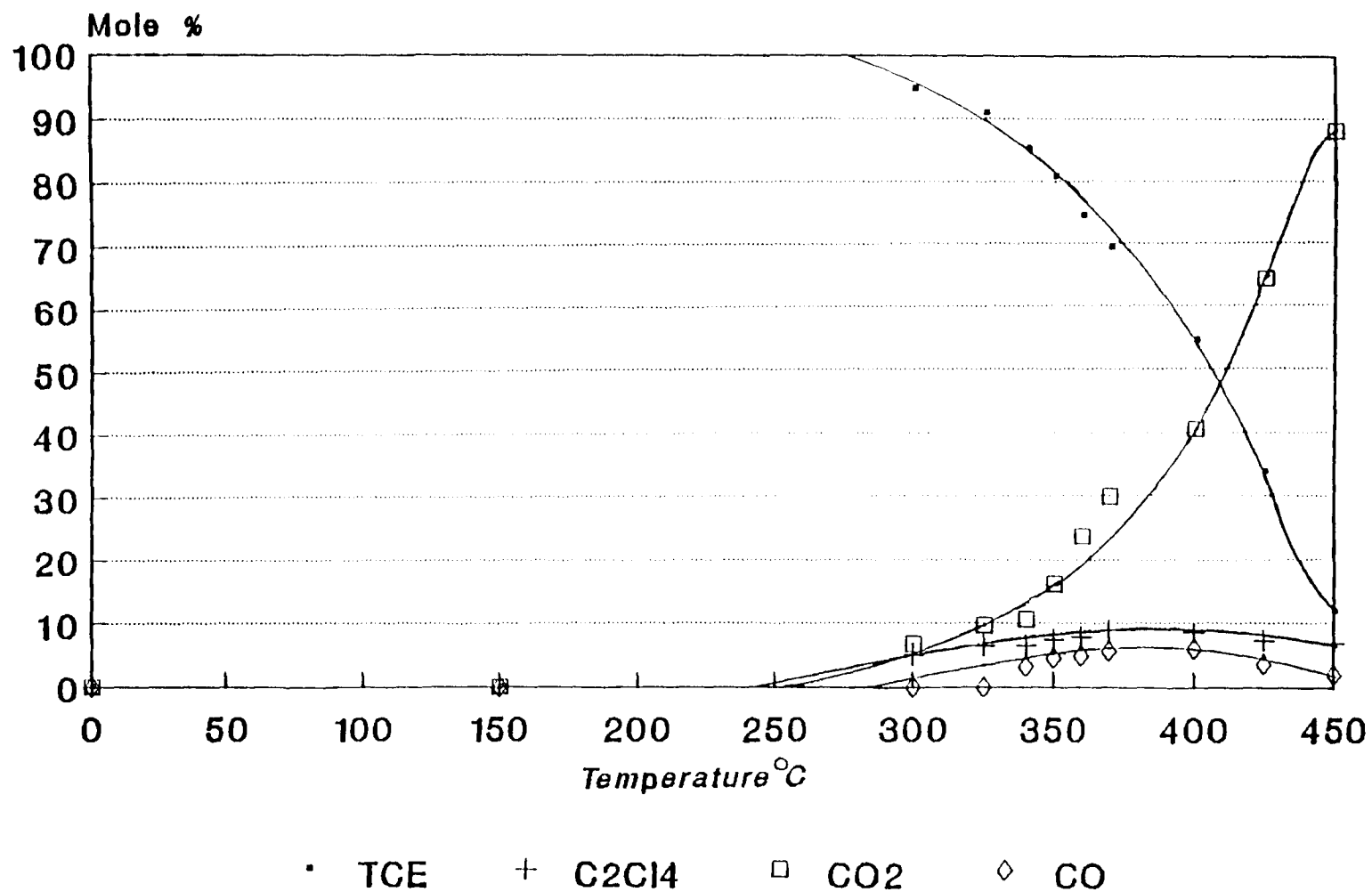
Products are represented by mole%

Table 7.

Product distribution after 75 hours of operation at 450°C.

Temp. (°C)	TCE	C ₂ Cl ₄	CO ₂	CO	Conv. (%)	C Bal (%)
150	62	0	0	0	0	100
250	62	0	0	0	0	100
300	57.6	3.87	0	0	6.8	99
325	54.7	5.0	10.4	2.1	11.5	96
340	51.6	5.85	18.6	3.4	16.8	108
350	48.4	6.61	23.8	3.6	21.8	108
360	45.5	7.1	28.3	4.3	26.3	108
370	43.2	7.58	33.4	6.1	30.2	109
400	31.8	7.75	56.6	6.5	48.5	103
450	8.0	5.73	108.6	3.0	87.1	94

Figure 16. Products Distribution : 100 hours Aged
 1.5%Pt- γ -Al₂O₃/400cpsi SV=30,000/hr



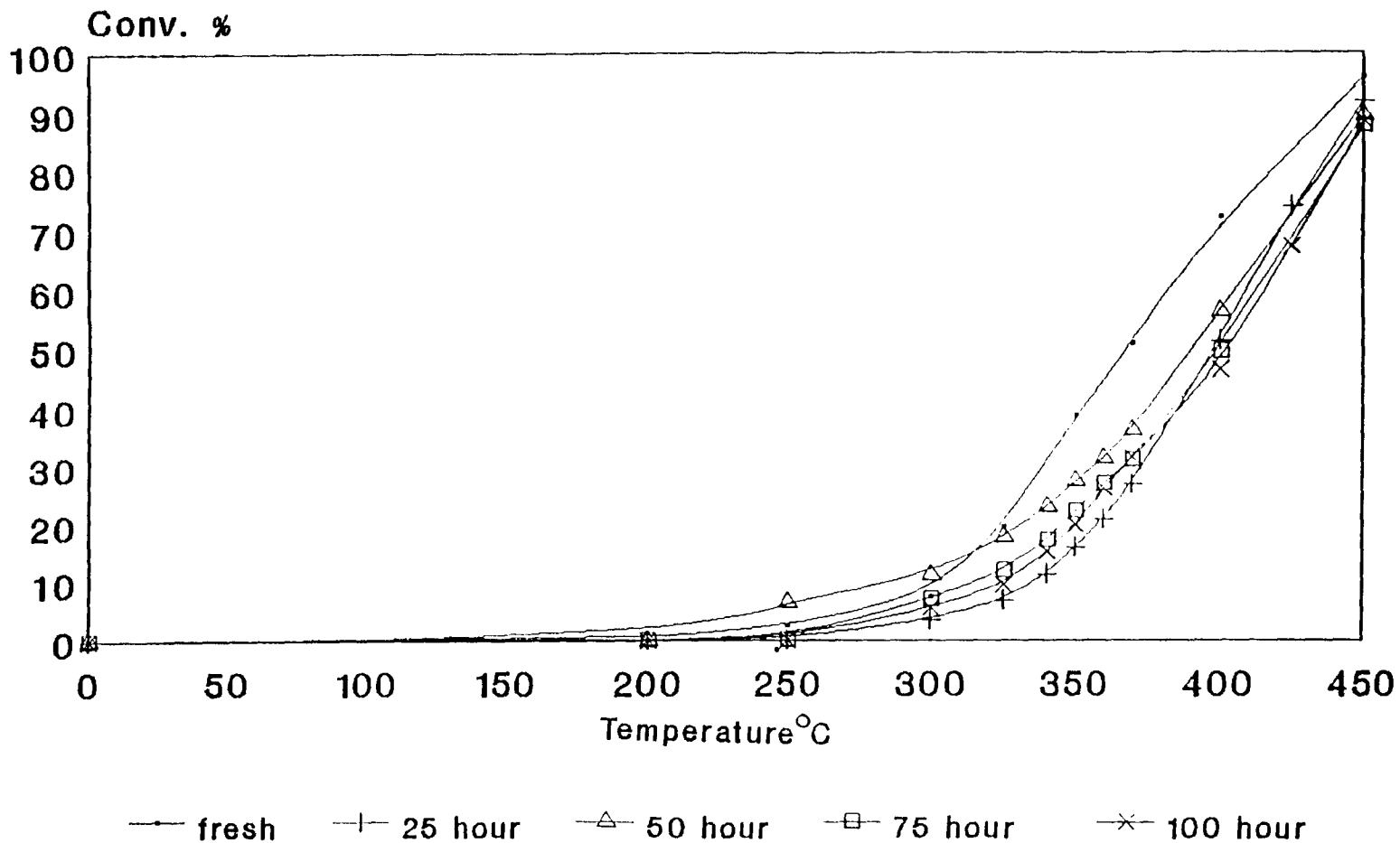
Products are represented by mole%

Table 8.

Product distribution after 100 hours of operation at 450°C.

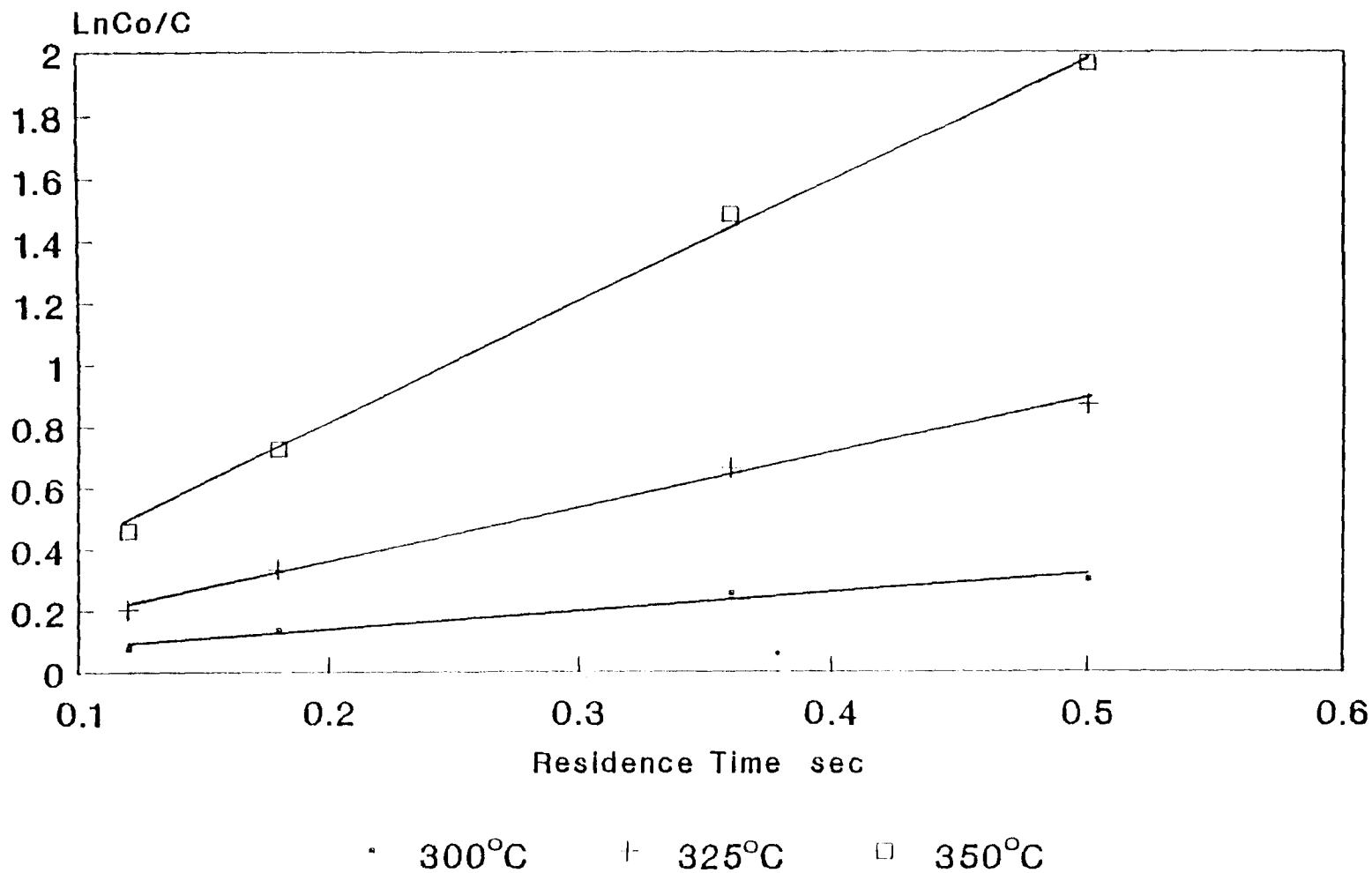
Temp. (°C)	TCE	C ₂ Cl ₄	CO ₂	CO	Conv. (%)	C Bal (%)
150	57	0	0	0	0	100
250	57	0	0	0	0	100
300	54	2.93	7.8	0	5.3	107
325	51.8	3.71	11.0	0	9.1	107
340	48.6	3.75	12.2	3.7	14.7	103
350	46	4.32	18.4	5.3	19.3	105
360	42.5	4.47	27.0	5.7	25.4	107
370	39.5	5.1	34.1	6.4	30.7	109
400	31.1	4.94	46.3	6.8	45.4	105
425	19.2	4.22	73.2	4.2	66.3	105
450	6.8	3.97	100.4	2.3	88.0	107

Figure 17. AGING EXPERIMENTS WITH TCE AT 450°C
SV=30,000/hr 1.5%Pt/Al₂O₃/400cps



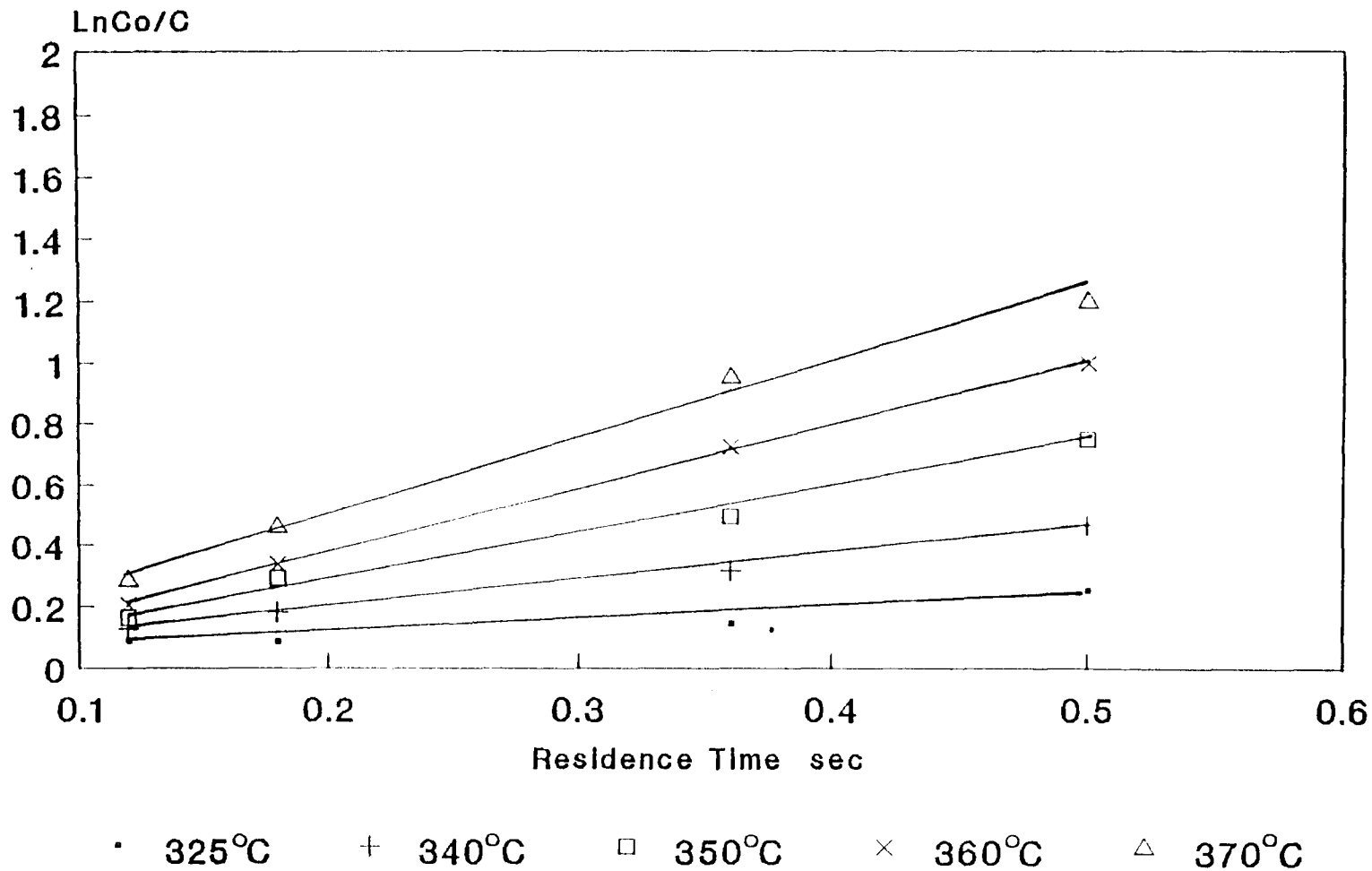
Feed Conc. = 50 - 60ppm

Figure 18. Determination of rate constant k
Fresh catalyst



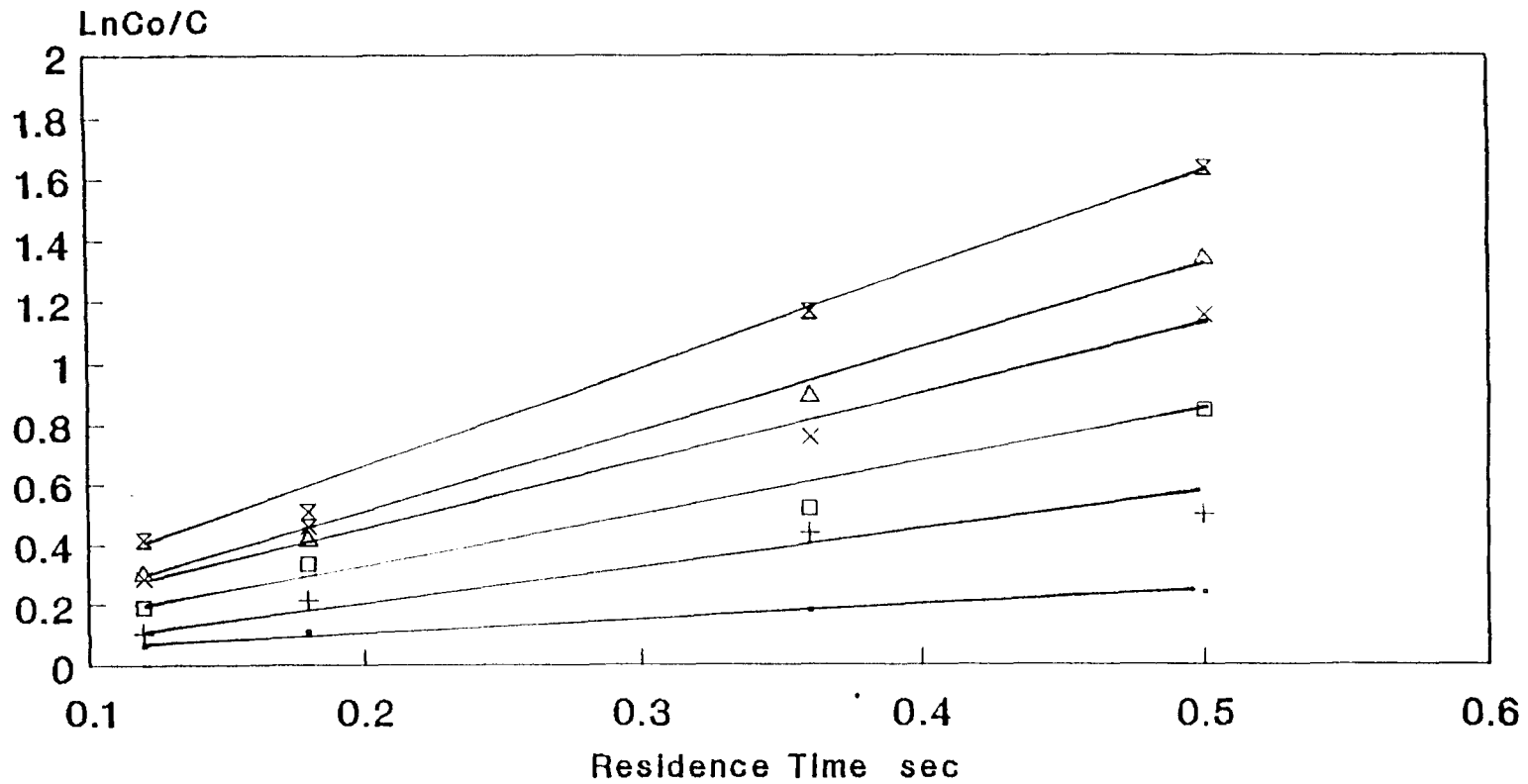
Reactant: 40ppm TCE

Figure 19. *Determination of Rate Constant k*
25 uours adged catalyst



Reactant: 50ppm TCE

Figure 20. *Determination of Rate Constant k*
50 hours aged catalyst

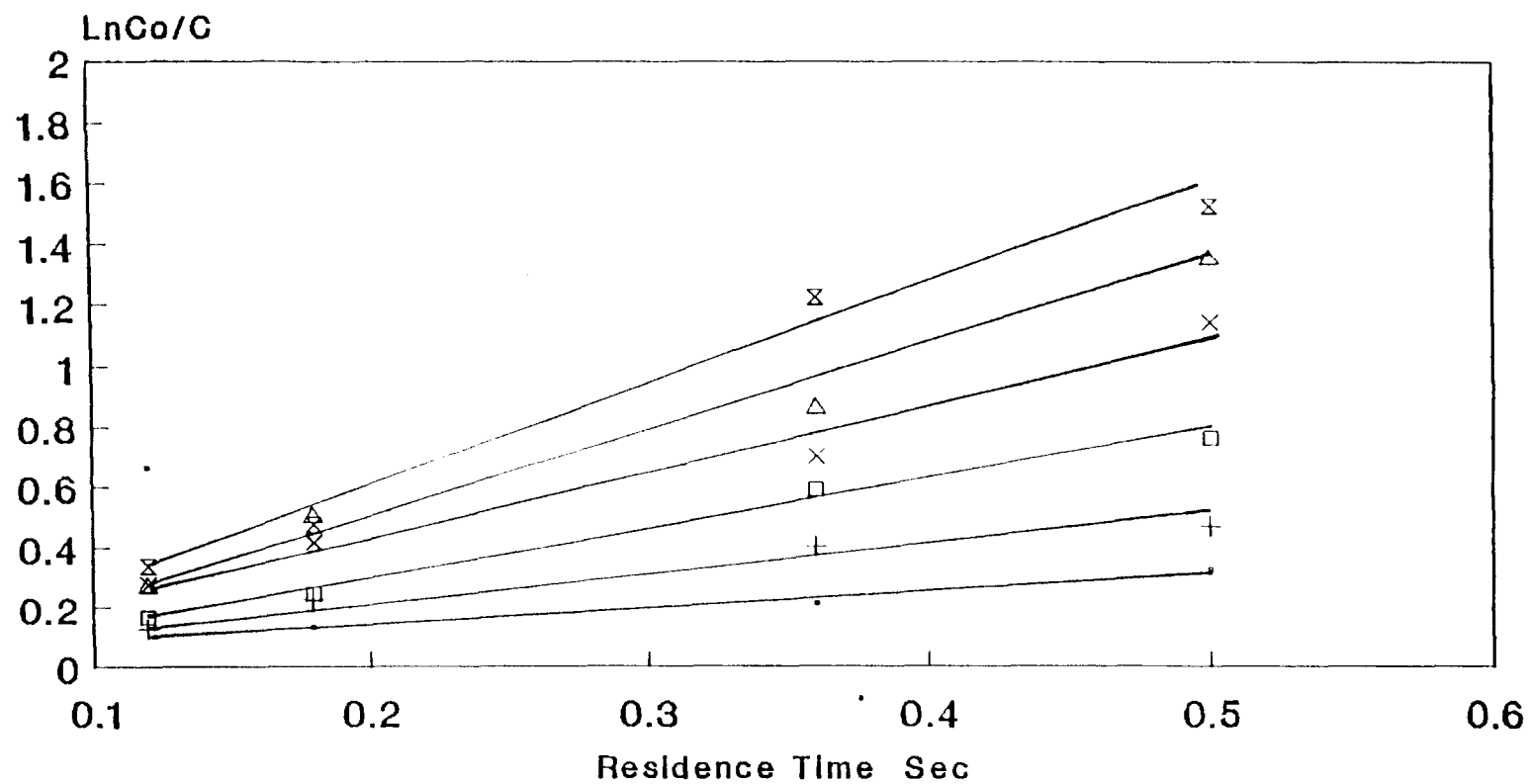


51

· 300°C	+ 325°C	□ 340°C
× 350°C	△ 360°C	⊠ 370°C

Reactant: 53ppm TCE

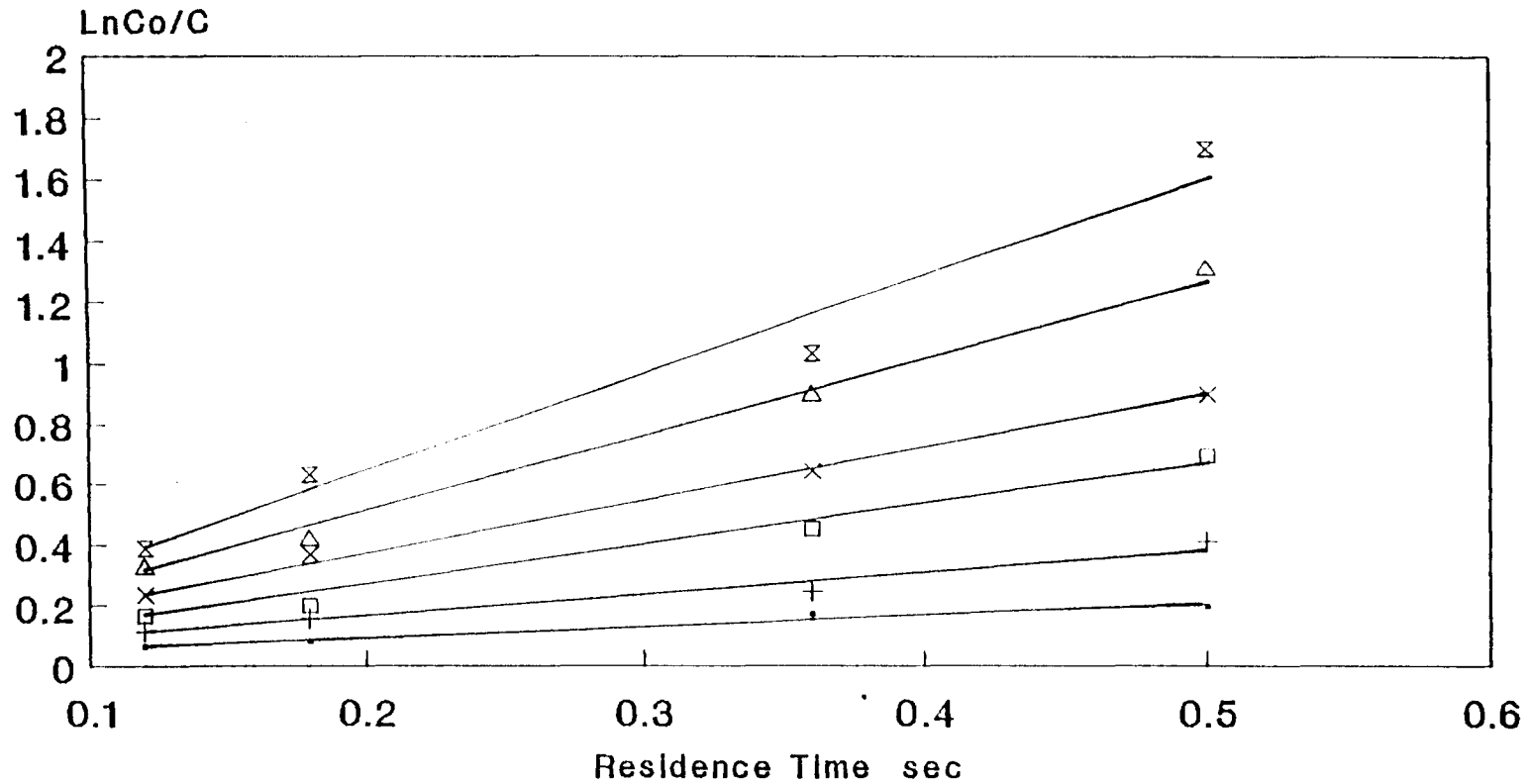
Figure 21. Determination of Rate Constant k
75 hours aged catalyst



· 300°C	+ 325°C	□ 340°C
× 350°C	△ 360°C	⊠ 370°C

Reactant: 62ppm TCE

Figure 22. *Determination of Rate Constant k*
100 hours aged catalyst



• 300°C

+ 325°C

□ 340°C

× 350°C

△ 360°C

⊗ 370°C

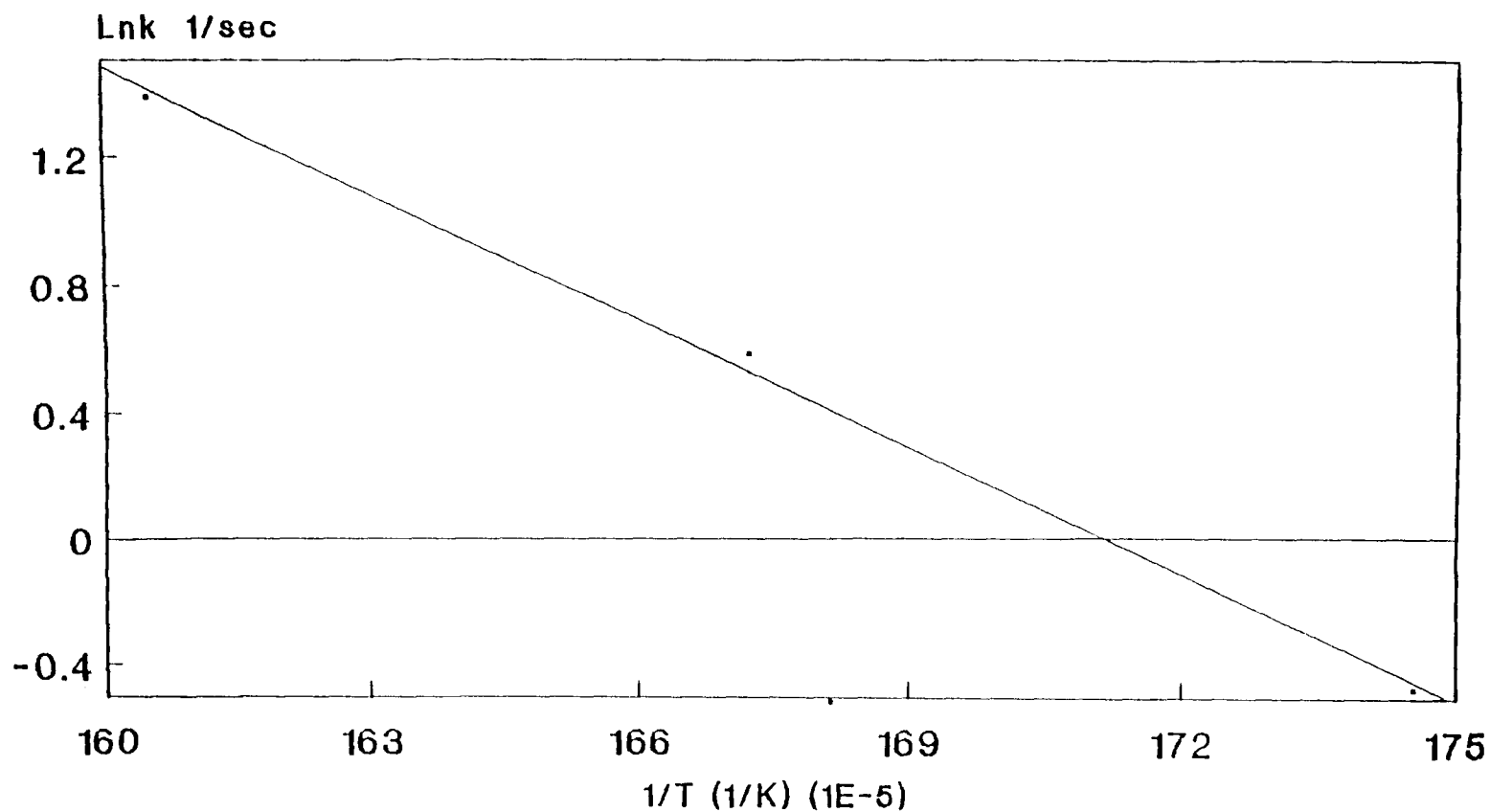
Reactant: 57ppm TCE

the plots of the logarithm of the rate constant k versus the inverse of temperature K for each cases are shown in Figures 23, 24, 25, 26 and 27. The activation energies E_a and pre-exponential factors A for each cases were calculated and listed in Table 9.

C. The Effect of Additives on C_2HCl_3 Oxidation

Trichloroethylene contains only one hydrogen atom. Consequently, upon oxidation, TCE would yield equal molar concentrations of HCl and Cl_2 . Thus, for complete conversion of TCE, one would obtain 25% HCl, 25% Cl_2 and 50% CO_2 . Due to this limitation, only 22% selectivity to HCl is obtained. To improve the selectivity to HCl, either a hydrogen-rich fuel such as methane or water vapor were added to the feed. The influence of both water and methane on products distribution of C_2HCl_3 oxidation are shown in Figures 28 and 29 and Tables 10 and 11. With methane as the additive, the selectivity to HCl improves to more than 80% at $450^\circ C$, and the selectivity to HCl increases gradually with increasing temperature. Methane also inhibits perchloroethylene production. In the case with water as the additive, the results are even better, 100% selectivity to HCl is reached at $450^\circ C$. The selectivity also increases with increasing temperature and water also inhibits perchloroethylene production. The comparison of conversion versus temperature

Figure 23. Arrhenius Plot for k in the First Order
Fresh Catalyst

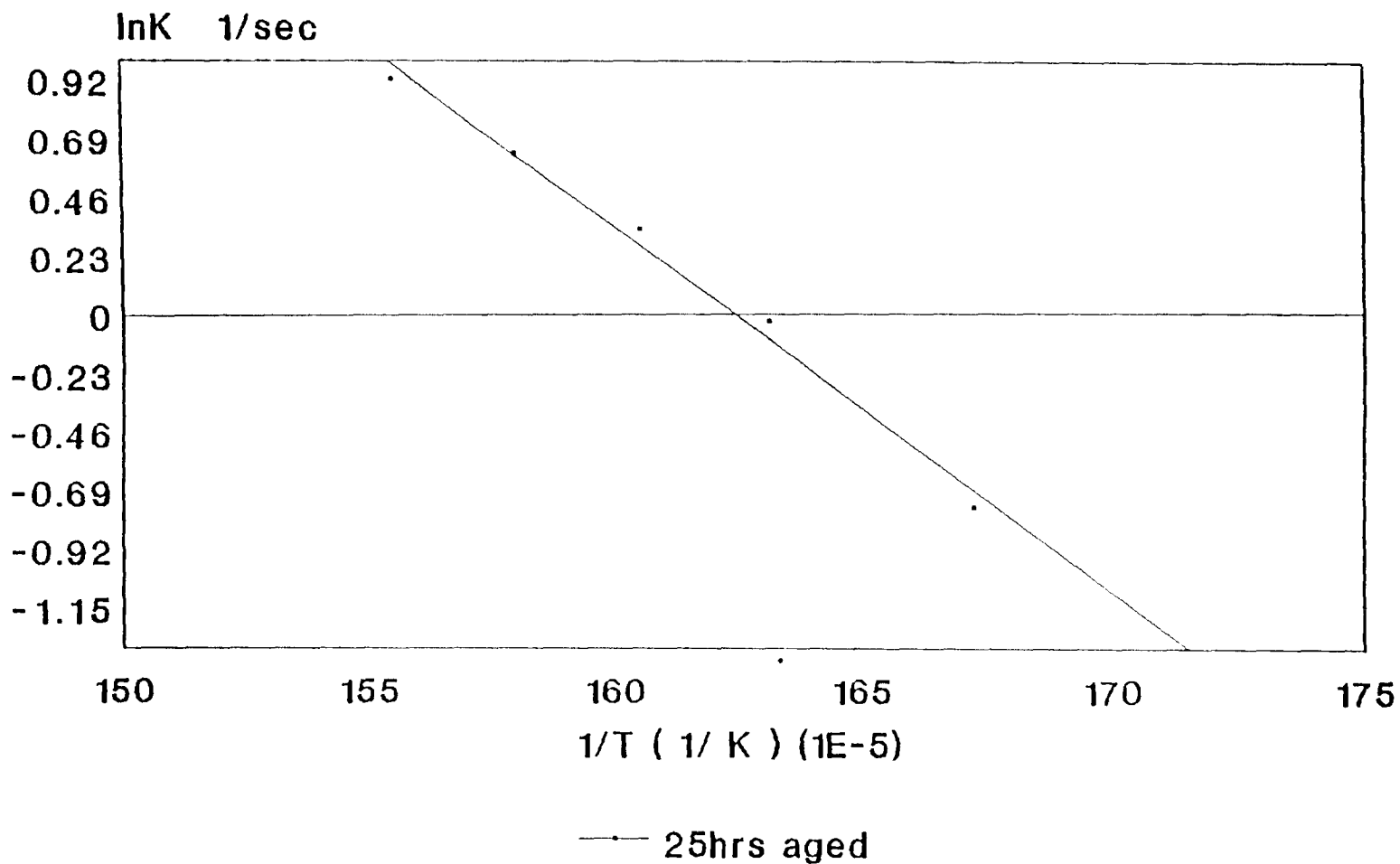


55

— Fresh

$E_a = 19.44 \text{ Kcal/mole}$
 $A = 2.23 \cdot 10^7 \text{ 1/sec}$

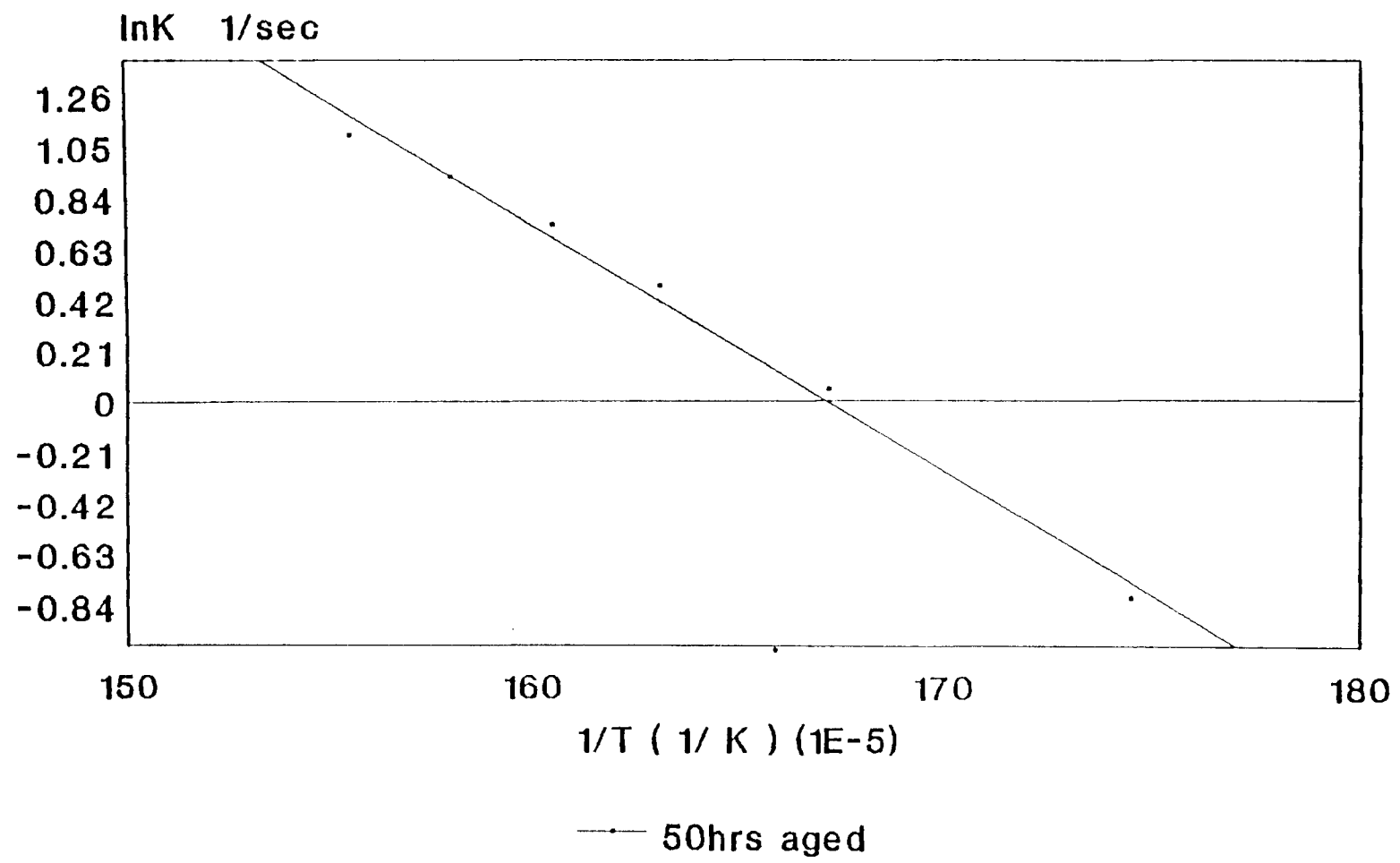
Figure 24. Arrhenius plot for K in the first order catalyst after 25hrs aged



56

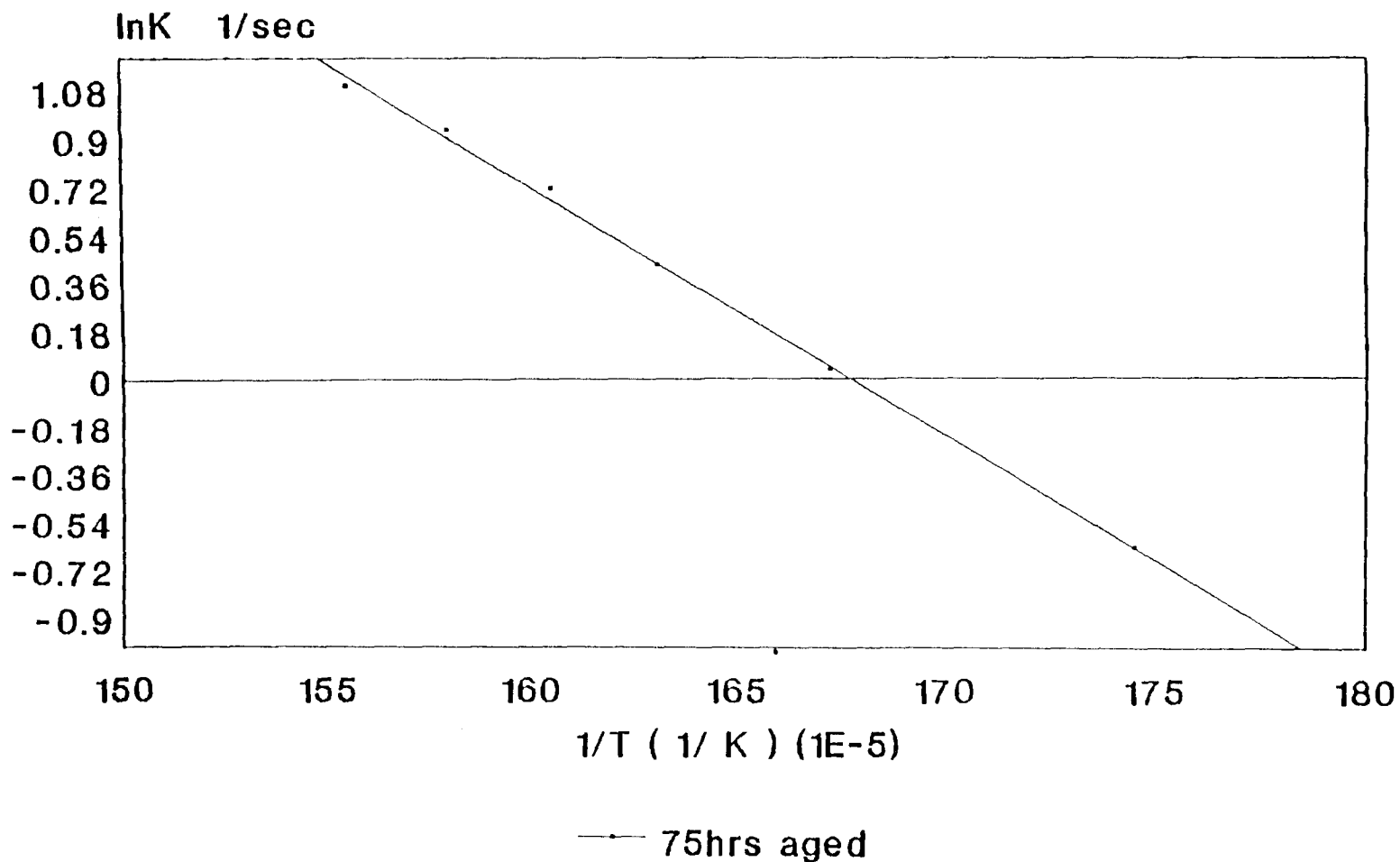
$E_a = 28.39 \text{ kcal/mole}$
 $A = 1.19 \cdot 10^{10} / \text{sec}$

Figure 25. Arrhenius plot for K in the first order catalyst after 50hrs aged



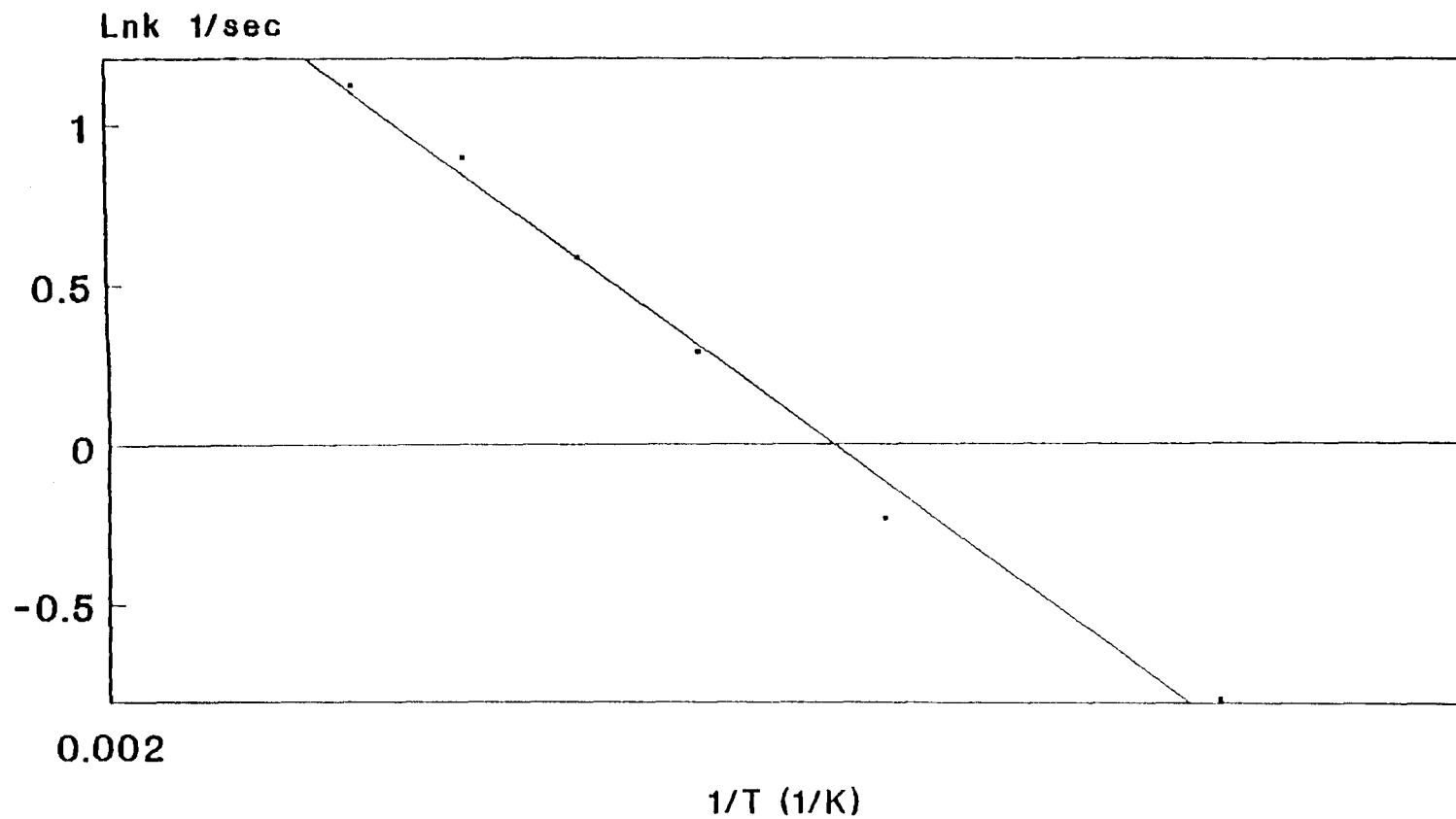
Ea = 20.12kcal/mole
A = 2.25*10^7/sec

Figure 26. Arrhenius plot for K in the first order catalyst after 75hrs aged



Ea = 18.51kcal/mole
A = 2.68*10⁶/sec

Figure 27. Arrhenius Plot for k in the First Order Catalyst After 100 Hour Aged



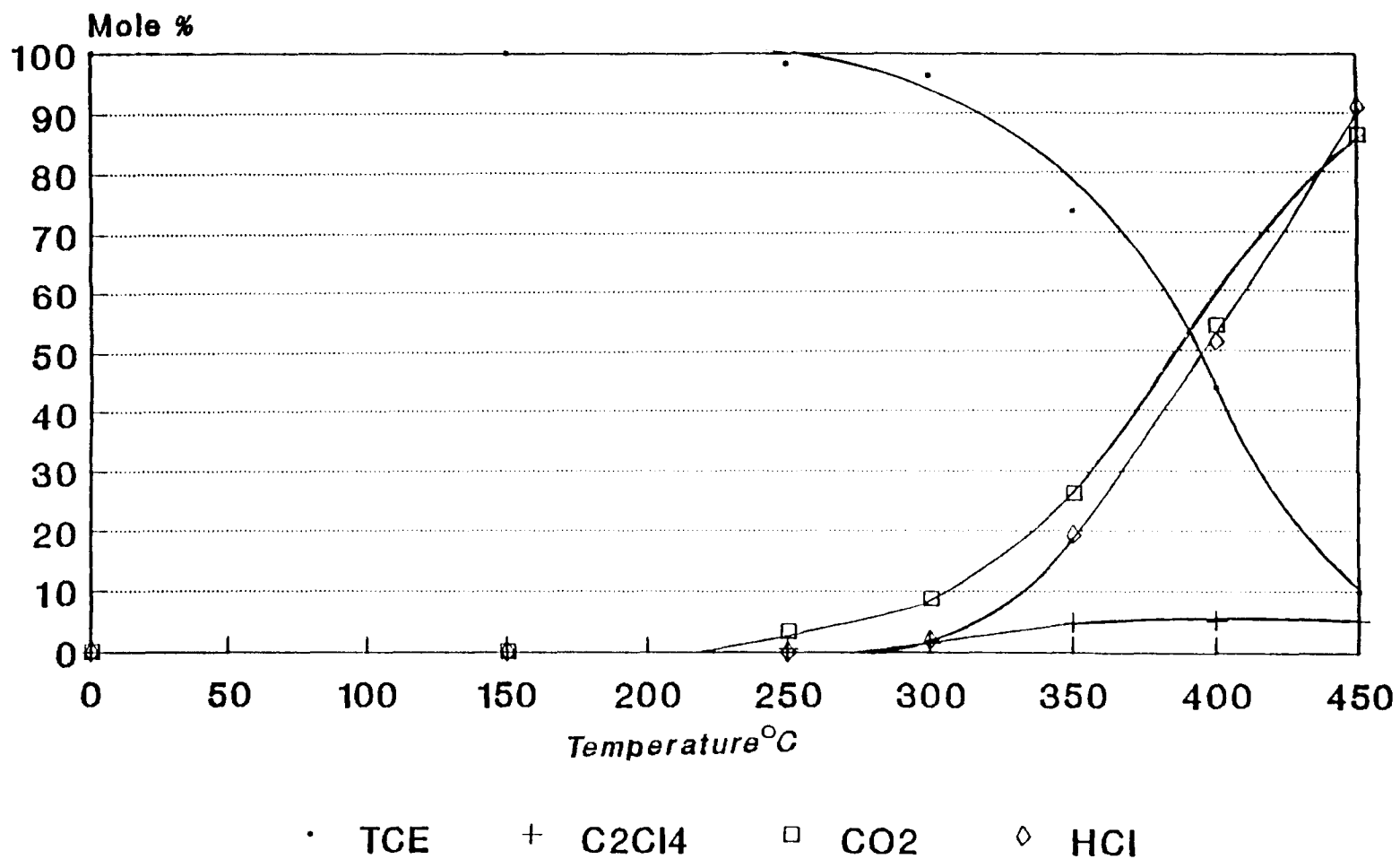
59

$E_a = 20.55 \text{ Kcal/Mole}$
 $A = 2.89 \cdot 10^7$

Table 9. Arrhenius Activation Energies and Pre-exponential Factors at Different Aging Time

	<i>Aging Times</i>				
	<i>fresh</i>	<i>25hrs</i>	<i>50hrs</i>	<i>75hrs</i>	<i>100hrs</i>
<i>Ea(Kcal/mol)</i>	19.44	28.39	20.12	18.51	20.55
<i>A factor</i>	$2.23 \cdot 10^7$	$1.19 \cdot 10^{10}$	$2.25 \cdot 10^7$	$2.68 \cdot 10^6$	$2.89 \cdot 10^7$

Figure 28. Water Effect on Products Distribution
 1.5%Pt- γ -Al₂O₃/400cpsi SV=30,000/hr



TCE Feed=235.6ppm 1.5% Water
 Products are represented by mole%

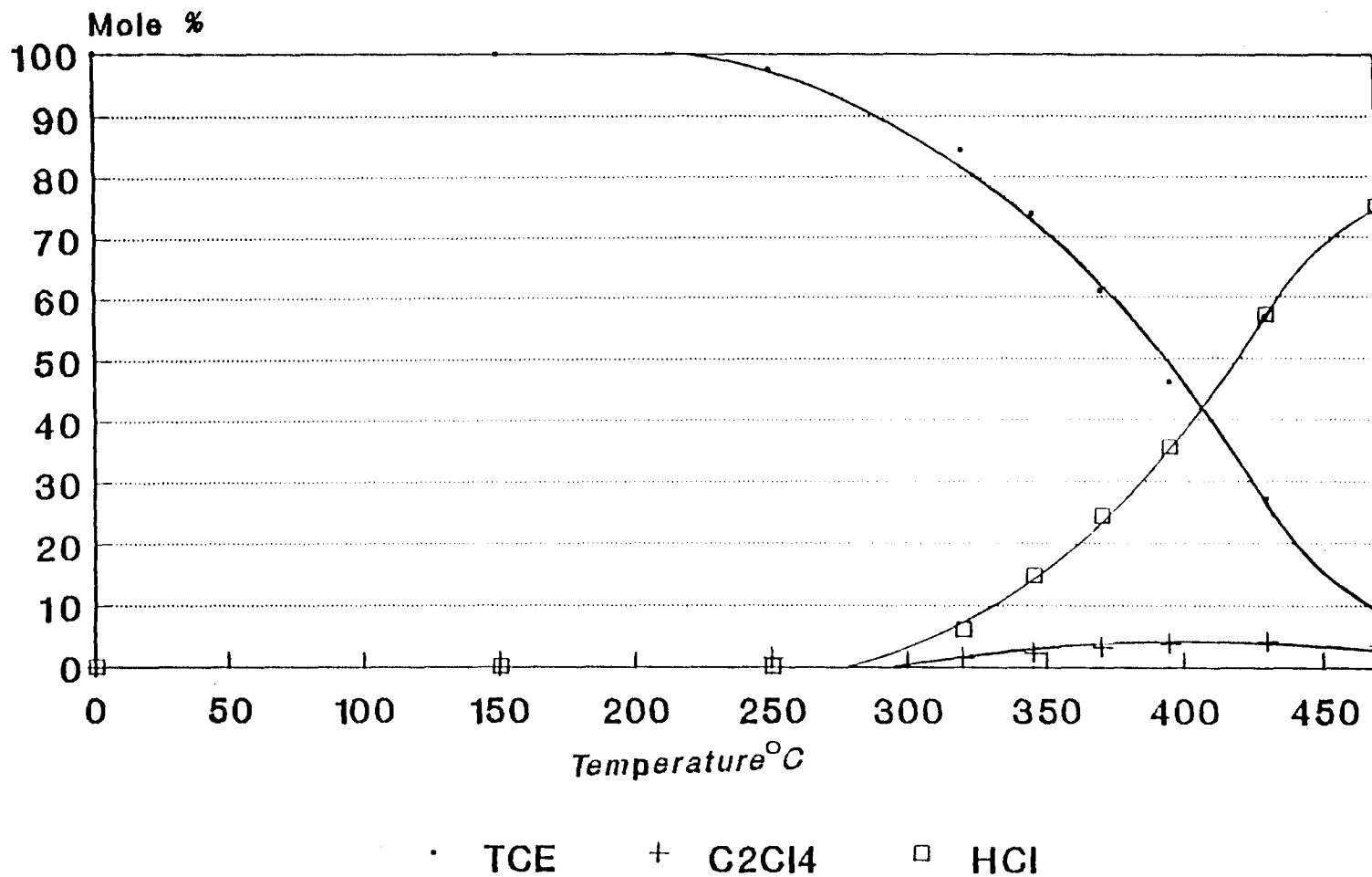
Table 10. Catalytic Oxidation of TCE with 1.5% Water : Products distribution
 1.5%Pt- γ Al₂O₃/monolith/400cpsi SV=30,000v/v/hr

Temp. (°C)	TCE (ppm)	C ₂ Cl ₄ (ppm)	CO ₂ (ppm)	HCl (ppm)	C Bal. (%)	Cl Bal. (%)	HCl Sel. (%)	CO ₂ Sel. (%)	Conv. (%)
150	242	0	0	0	100	100	0	0	0
265	242	3.2	0	0	101	100	0	0	0
315	235	4.2	17.4	12.3	102	101	58.7	124	2.9
365	174.2	10.7	153.5	186.3	108	104	91.6	113	28
415	93.7	11.9	303	461	106	109	103.6	102	61.3
465	29.8	13.5	404.5	638.7	102	108	100	95.3	87.7

Note:

1. temp. : temperature
2. bal. : balance
3. sel. : selectivity
4. conv. : conversion

Figure 29. Methane Effect on Products Distribution
 1.5%Pt- γ Al₂O₃/400cpsi SV=30,000/hr



TCE Feed = 240ppm 0.54% Methane
 Products are represented by mole%

Table 11. Catalytic Oxidation of TCE with 0.6% Methane : Products Distribution
 1.5%Pt- γ Al₂O₃/monolith/400cpsi SV=30,000v/v/hr

Temp. (°C)	CH ₄ (ppm)	TCE (ppm)	C ₂ Cl ₄ (ppm)	CO ₂ (ppm)	HCl (ppm)	C Bal. (%)	Cl Bal. (%)	HCl Sel. (%)	Conv. (%)
150	6100	253	0	0	0	100	100	0	0
265	6072	248.5	0	15	0	100	100	0	1.8
325	6121	208.7	4.7	54	47.3	100	91.2	35.6	17.5
345	6087	190.8	5.1	131	72.4	100	87.7	40.1	24.6
370	6011	148.4	6.4	237	200.2	99	88.4	63.8	41.3
395	5921	112.7	8.8	472	302.2	100	89	71.8	55.4
420	5252	80.2	8.5	1147	398	99	88.6	76.8	68.3
470	4288	27.8	6.4	2407	561.2	102	88.3	83.1	89

64

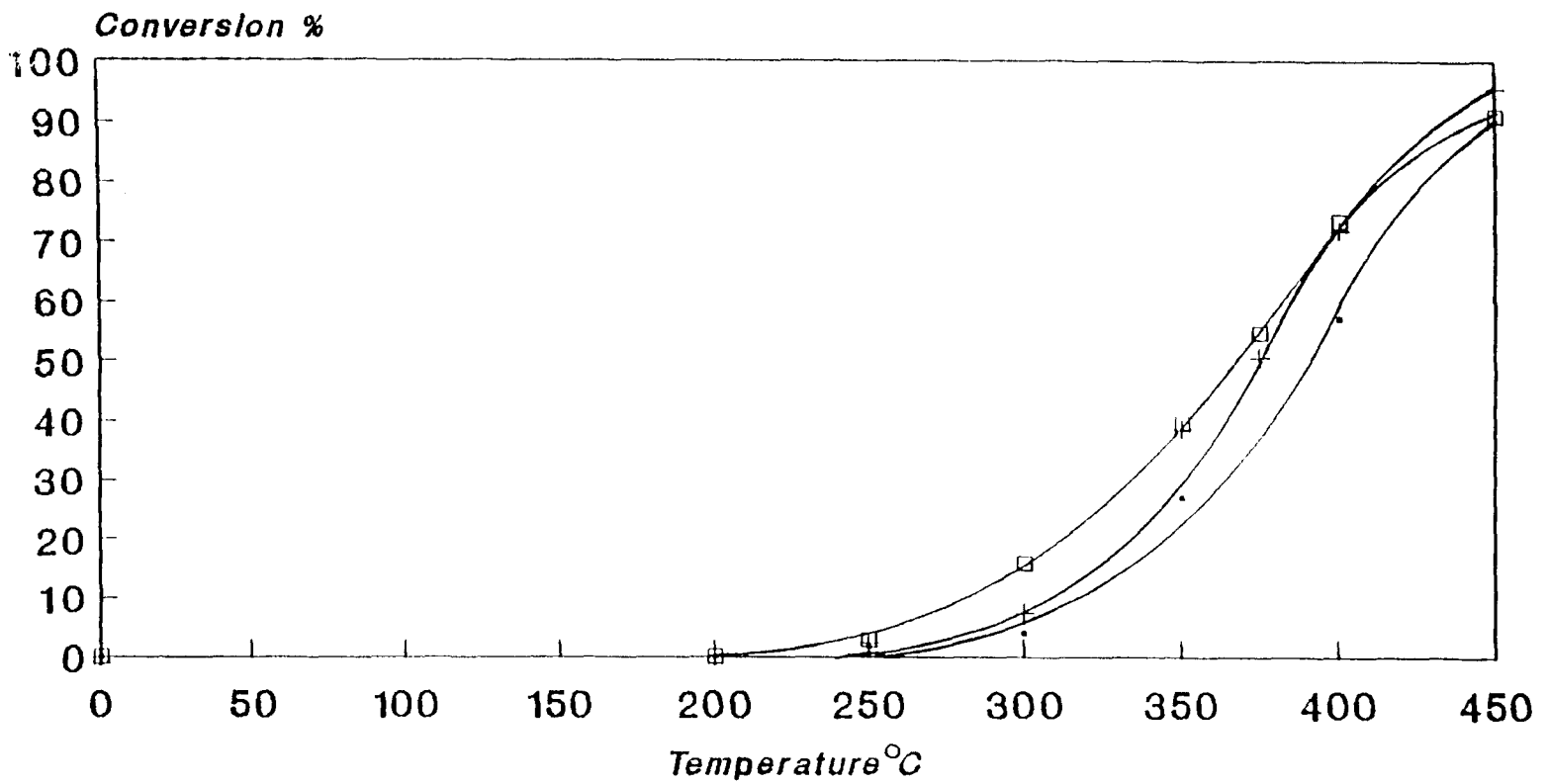
Note:

1. temp. : temperature
2. bal. : balance
3. sel. : selectivity
4. conv. : conversion

curves for the cases with no additive, water and methane is shown in Figure 30. The results indicate that methane can accelerate C_2HCl_3 oxidation reaction, while, water slightly inhibits this reaction.

Figure 30. Effect of Additive on Oxidation of TCE

SV = 30,000v/v/hr 1.5%Pt/400cpsi



· water + no additive □ methane
Fresh

No additive : feed=50ppm
Methane : 0.6% methane feed=240ppm
Water : 1.5% water feed=236ppm

DISCUSSION

1. Reactants

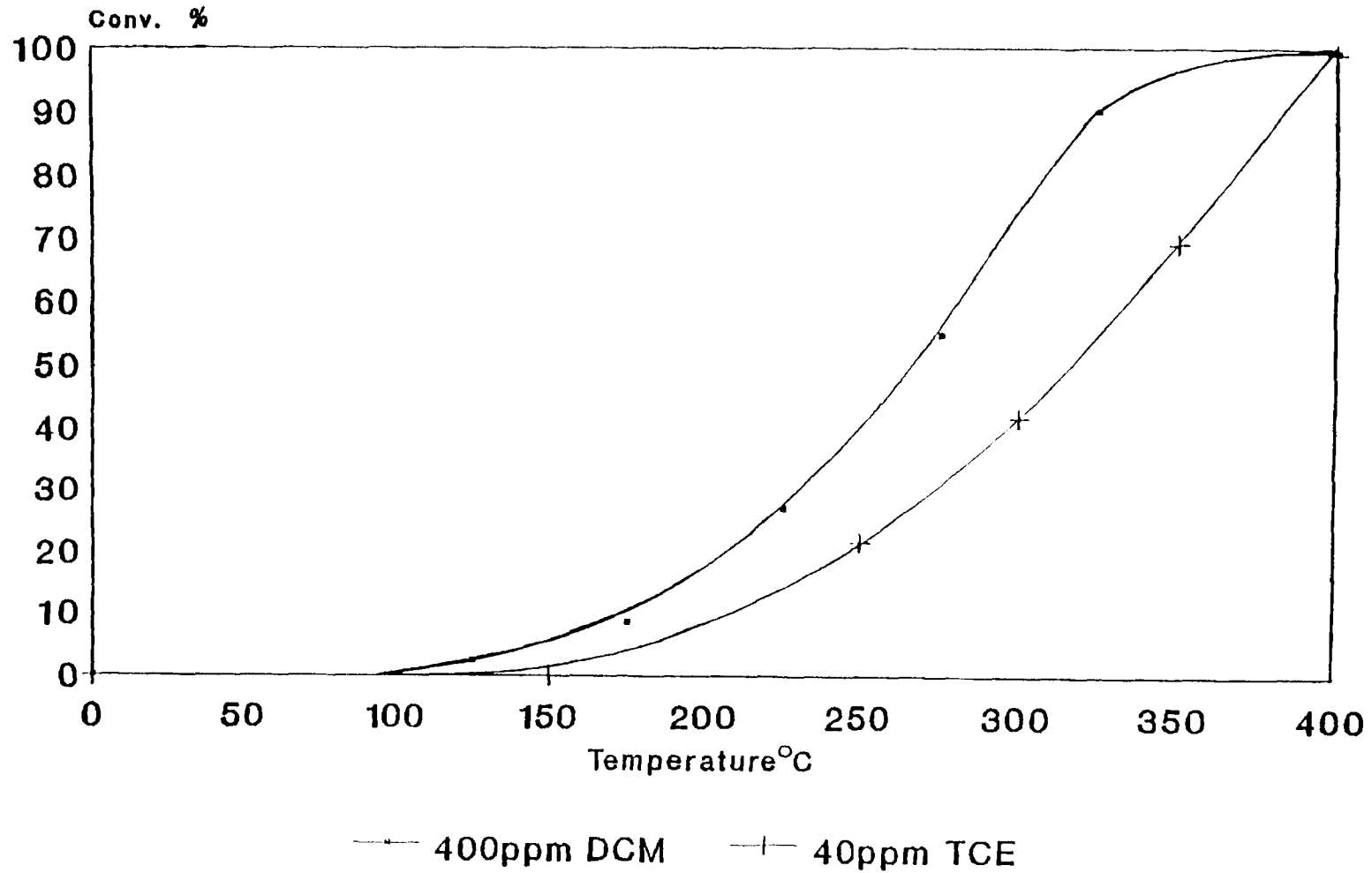
Dichloromethane was chosen as reactant in the initial experiments. Since a single carbon organic molecule has high bond energies, especially carbon-hydrogen bonds, high temperatures are needed to completely oxidize the molecule. Therefore, dichloromethane was chosen as a suitable reactant to evaluate the potential for platinum catalyzed incineration.

Trichloroethylene oxidation experiments were also conducted. Trichloroethylene was chosen as a reactant because it has been found in high concentration in ground water throughout United States, and incineration is a desirable method for disposal of this compound.

Figure 31 presents conversion as a function of temperature for both CH_2Cl_2 and C_2HCl_3 at the same space velocity and the same operating condition, but different feed concentrations. The comparison shows that C_2HCl_3 is more difficult to oxidized than CH_2Cl_2 . One can explain these results based on bond energies of C_2HCl_3 and CH_2Cl_2 . The structure and bond energies for both compounds are shown in Figure 32 (Carey, 1990).

The weakest bond in CH_2Cl_2 structure is C-Cl bond, where the bond energy is 84 kcal/mol. The weakest bond in C_2HCl_3 structure is also the C-Cl bond, the C-H bond is weaker by 6 kcal

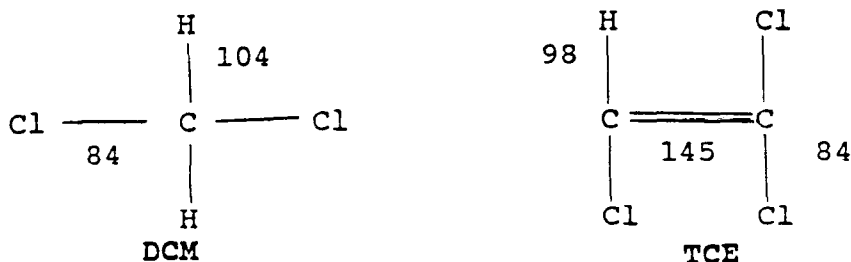
Figure 31. Comparison of DCM vs TCE Conversion



89

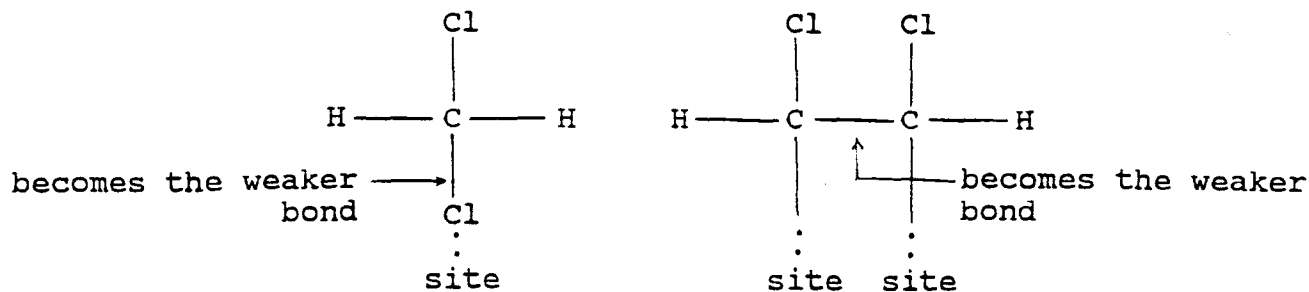
1.5%Pt-rAl₂O₃/monolith/200cpsl
SV = 1020 v/v/hr

Figure 32 Bond energies in kcal for DCM and TCE



than the similar bond in DCM. From this point of view, C_2HCl_3 should be slightly easier to oxidize than CH_2Cl_2 . Since a platinum catalyst was used in the reaction, the heat released by different reactant in the process of being adsorbed on a platinum site may be different. If one of these molecules releases more heat on adsorption, it will have a lower activation energy or will achieve the same oxidation rate at a lower temperature. In other words, the platinum catalyst may modify the overall kinetics if the adsorption kinetics are rate determining. This effect may appear as an apparent weaker bond energy in CH_2Cl_2 when compared to the one in C_2HCl_3 after adsorption. An example could be:

Figure 33 The weaker bond in DCM and TCE after adsorption



Another possibility may be the poisoning of platinum catalyst by chlorine. According to Hung and Pfefferle (1990) and (Hung et al., 1990) in the absence of any chlorinated fuel, lith was found to be adequate for stable gas-phase combustion of propane. However, as a small amount of CHCl_3 was added into the propane/air mixtures, it reduced the rate of propane combustion. This effect was reversible, since the rate of combustion of propane recovered by turning off the CHCl_3 . Cullis and Willatt (Hung et al., 1990) also reported the reversible deactivation of platinum (supported on alumina) by chlorinated methanes for hydrocarbon oxidation. In our case, C_2HCl_3 containing three chlorine atoms, may be a more effective poison, therefore, higher temperature may be required to achieve a desired rate.

2. Catalytic Oxidation of Trichloroethylene

A. Explanation on Products Distribution

The overall stoichiometry of oxidation of trichloroethylene at 1 atm and at the temperature range used in this study may be represented by the following global reaction:



However, trace amount of CO and C_2Cl_4 also were found.

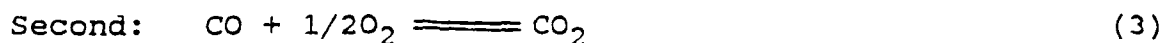
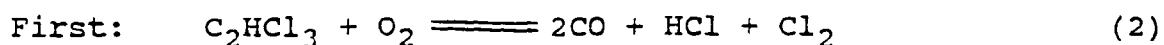
For complete oxidation, each mole of C_2HCl_3 would yield two moles of CO_2 . Neglecting the change in total volume of gas due to

the large excess of the air, the CO_2 concentration should be twice the amount of inlet concentration of C_2HCl_3 , if all carbons were converted to CO_2 . Table 5 shows that this is indeed the case at 450°C , with 75 ppm CO_2 being formed from 39 ppm of C_2HCl_3 .

The selectivity to HCl was calculated only 23% at 450°C . This, however, is not surprising since C_2HCl_3 is a hydrogen-lean reactant containing only one hydrogen but three chlorine atoms. Thus, equal atoms of chlorine are converted to Cl_2 .

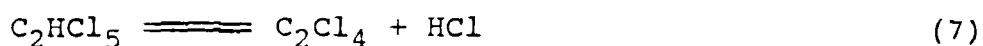
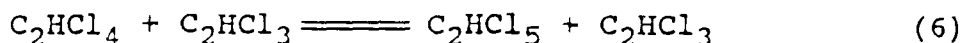
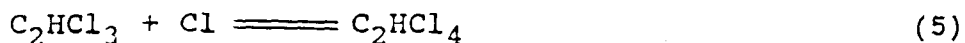
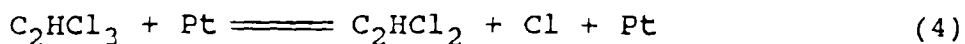
In practical systems, the formation of Cl_2 is undesirable because it is difficult to remove from the exhaust gases by simple aqueous scrubbing. However, at the low temperatures encountered in catalytic combustion, the formation of Cl_2 is inevitable, particularly with hydrogen-lean fuel and when excess air is present. Consequently, the selectivity to Cl_2 must be considered in chlorinated hydrocarbon oxidation study. This will be discussed later.

The formation of CO at low temperature was not surprising in view of the two-step oxidation reaction of chlorinated hydrocarbons (Bose, 1983):

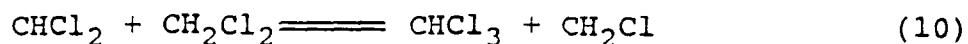
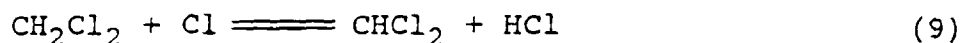
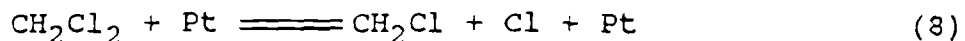


The concentration of CO decreases with increasing temperature because reaction (3) is favored at high temperatures.

The formation of C_2Cl_4 can be explained by the possible activity of platinum catalyst for the following reactions (Saken, 1986):



The formation of $CHCl_3$ in the oxidation reaction of CH_2Cl_2 can support this assumption.



B. Effect of Aging Time on Reaction

The aging experiments were conducted to help identify catalyst deactivation rate parameters. Four aging times were investigated.

As shown in Figure 17, only fresh catalyst was obviously deactivated, in the other four cases, there was only a very slight change in conversion versus temperature curves, and the catalyst was not obviously deactivated. Hung and Pfefferle's paper can be used to explain this phenomena. As described above, their research shows that the deactivation of platinum-alumina cata-

lyst by chlorinated hydrocarbon is reversible for hydrocarbon oxidation. In this research, one can speculate that each time C_2HCl_3 was fed into the reactor system, the catalyst would deactivate. However, once the experiment was finished and the TCE source removed from the carrier gas, the catalyst could recover. This could explain why the four conversion curves were not fitted very well is because of the deactivations other than poisoning and experimental error.

The only exception is the case with fresh catalyst. In this case, the fresh catalyst was obviously deactivated, the reason for this is because for most catalysts the activity decline sharply at first due to redispersion and irreversible poisoning and then reaches a state where the catalyst activity decreases much more slowly with time (Hughes, 1984).

C. Kinetic Study with Oxidation of Trichloroethylene

The measured data for the oxidation of C_2HCl_3 in air were correlated first using the empirical power law kinetics of the form:

$$-r_{C_2HCl_3} = k \cdot C_{C_2HCl_3}^a \cdot C_{O_2}^b$$

Where $C_{C_2HCl_3}$ and C_{O_2} are the concentrations for C_2HCl_3 and O_2 respectively.

Experiment were conducted in large excess oxygen one can therefore assume that the oxidation of TCE obeys first order

reaction kinetics with respect to the TCE. The linearity of the plots of the logarithm of measured retention of reactant versus retention time (Figures 18 to 22) show excellent agreement with this assumption.

The reaction order with respect to O_2 was also studied. The effect of different percentage of oxygen in helium on conversion- was investigated and illustrated in Figure 34. It was found that, changing the concentration of oxygen in the 5 to 20% range had no marked effect on the rate of oxidation of C_2HCl_3 . Therefore, it was concluded that it is reasonable to assume that the rate of C_2HCl_3 oxidation was zeroth order with respect to oxygen within the experimental condition studied.

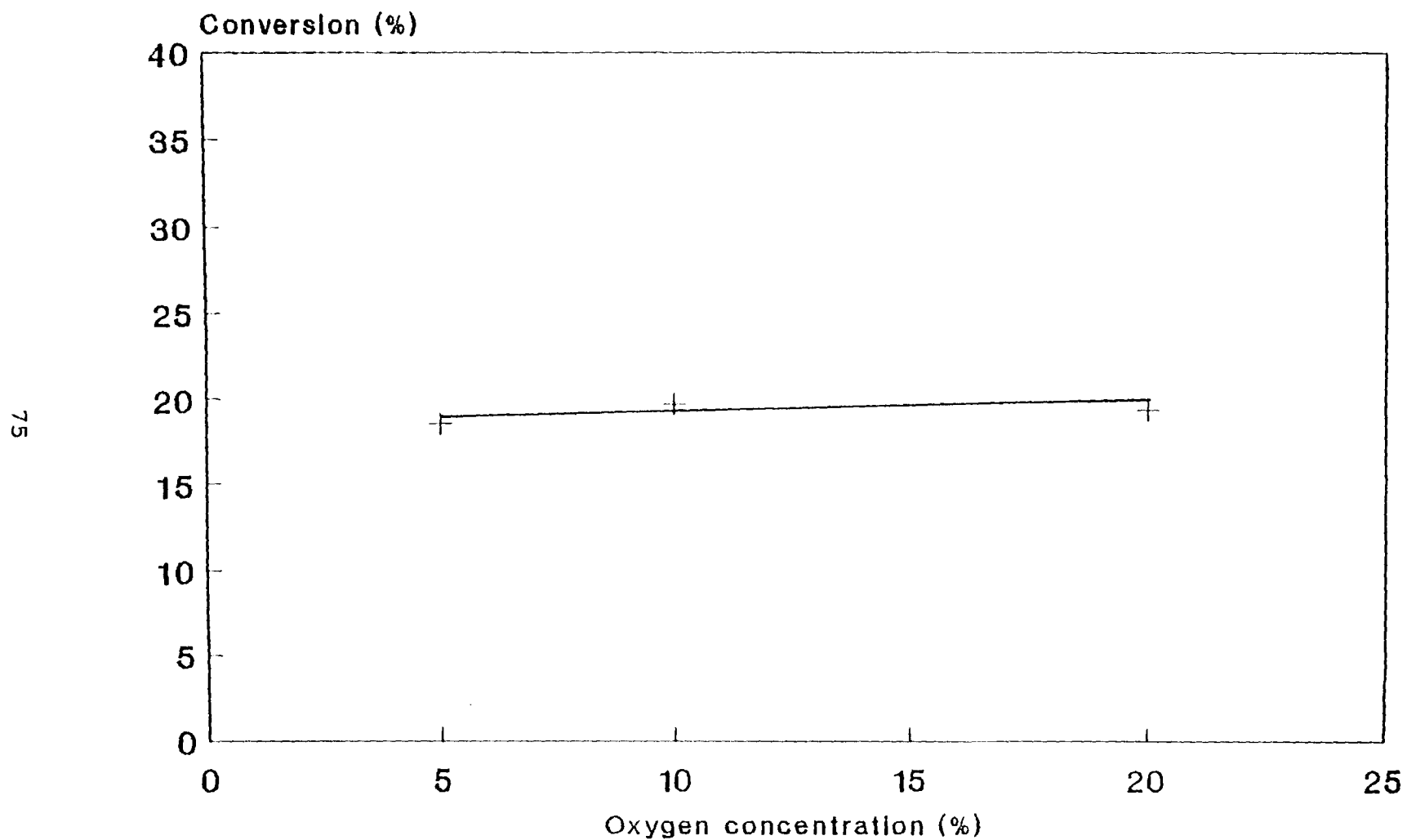
The following rate expression correlated the experimental data for fresh catalyst:

$$-r_{C_2HCl_3} = 2.23 \cdot 10^7 \exp(-19440/RT) \cdot C$$

For the other four reactions at 25, 50, 75 and 100 hours of aging time, the active energies and pre-exponential factors were calculated and all listed in Table 9.

Since active energy E_a represents the energetics of the rate determining step on the surface of the catalyst, and the pre-exponential factor, A , represents catalyst characteristics. The deactivation study was focused on measuring changes in the A factor.

Figure 34. Effect of Oxygen on Oxidation of TCE
1.5%Pt-Al₂O₃/monolith/400cpsi 325°C



TCE Feed = 40ppm

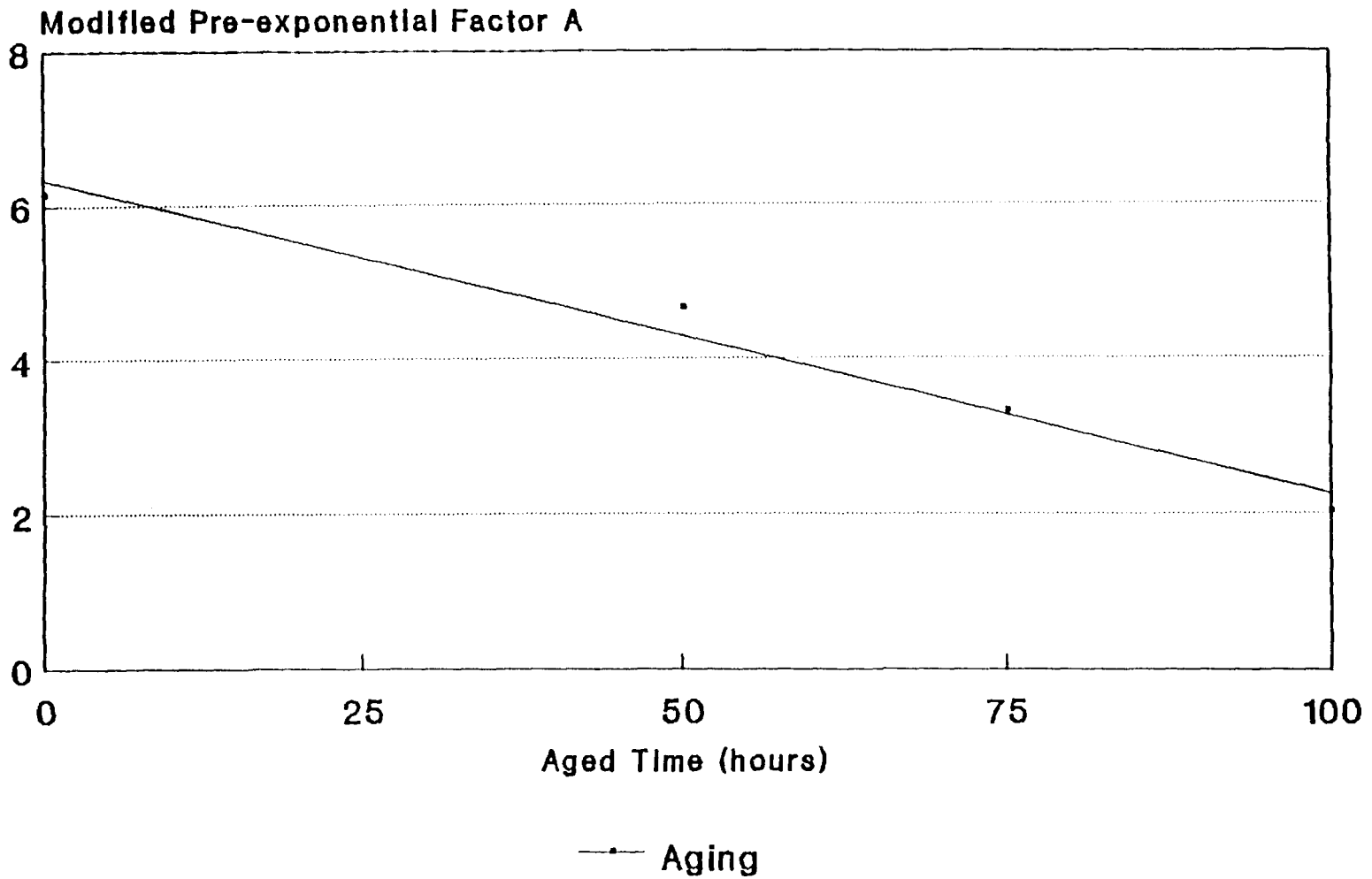
The activation energies of the five different experiments were averaged, and this modified active energy E_a' was used in the Arrhenius equation to estimate 5 A factors. At same temperature, the five modified A factors were calculated using 5 measured rate constants at that temperature. The plot of modified A factors versus aging times are shown in Figure 35. The modified A factor indeed decreased with increasing temperature which indicate that the catalyst was being deactivated. The mechanism of deactivation are still unknown, and further investigation is necessary.

D. The Effect of Additives on Oxidation of Trichloroethylene

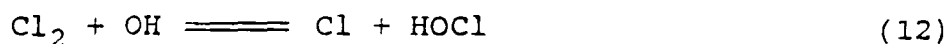
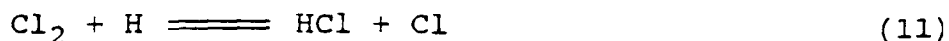
Since C_2HCl_3 is a hydrogen-lean reactant, to improve the selectivity to HCl, hydrogen-rich additives are required. As described above, in the catalytic oxidation of C_2HCl_3 reactions without any additive, 2/3 of the chlorine atoms are converted to Cl_2 which is an undesirable product because it is difficult to remove from the reactor exhaust gases by simple aqueous scrubbing. Consequently it is very important to develop a method to decrease the formation of Cl_2 . Based on this consideration, methane and water were introduced into the reactor system as source of hydrogen.

To determine the effect of additives, 1.5% water vapor was added to the system. Water was chosen as a hydrogen source is

Figure 35. Variation of Pre-Exponential with Aging
Average Active Energy $E_a = 20.04\text{Kcal/mol}$



because decomposes at high temperature into H and OH radicals which serve as hydrogen sources, especially when platinum catalyst is present in the system. To the extent that chlorine atoms are present on the surface, we can assume that the following reaction take place:



In the second case, 0.6% methane were added into the system. There are two reason for choosing CH_4 as a additive. First, methane is a hydrogen-rich molecule which can donate hydrogen. Second, it can be used to provide heat by combustion to accelerate the reaction. The reaction mechanism can be proposed as:



Figure 36 shows the effect of both additives on selectivity to HCl. Both water and methane can dramatically increase the HCl production. The case with water as additive obviously better than methane. This may be a consequence that both H and OH radicals participate in the formation of HCl, or because platinum catalysts favor water decomposition.

The addition of water and methane also influence the production of C_2Cl_4 (see Figure 37). Both of additives reduce C_2Cl_4 production. The reaction mechanism probably involves removing Cl-containing intermediates, and converting them to HCl. Thus, preventing the formation of C_2Cl_4 .

Figure 36. Comparison of HCl Selectivity
1.5%Pt- γ Al₂O₃/400cpsi SV=30,000/hr

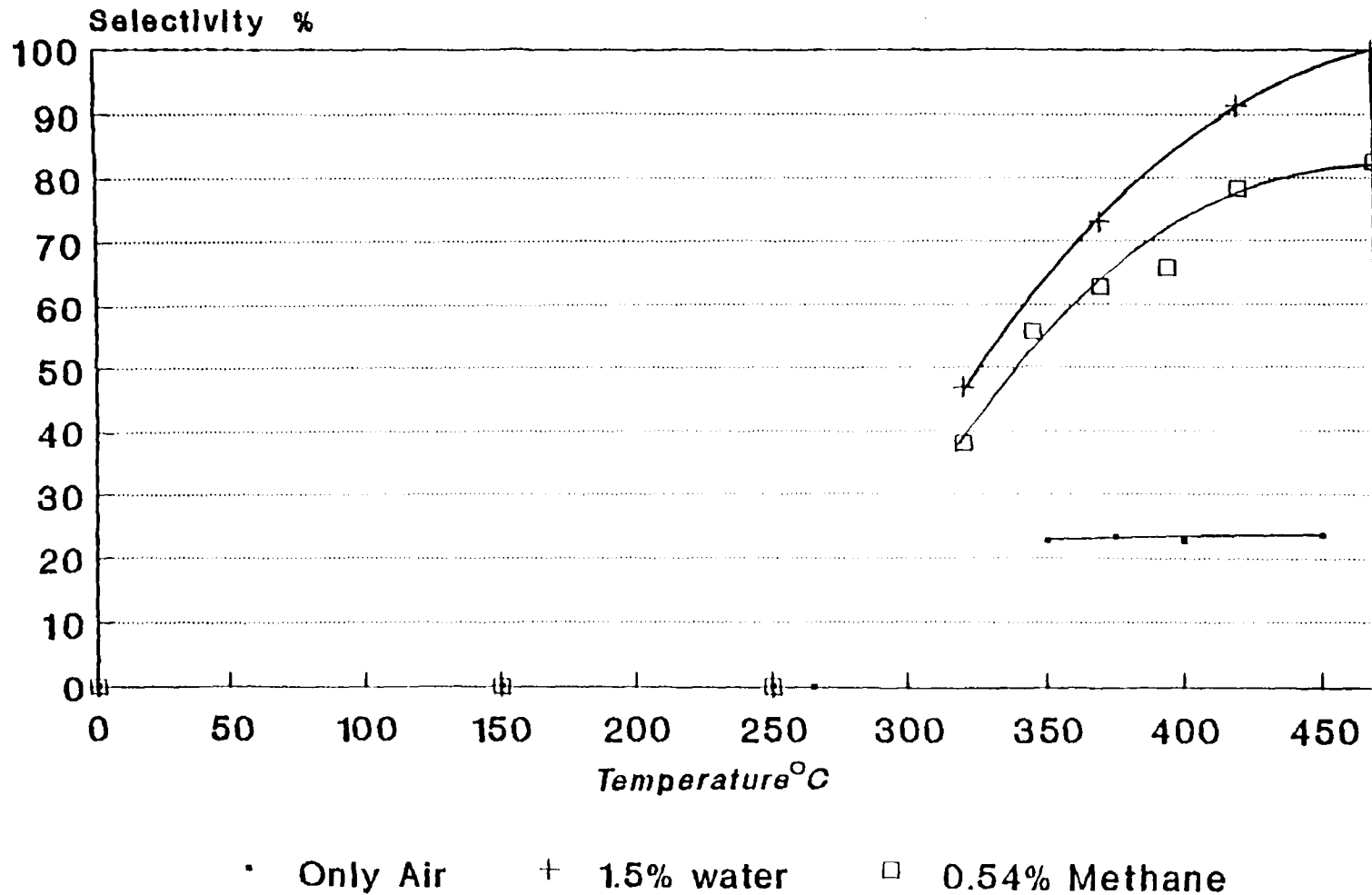
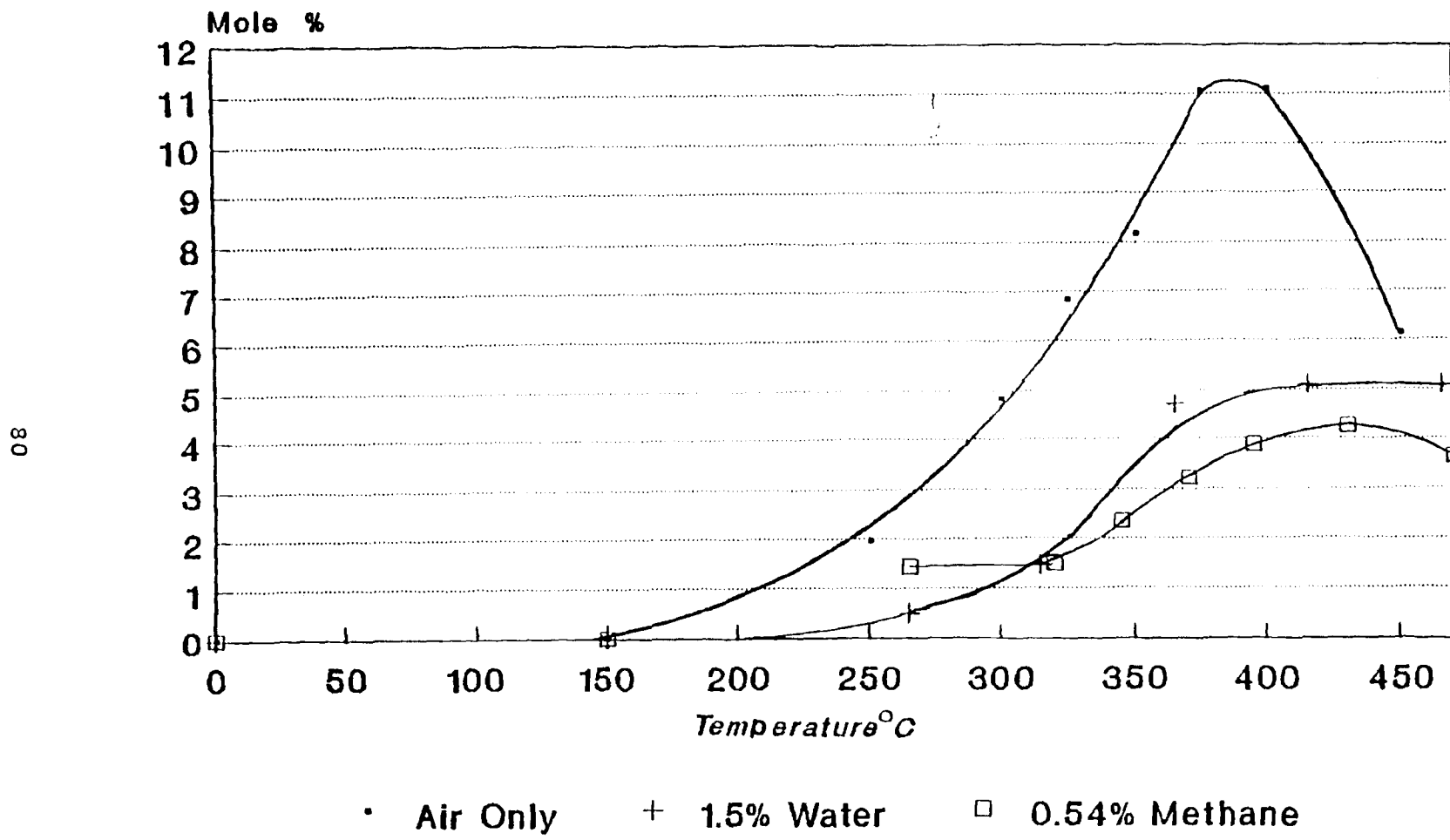


Figure 37. Comparison of C₂Cl₄ Mole %
1.5%Pt-/Al₂O₃/400cpsi SV=30,000/hr



Reaction rate data show that the addition of methane can slightly accelerated oxidation reaction of C_2HCl_3 . This is a consequence of the exothermicity of the oxidation of methane, after light-off, increases the surface temperature of the catalyst, and thus, increase the rate of conversion of C_2HCl_3 . The addition of water on the other hand slightly inhibits the reaction rate. Water decomposition is an endothermic heat consuming reaction which will absorb heat from reactor system and inhibit conversion of C_2HCl_3 . Both effects are shown in Figure 31.

CONCLUSION

As a consequence of the research, the following conclusion were reached:

- o The complete oxidation of chlorinated hydrocarbons over 1.5%Pt- Al₂O₃ occurs at a much lower temperature than homogeneous thermal incineration.

- o The light-off temperature for oxidation of 450 ppm dichloromethane over 1.5%Pt- Al₂O₃/monolith/200cpsi at 1020 v/v/hr is 200°C, and 100% conversion is achieved at 400°C.

- o The main products from the oxidation of dichloromethane are carbon dioxide and hydrogen chloride. However, trace amount of chloroform as an intermediate product was also found.

- o The light-off temperature for oxidation of 50 ppm trichloroethylene over 1.5%Pt-Al₂O₃/monolith/400cpsi at 30,000v/v/hr is 325°C, and 100% conversion is achieved at 550°C.

- o The main products from the oxidation of trichloroethylene are carbon dioxide, chlorine gas and hydrogen chloride. However, trace amount of carbon monoxide and perchloroethylene as intermediate product were also found.

- o The Pt- Al₂O₃ catalyst is more efficiency for oxidizing dichloromethane than trichloroethylene.

- o Both carbon and chlorine balance for oxidation of trichloroethylene over 1.5%Pt- Al₂O₃/monolith/400cpsi at 30,000v/v/hr were satisfied within 100±10%.
- o The oxidation reaction of trichloroethylene obeys first order reaction kinetics with respect to trichloroethylene.
- o Trichloroethylene oxidation rates were independent of the concentration of oxygen over the range of 5 to 21%.
- o The activation energy, E_a, for the oxidation of trichloroethylene is 20kcal/mole, and the pre-exponential factor, A, is 2.23*10⁷ sec⁻¹.
- o Aging time of 100 hours at 450°C had no substantial effect on products distribution.
- o A deactivation parameter with respect to aging time was developed using the pre-exponential factor changes if the activation energy was assumed constant.
- o Both water and methane, introduced as additives in the oxidation reactions of trichloroethylene, increase the formation of HCl and inhibit the production of perchloroethylene.
- o The addition of methane slightly accelerated the oxidation reaction of trichloroethylene, and water slightly inhibited the reaction.

FUTURE WORK

1. Get better data on kinetics and mechanism of catalytic oxidation of chlorinated hydrocarbons.
2. Study mechanism of Pt catalyst deactivations with respect to chlorinated hydrocarbon, including dispersion, sintering, poisoning, etc.
3. Study kinetics of the oxidation of DCM and TCE by changing feed concentration instead of varying space velocity.
4. Devise methods to regenerate catalyst.
5. Study catalytic deactivation due to sulfur and phosphorous compounds.

REFERENCES

Augustine, R. L., Rylander, P. N., and Greenfield, H., (1988), "Catalysis of Organic Reaction" Marcel Dekker, Inc., NY.

Baker, E. G. et al., (1989), "Catalytic Destruction of Hazardous Organic in Aqueous Wastes: Continuous Reactor system Experiments" Hazardous Waste & Hazardous Materials. Vol. 6, No. 1.

Bonacci, J. C., Farrauto, R. J., and Heck. R., (1988), "Catalytic Incineration of Hazardous Waste" Environmental Science, Vol I, Thermal Treatment. Gulf Publication.

Bond, G. C., (1973), "Catalytic Destruction of Chlorinated Hydrocarbons" U.S. Patent No. 1485735.

Bose, D., and Senkan, S. M., (1983), "On the Combustion of Chlorinated Hydrocarbon: Trichloroethylene" Combustion Sci. & Tech., Vol. 35, pp. 187 - 202.

Carey, F. A., and Sundberg, R. J., (1990), "Advanced Organic Chemistry" Plenum Press. New York & London.

Du, J., (1990), "The Treatment of Trace Concentration of Chlorinated Hydrocarbon by Catalytic Oxidation" Master Thesis, New Jersey Institute of Technology, May, 1990.

Heras, J. M., and Viscido, L., (1988), "The Behavior of Water on Metal Surface" Cata. Rev. & Sci. Eng., 24(2), pp. 233 - 309.

Huang, S. L., and Pfefferle, L. D., (1989), "Methyl Chloride and Methylene Chloride Incineration in a Catalytically Stabilized Thermal Combustor" Environ. Sci. & Tech., Vol. 23, No. 9.

Hughes, R., (1984), "Deactivation of Catalysts" Academic Press Inc. London.

Jennings, M. S., and Palazzolo, M. S., (1985), "Catalytic Incineration for Control of Volatile Organic Compound Emission" Pollution Tech. Rev., No. 121, Noyes Publication, NJ.

Johnston, E. L., et al., (1976), "Low Temperature Catalytic Oxidation of Chlorinated Compound to Recover Chlorine Values Using Chromium-Impregnated Supported Catalysts" USA Patent 3989807, Nov. 2, 1976.

Lavanish, J. M., et al., (1976), "Catalytic Oxidation of C₂-C₄ Halogenated Hydrocarbons" USA Patent 4039623, Aug. 16, 1976.

Lee, C. C., Talyor, P. H., and Dellinger, B., (1990), "Development of a Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability" Environ. Sci. & Tech., 24, pp. 316-328.

Lester, G. R., (1990), "Catalytic Destruction of Organhalgen Compound" International Patent BOID 53/36, BOIJ 23/64, A62D3100, International Publication Number WO 90/13352.

New Jersey Department of Health (1986), "Hazardous Substance Fact Sheet: Methylene Chloride" Trenton, NJ 08625.

New Jersey Department of Health (1986), "Hazardous Substance Fact Sheet: Trichloroethylene" Trenton, NJ 08625.

Novinson, T., (1989), "Chemical Detoxification of Polychlorinated Biphenyls (PCBs)" USA Patent 4804779, Feb. 14, 1989.

Olfenbittel, B. "New Technologies for Cleaning Up Contaminated Soil and Groundwater" A Battelle Special Report on Soil Remediation.

Pope, D., Walker, D. S., and Moss, R. L., (1978), "Evaluation of Platinum-Honeycomb Catalysts for The Destructive Oxidation of Low Concentrations of Odorous Compounds in Air" Atm. Environ., Vol. 12, pp. 1921 - 1927.

Ramanathan, K., and Spivey, J. J., (1989), "Catalytic Oxidation of 1,1-Dichloroethane" Combustion Sci. & Tech., Vol. 63, pp. 247-255.

Reid, R. C., Prausnitz, J. M., and Poling, B. E., (1987), "The Properties of Gases and Liquids" McGraw-Hill, NY.

Satterfield, C. N., (1980), "Heterogeneous Catalysis in Practice" McGraw-Hill NY.

Sare, E. J. et al., (1977), "Catalytic Oxidation of C₂-C₄ Halogenated Hydrocarbons" USA Patent 4059677, Nov. 22, 1977.

Senkan, S. M., Chang, W. D., and Karra, S. B., (1986), "A Detailed Mechanism for The high Temperature Oxidation of C₂HCl₃" Combustion Sci. & Tech., Vol. 49, pp. 107 - 121.

Schaumburg, F. D., (1990), "Banning Trichloroethylene: Responsible Reaction or Overkill" Environ. Sci. & Tech. Vol. 24, No. 1.

Tanguay, J. F. et al., (1989), Photodegradation of Dichloromethane with Titanium Catalysts" American Chemical Society, Miami Beach Meeting. Sep. 10-15, 1989.

Weldon, J., and Senkan, S. M., (1986), "Catalytic Oxidation of CH₃Cl by Cr₂O₃" Combustion Sci. & Tech., Vol 47, pp. 229 - 237.

Yu T. C., (1991), "Catalytic Oxidation of Chlorinated Compounds Over PdO/Al₂O₃ on Monolith" Master Thesis. New Jersey Institute of Technology May, 1991.

Appendix I

Product Distribution for Oxidation of DCM at 1020v/v/hr : Repeat

<i>Temp.(C)</i>	<i>Concertration (ppm)</i>				<i>Conversion (%)</i>	
	<i>CH2CL2</i>	<i>CHCL3</i>	<i>CCL4</i>	<i>CO2</i>	<i>FID</i>	<i>ECD</i>
<i>20</i>	<i>350</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
<i>150</i>	<i>350</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
<i>200</i>	<i>313</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>8.86</i>	<i>10.6</i>
<i>250</i>	<i>261</i>	<i>0.08</i>	<i>0</i>	<i>0</i>	<i>25.9</i>	<i>25.4</i>
<i>300</i>	<i>186</i>	<i>0.21</i>	<i>0</i>	<i>197</i>	<i>55.8</i>	<i>46.8</i>
<i>400</i>	<i>15</i>	<i>0.61</i>	<i>0</i>	<i>347</i>	<i>100</i>	<i>95.7</i>
<i>500</i>	<i>11</i>	<i>0.46</i>	<i>0</i>	<i>356</i>	<i>100</i>	<i>97.6</i>

Appendix II

Product Distribution for Oxidation of DCM at 2040v/v/hr : Repeat

<i>Temp.(C)</i>	<i>Concentration (ppm)</i>				<i>Conversion (%)</i>	
	<i>CH₂CL₂</i>	<i>CHCL₃</i>	<i>CCL₄</i>	<i>CO₂</i>	<i>FID</i>	<i>ECD</i>
<i>20</i>	<i>332</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
<i>150</i>	<i>332</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
<i>200</i>	<i>330</i>	<i>0.18</i>	<i>0</i>	<i>0</i>	<i>5.4</i>	<i>2.4</i>
<i>250</i>	<i>289</i>	<i>1.48</i>	<i>0</i>	<i>0</i>	<i>16.5</i>	<i>12.8</i>
<i>300</i>	<i>87</i>	<i>0.88</i>	<i>0</i>	<i>264</i>	<i>80.8</i>	<i>74</i>
<i>400</i>	<i>1</i>	<i>0.29</i>	<i>0</i>	<i>348</i>	<i>100</i>	<i>99</i>

Appendix III

Repeat Experiment : Methane Effect

Temp. (°C)	C ₂ HCl ₃ (ppm)	CH ₄ (ppm)	C ₂ Cl ₄ (ppm)	CO ₂ (ppm)	HCl (ppm)	C bal (%)	Cl bal (%)	Conv. (%)
150	253	6100	0	0	0	100	100	0
265	249	6072	0	15	0	100	100	2.0
325	209	6121	4.7	54	47	100	91	17.5
345	191	6087	5.1	131	72	100	88	24.6
370	148	6011	6.4	237	200	99	88	41.3
395	113	5921	8.8	472	302	100	89	55.4
420	80	5252	8.5	1147	398	99	89	68.3
470	28	4288	6.4	2407	561	102	88	89.0

Note : Using same operating condition.

Appendix IV

Repeat Experiment : Water Effect

C bal (%)	Temp. (°C)	C ₂ HCl ₃ (ppm)	C ₂ Cl ₄ (ppm)	CO ₂ (ppm)	HCl (ppm)	Cl bal (%)	Conv. (%)
150	242	0	0	0	100	100	0
265	242	3.2	0	0	101	100	0
315	235	4.2	17	12	102	101	2.9
365	174	10.7	153	186	108	104	28
415	94	11.9	303	461	106	109	61
465	30	13.5	404	639	101	108	88

Note : Using same operating condition.

Appendix V

Calculated Rate Constants k at Different Aging Time

Temp. (°C)	rate constants k				
	fresh	25hr	50hr	75hr	100hr
300	0.6227		0.4450	0.5869	0.4538
325	1.7766	0.4714	1.0464	1.0181	0.7951
340		0.9711	1.6031	1.5327	1.3250
350	3.9971	1.4035	2.0705	2.0492	1.7869
360		1.9013	2.5092	2.5431	2.4419
370		2.5318	2.9961	2.9961	3.0560