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# Hydrodechlorination reactions on silica-supported rhodium catalysts

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# ABSTRACT

Title of Thesis: Hydrodechlorination Reactions on Silica-
supported Rhodium Catalysts

Chen, Yung-Ming, Master of Science, 1987

Thesis directed by: Dr. Joseph W. Bozzelli
Professor in Department of Chemistry and Chemical Engineering
N. J. I. T.

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The objectives of this study were to investigate the pathways of the hydrodechlorination reactions over silica-supported Rh catalysts as well as identify selectivities and deactivation properties.

Reaction of 1,2-dichloroethane with hydrogen over $Rh/SiO_2$ catalyst was studied in the temperature range 200 to 300°C. Formation of two intermediates was proposed while 1,2-dichloroethane was adsorbed on the catalyst, the reactive intermediates then produce ethane, ethylene, chloroethane and methane. From the methane formation, it was inferred that the ethane hydrogenolysis occured over the $Rh/SiO_2$ catalysts. Higher conversion to $C_1$ and $C_2$ hydrocarbons was observed at higher reaction temperature. The activation energy was found to be 13 Kcal/mole.

Hydrodechlorination of trichloroethylene was studied to gain information on controlling parameters to manage trichloroethylene pollution emissions in vapor-degreasing applications. Reaction temperature above 150°C, longer contact time, and reactant partial pressure below 100 torr

effectively promoted the conversion to hydrocarbon formation. The activation energy was 13.9 Kcal/mole. The data showed that two Cl atoms on the $\alpha$ carbon did not need to be removed simultaneously during the reaction.

The deactivation on $Rh/SiO_2$ catalyst was also studied. A comparion of the ethylene hydrogenation on fresh and contaminated catalysts (after reaction with 1,1-dichloroethane) showed a negative effect on the product selectivity to ethane formation, for the deactivated catalyst. The varied selectivity for $CH_4$ and $C_2H_6$ demonstrated that at least two distinct types of active sites existed on the catalyst surface.

# HYDRODECLORINATION REACTIONS
# ON
# SILICA-SUPPORTED RHODIUM CATALYSTS

by

Yung-Ming Chen

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
1987

# APPROVAL SHEET

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# CHAPTER 1: HYDRODECHLORINATION OF 1,2-DICHLOROETHANE OVER RHODIUM SUPPORTED ON SILICA GEL

## 1-1 INTRODUCTION

Catalysis plays an important role in pollution problems, not only in the removal of pollutants, such as $NO_x$, CO, sulphur compounds and chlorocarbon species from effluent streams, but also in the improvement of the selectivity of manufacturing processes. Rhodium is an important component in automotive exhaust catalyst [1,2], especially in the catalytic reduction of nitric oxide.

Chlorinated organic solvents and other chemicals are used by many industries, and disposal of these chemicals after use has become a significant problem. There are several techniques now in development to solve this growing disposal destruction problem; such as biodegradation, incineration, and hydrodechlorination. Catalytic conversion of halocarbons to useful fuels has received much attention specifically the catalyts: palladium and platium, but there is little known on understanding the Rh catalyst in the hydrodechlorination reactions. A study on reaction of 1,2-dichloroethane with hydrogen over silica-supported rhodium catalyst may be useful in gaining information of mechanistic pathways and controlling parameters for Rh catalytic hydrodechlorination and its economic viability.

## 1-2. LITERATURE SURVEY

### 1.2.1 Rhodium/$SiO_2$ Catalysts

Practical catalysts using the group VIII metals always have the metals dispersed on a support or carrier. This is a convenient technique for obtaining a relatively large metal area which is resistant to sintering during use or regeneration. Other important functions of the support are to physically separate small metal crytallites and to hinder the agglomeration of the small crystallites into larger crystallites. This would decrease the number of the surface metal atoms per unit mass of metal, and thereby decrease the activity of the catalyst. The structure of the metal particles dispersed on a silica powder support has been studied by Avery and Sanders [3], using the electron microscopy to determine particle sizes and extent to which the metal particles were multiple twinned or in an ideal structure. Their catalysts were prepared by impregnation using an aqueous solution of metal halide derivatives, dried at $100^{o}$-$150^{o}$C and hydrogen reduced at $300^{o}$C. The proportion of metal was in the range 5-15%, and the range of electron microscopically visible metal particle diameters were

| | |
|---|---|
| platinum | 10 - 80 $A^{o}$ |
| palladium | 21 - 100 $A^{o}$ |
| gold | 100 - 350 $A^{o}$ |

### 1.2.2 Catalytic Activity of Rhodium in Relation to Its State of Dispersion [4,5]

The degree of dispersion for a supported metal, defined as ratio of surface metal atoms to total number of metal atoms, is known to be extremely high in these noble metals [6]. The dispersion of a supported metal can have any value between 0 and 1. Low dispersion values (less than 0.3) indicate that the metal is composed of relatively large crystallites with most atoms occupying internal positions. Dispersion values between 0.4 and 0.7 indicate the metal is exposed as very small crystallites. Dispersion values approching unity mean that nearly all metal atoms are exposed as a completely atomized condition.

In discussing catalytic activity in relation to its state of dispersion, Yates and Sinfelt [4] have investigated the catalytic activity of rhodium as a function of its dispersion, using hydrogenolysis of ethane as a test reaction. The catalysts included: bulk rhodium and a series of rhodium-silica catalysts of varying rhodium concentration. The results of their study are summarized in Table 1-1. The specific activities of bulk rhodium and severely calcined rhodium (both having large crystallite sizes) on silica were substantially lower than those of highly dispersed rhodium. It appears that the reaction is structure sensitive, or in Boudart's terminology, " a demanding reaction". They also suggested that the catalytic activity ultimately decreases as the metal dispersion is increased to an extremely high degree(by decreasing the rhodium concentration to 0.3% or less). The fraction surface area of the rhodium increased smoothly with decreasing rhodium concentration, beginning with the unsupported rhodium sample. The surface area approached a limiting value at about 1% Rh concentration, below which it changed very little with further decreases in concentration. The highest catalytic activity was associated with an intermediate state of dispersion (1-10%) of the metal. They calculated a chemisorption stoichiometry Xm of 2 for a series of Rh-on-silica catalysts, and in no case did the ratio of hydrogen atoms to total rhodium atoms exceed unity. Obviously the silica surface sites are not able to fully stabilize atomically dispersed rhodium centers.

### 1.2.3 Hydrodehalogenation of Some Simple Halocarbons

The removal of halogen from an organic compound by catalytic hydrogenation is usually accomplished under mild conditions (lower temperature) relative to thermal decomposition reactions. As a rule dehalogenation, RX to RH, the ease of reaction order is RI>RBr>RCl [7]. The rupture of the carbon-fluorine bond does not take place except in certain highly activated systems or during reduction of an aromatic ring containing fluorine [8].

Some aliphatic chlorides have been hydrodehalogenated by various methods to produce lower Cl content compounds. Yang and Bozzelli [9] studied the reaction of 1,2-dichloroethane with hydrogen over H-Y mordenite zeolite, they found that the major products are vinyl chloride, and a trace amount of $C_2$ hydrocarbons. One appealing observation is the high initial conversion, but a rapid loss of catalyst activity occurs via coke formation. In the hydrodechlorination of 1,2-dichloroethane over palladium on alumina catalyst, ethane, ethylene, and chloroethane were observed at temperatures from 100 to 245°C. The apparent activation energy was 15 kcal/mole. Yang and Bozzelli [9] indicated that higher reaction temperatures led to more conversion for $C_2$ hydrocarbons. The palladium catalyst showed some sintering and fouling at the surface, for the catalyst at the reaction time 36.8 h after 12 h regeneration, and the activity only recovered to 56% of the initial value. Chuang, S. C. and Bozzelli, J. W. [10,11] have done several hydrodechlorination thermal-reaction studies. They provided some kinetic data and products distribution information and gave a better understanding of the kinetics and mechanism of these non-catalytic reactions.

Campbell and Kemball [7] studied the reaction of ethyl chloride and ethyl bromide with hydrogen on evaporated metal films(Pt, Pd, Ni, Fe, Rh). They pointed out that the metals which catalyzed the decomposition of the ethyl halides did so only at higher temperatures and the main reaction was formation of ethane and hydrogen halide. One interesting point is that the catalytic activity of rhodium departed from the usual pattern of other group VIII metals by giving the methane formation. They proposed that the dissociation of carbon-hydrogen bonds was a necessary preliminary step in the dissociation of the carbon-carbon bond, and from the distribution of methanes they determined that species responsible for the formation of methane undergo substantial exchange before leaving the surface.

In the study of heterogenous hydrogenolysis of some fluorocarbons over active carbon-supported Pd catalyst, Witt et al. [12] showed that C-F hydrogenolysis took place most readily for compounds with only one F atom attached to each carbon and least readily for compounds with more than two F atoms attached to the carbon. The apparent activation energy (Ea) values for a maximum of one F atom on each carbon $CH_2=CHF$, $C_2H_5F$, and $CHF=CHF$ are in the range of 12-17 kcal/mole. With two or more F atoms on one of carbon atoms, $CH_2=CF_2$, $CH_3CHF_2$, and $CH_3CF_3$, Ea values are in the range of 20-26 kcal/mole.

Baltzly and Phillips [13] studied dehalogenation of halogen-substituted compounds over palladium on charcoal. They found that saturated aliphatic bromides, such as isobutyl bromide, t-butyl bromide, and cyclohexyl bromide, did not undergo hydrogenolysis. Aromatic halides, such as bromo-benzene, allyl chloride, and benzyl chloride, were, however, readily dehalogenated, indicating an interaction of catalyst with Pi bonding orbitals.

In the selective hydrogenation of haloalkenes to haloalkanes using rhodium catalysts, Ham and Coker [14] found that rhodium on alumina is a superior catalyst for the hydrogenation of a vinylic or allylic halogen-substituted olefins to haloalkanes, but under hydrogenation conditions used, hydrogenolysis of the chloroalkanes did not occur. The yield of chloroalkanes, as well as the rate of hydrogenation, was effected by the catalyst support.

Table 1-1 Ethane Hydrogenolysis Activity of Rhodium in Relation to Its State of Dispersion[1]

| States of Dispersion[2] | Crystallite Size(A$^o$) | Specific[3] Activity |
|---|---|---|
| Bulk Rh | 2560 | 0.79 |
| 1-10% Rh on $SiO_2$ | 12-41 | 8-16 |
| 5% Rh on $SiO_2$ (calcined at 800$^o$C) | 127 | 0.41 |
| 0.1-0.3% Rh on $SiO_2$ | <12 | 4.3-4.4 |

1. D. J. C. Yates and J. H. Sinfelt, J. Catal., 8, 348-358(1967).
2. Dispersion, D

$$D = \frac{\text{no. surface metal atoms}}{\text{total no. of metal atoms}}$$

3. Specficactivity is defined as the reaction rate per unit surface area of metal at a given temperature.

Table 1-2 Percentage d-Character in the Metallic Bond of Transition Elements [15]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sc<br>20 | Ti<br>27 | V<br>35 | Cr<br>39 | Mn<br>40.1 | Fe<br>39.5 | Co<br>39.7 | Ni<br>40 | Cu<br>36 |
| Y<br>19 | Zr<br>31 | Nb<br>39 | Mo<br>43 | Tc<br>46 | Ru<br>50 | Rh<br>50 | Pd<br>46 | Ag<br>36 |
| La<br>19 | Hf<br>29 | Ta<br>39 | W<br>43 | Re<br>46 | Os<br>49 | Ir<br>49 | Pt<br>44 | Au<br>-- |

## 1.3 EXPERIMENTAL

### 1.3.1 Catalyst Preparation

$Rh/SiO_2$ (3 wt%) catalyst was prepared by impregnating silica with a solution of $RhCl_3$ $3H_2O$ at PH 2. The Rhodium(III) chloride-hydrate(40-43% Rh) was obtained from Strem Chemicals Inc., Newburyport, MA. The silica used as a support was silica gel, large pore #14-742(350 $m^2/g$ surface area, average pore diameter 200 $A^o$) obtained from the Strem Chemicals, Inc. 2 to 4 ml impregnating solution of appropriate concentration for desired wt% was employed per gram of silica, and the catalyst was then dried 24 h at $100^oC$. After the preparation described above, the catalyst was reduced in flowing hydrogen at $400^oC$ for 24 h. For each run, the reactor was loaded with the appropriate 0.150 g of the catalyst, reduced a second time under a $H_2$ flow of 90 cc/min at $300^oC$ for 3 h, then the reactor was cooled down to the desired reaction temperature.

### 1.3.2 Particles Size of $Rh/SiO_2$ Catalyst

The particles size of Rh metal determined by X-ray diffraction is $62^oA$, and the particles size of Rh metal after the reaction is 61 $A^o$ as shown in Table 3-1, Figure 1-1, and Figure 1-2.

### 1.3.3 Apparatus and Procedure

0.7-cm-ID by 35-cm-length pyrex tube was used as the reactor, the temperature range studied was from 200 to $300^oC$. The catalyst was prepared as mentioned before. A schematic diagram of the apparatus is shown in Figure 1-3. Telfon tubing was used for connection to GC and it was heated by heating tapes (80°C) to avoid condensation or adsorption of products or reactants with high boiling point. Temperature measurement was carried out by thermocouples on both sides of the catalytic bed. Two impingers in series were used as saturators, and maintained in a 0°C ice bath. Hydrogen was used both as a carrier and as a reagent gas. One stream of $H_2$ brought 1,2-dichloroethane vapor into reactor. The second pure $H_2$ stream was used to change the mole ratio of reagents.

### 1.3.4 Products Analysis

A Perkin-Elmer model 900 gas chromatograph equipped with a flame ionization detector was used for all analyses. Seperation was effected by a 12 ft by 1/8 inch OD stainless steel tubing column packed with Porapak Q and operated at 50°C-190°C at a programming rate of 16°C/min. A Hewlett-Packard 3390A recorder/integrator was connected to the GC for quantitative determination of all reactants and products. The column was not capable of resolving ethylene and acetylene. A GC/MS spectrometer was used to help identify the sample products. The equipment used was a Carlo Erba strumentizione Fractovap 4160 series GC interfaced with a Kratos MS 25 double focus magnetic sector Mass Spectrometer, electron impact mode.

### 1.3.5 Materials

Hydrogen and nitrogen were purchased as commercial grade from MG Industries Company (North Branch,NJ). 1,2-dichloroethane was obtained from Aldrich Chemical Company, INC., and the purity was 99%. The catalyst used was prepared as mentioned before.

Figure 1-1 Particle Size of Reduced Rh (by X-ray Diffraction)

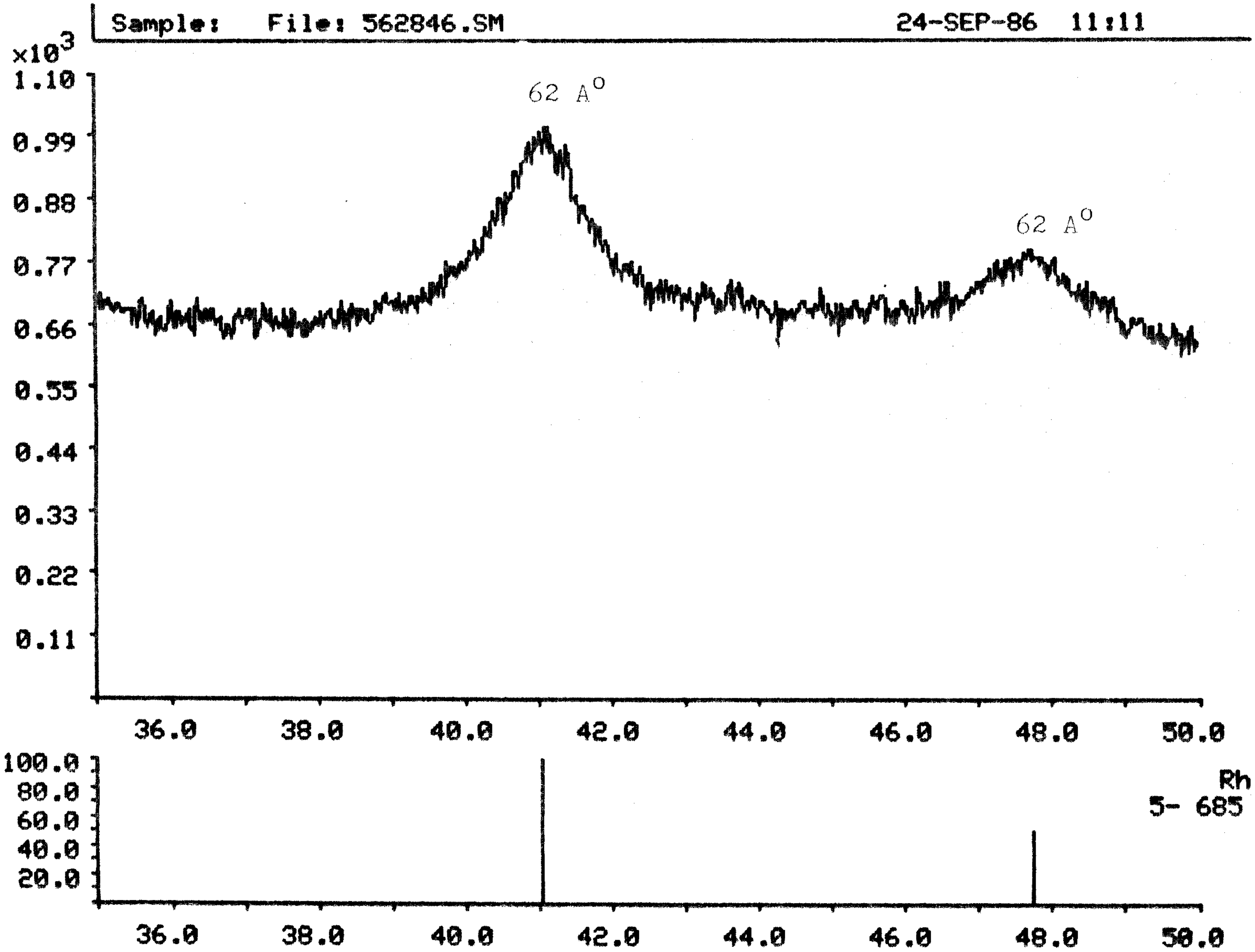
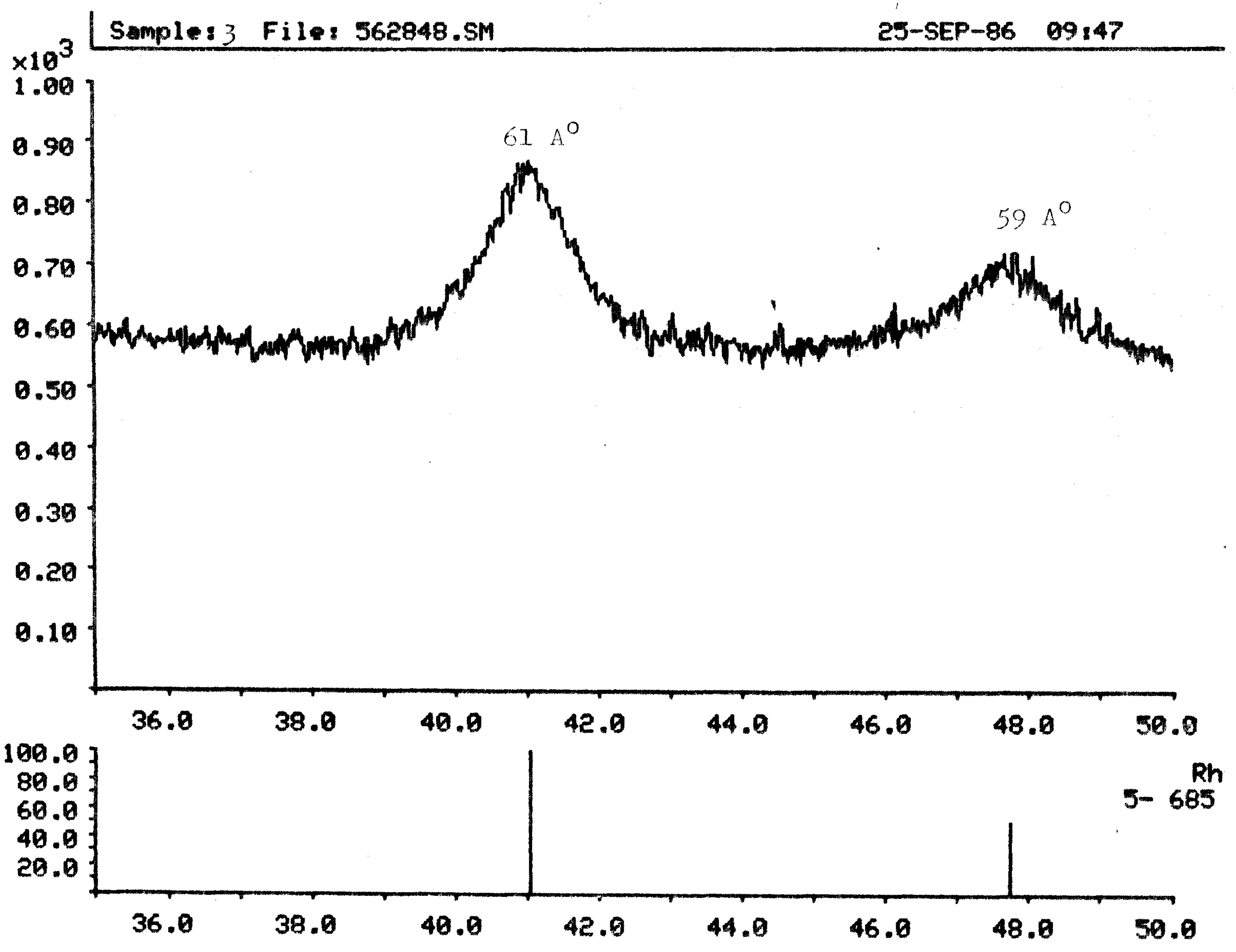


Figure 1-2 Particle Size of Rh (after reaction for 4 hr)
1,2-dichloroethane + $H_2$ ( T = 260 °C )



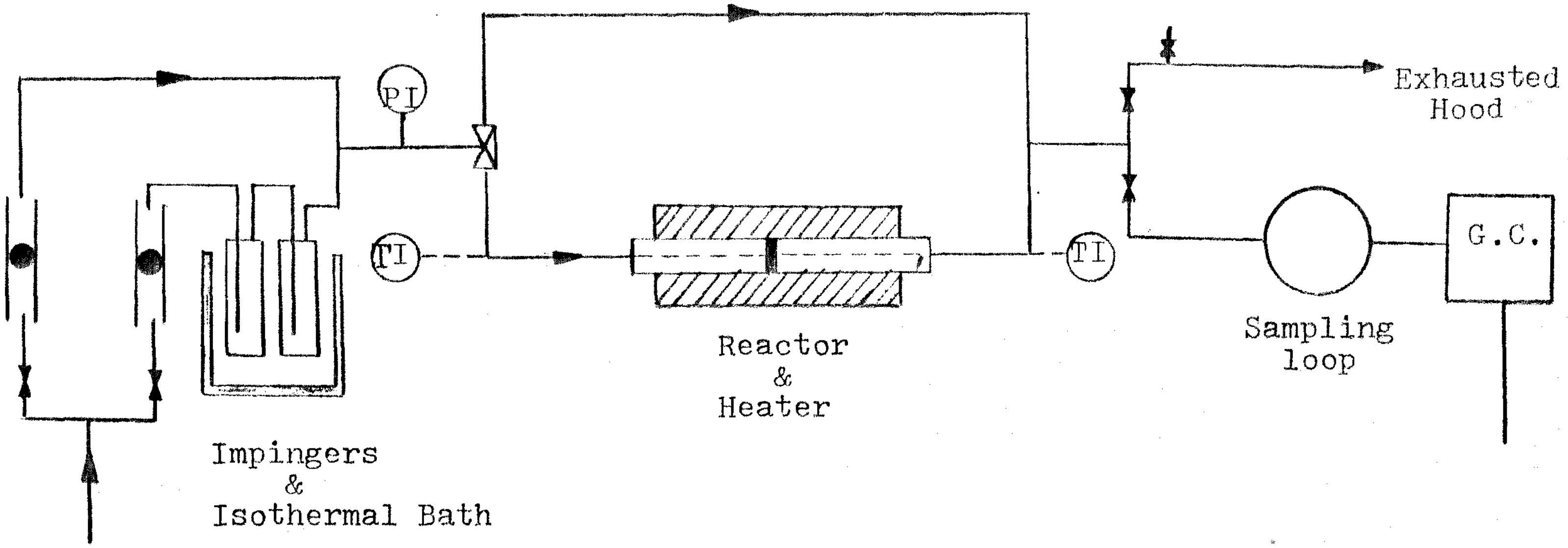


Figure 1-3 Schematic Diagram of Reactor System

## 1.4 RESULTS AND DISCUSSION

### 1.4.1 Temperature Effect on Selectivity and Reactivity

In the hydrodechlorination of 1,2-dichloroethane, it was found that only four products were formed in the temperature range of 200-300°C. The major products were ethane and chloroethane; the trace products were methane and ethylene. As the temperature increased Rh catalysts resulted in higher yields of methane. As in discussing the order of hydrogenolysis activities of the noble metal of group VIII by Sinfelt and Yates [4], it is of interest to consider the percentage "d" character of the metal bond as shown in Table 1-2 [15]. The hydrogenolysis activity increases with increasing d character. One striking observation is the extremely low activity of palladium and platium compared with the activities of the other noble metals of Group VIII. Figure 1-4 and Table 1-3 show the observed change in selectivity with respect to temperature. It is also interesting to note the higher conversion to $C_2$ and $C_1$ hydrocarbons is observed at higher reaction temperature, but the conversion to chloroethane decreases with the increased temperature. Rates of product formation as a function of proceeding reaction time are shown in Figure 1-5 and Figure 1-6. All showed a stable product selectivity after 4 h.

Figure 1-7 shows the observed change in total conversion of 1,2-dichloroethane and the loss of catalyst activity with respect to time at 245°C. It also shows the effect of regeneration (reduced under $H_2$ flow for 12 hr. each time at $300^{o}C$) on the catalyst activity. The catalyst activity declines rapidly in the first hr. The rapid decline in activity of Rh on silica gel might be due to the deactivation of the active rhodium by the hydrogen chloride produced and coke formation on the catalyst surface. After fourth regeneration the activity recovered to only 60% its initial value. This indicates that the catalyst may undergo sintering and some fouling (covered by carbonaceous material). The temperature and atmosphere are the most important factors affecting the deactivation.

Table 1-3 Effect of Temperature on 1,2-dichloroethane Hydrodechlorination Selectivity

| Catalyst | $Rh/SiO_2$(3 wt%) | | | |
|---|---|---|---|---|
| Dispersion(%) | | | | |
| Temperature ($^{o}C$) | 200 | 240 | 260 | 280 |
| Reaction rate (mole/kg/hr) | 3.13 | 8.36 | 9.26 | 17.34 |
| Total conversion | 0.04 | 0.109 | 0.121 | 0.227 |
| Selectivity(%) | | | | |
| $CH_4$ | 0.64 | 1.26 | 1.58 | 5.06 |
| $C_2H_4$ | 0 | 0 | 0.12 | 0.12 |
| $C_2H_6$ | 73.78 | 82.99 | 83.21 | 84.72 |
| $C_2H_5Cl$ | 25.58 | 15.75 | 15.09 | 10.10 |

Figure 1-4

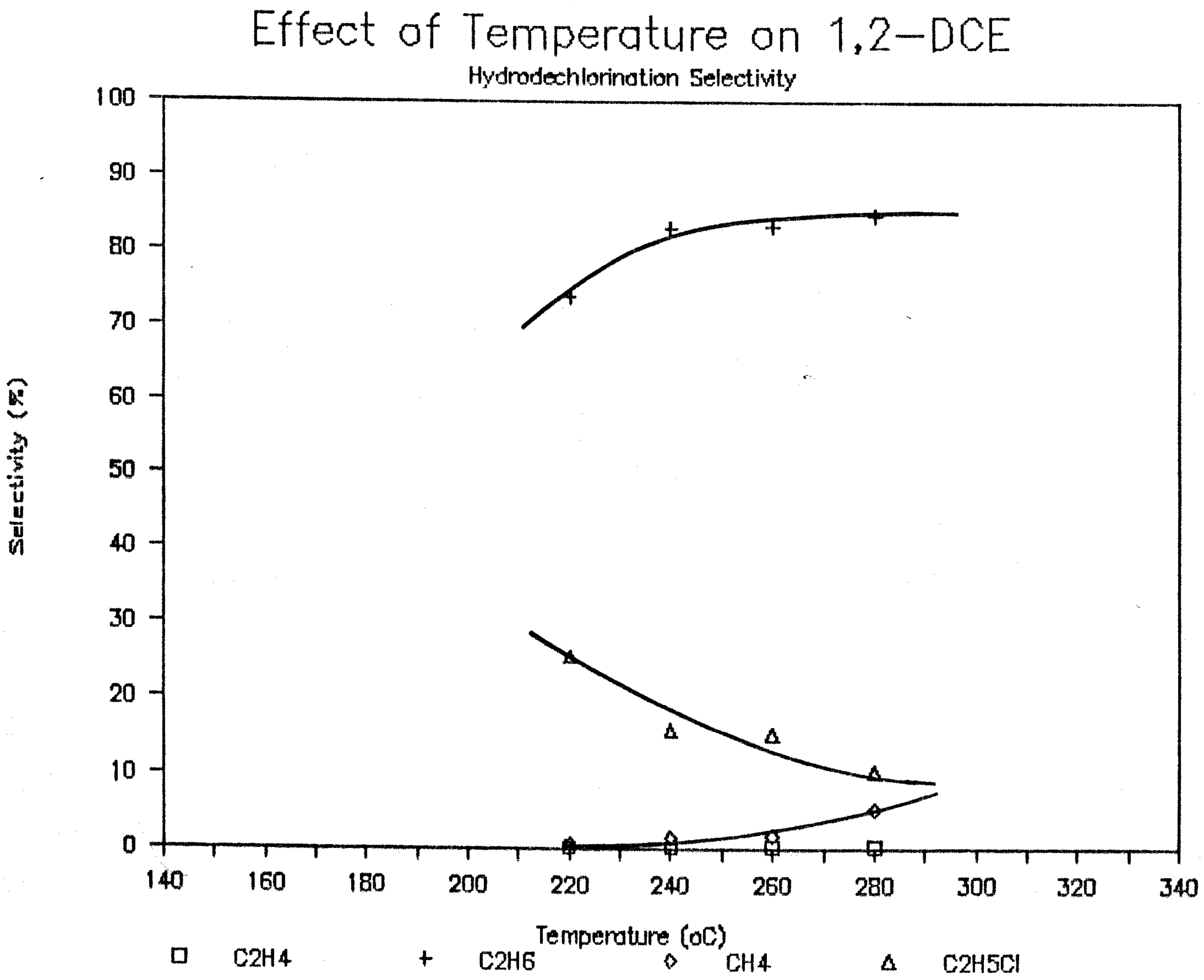

Effect of Temperature on 1,2-DCE
Hydrodechlorination Selectivity
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
140
160
180
200
220
240
260
280
300
320
340
Temperature (oC)
□ C2H4
+ C2H6
◇ CH4
△ C2H5Cl

Figure 1-5

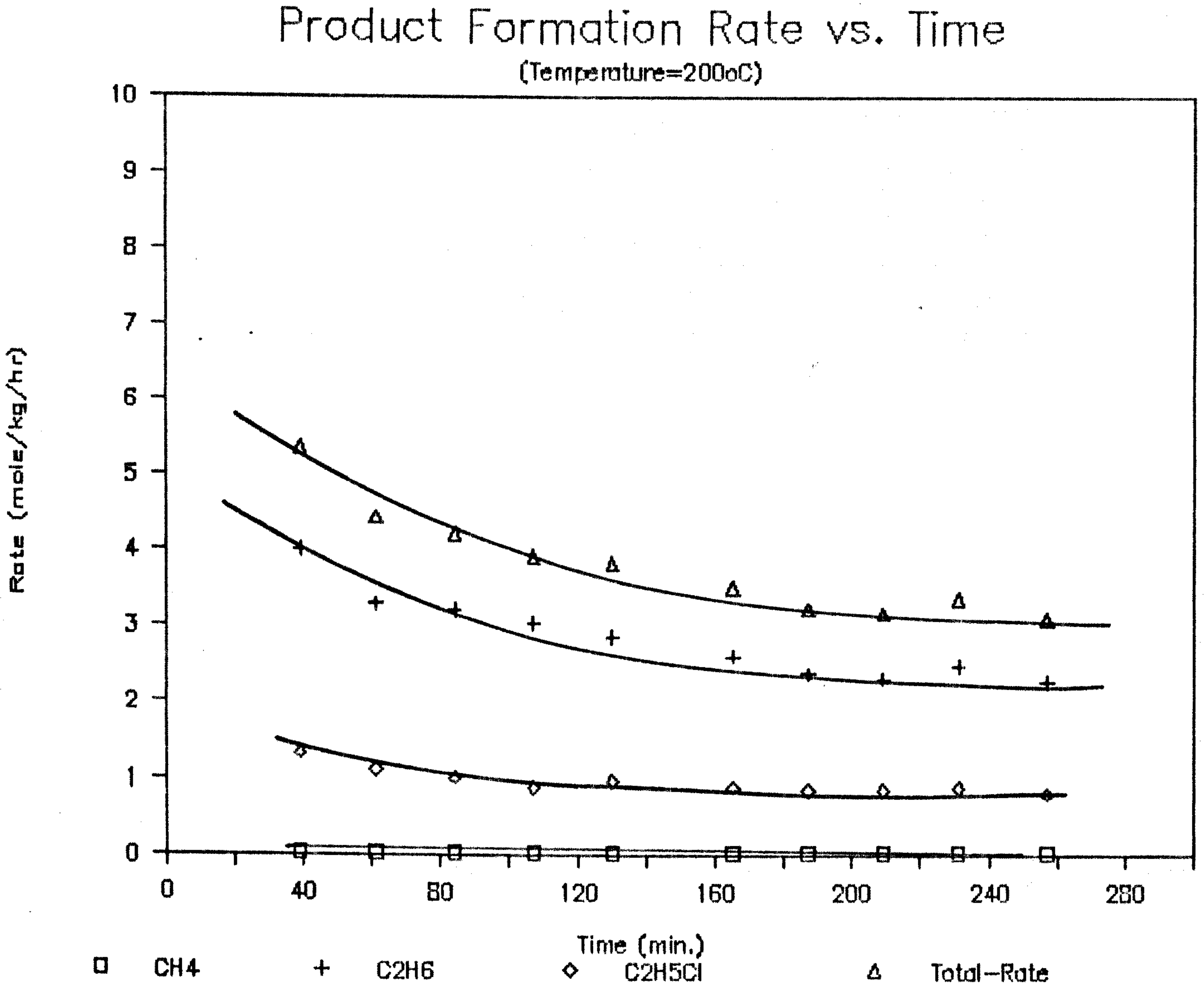

Product Formation Rate vs. Time
(Temperature=200oC)
Rate (mole/kg/hr)
10
9
8
7
6
5
4
3
2
1
0
0
40
80
120
160
200
240
280
Time (min.)
□ CH4
+ C2H6
◇ C2H5Cl
△ Total-Rate

Figure 1-6

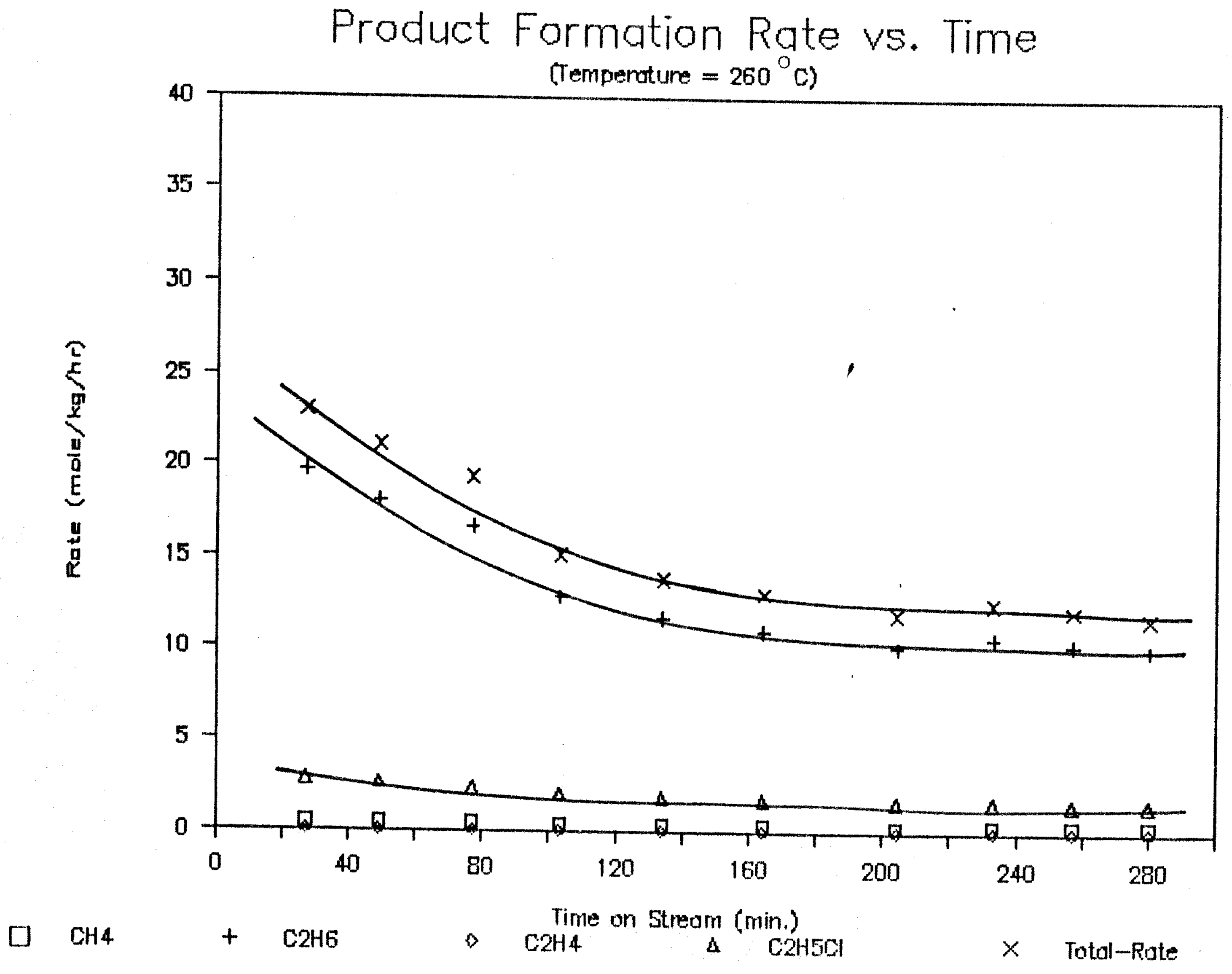
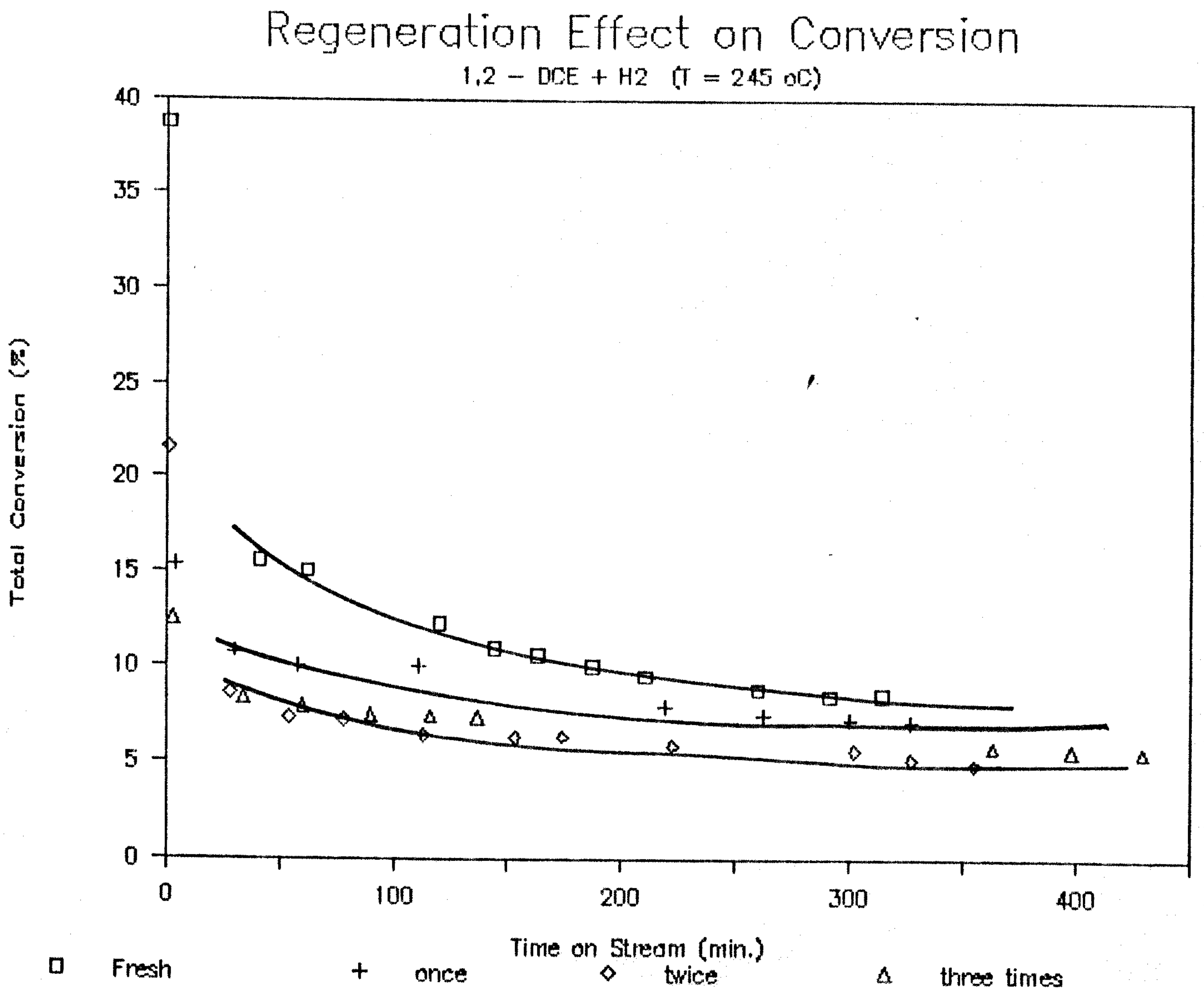

Product Formation Rate vs. Time
(Temperature = 260 °C)
Rate (mole/kg/hr)
0
5
10
15
20
25
30
35
40
Time on Stream (min.)
0
40
80
120
160
200
240
280
□ CH4
+ C2H6
◇ C2H4
Δ C2H5Cl
× Total–Rate

Figure 1-7


Regeneration Effect on Conversion
1,2 – DCE + H2 (T = 245 oC)
Total Conversion (%)
0
5
10
15
20
25
30
35
40
Time on Stream (min.)
0
100
200
300
400
□ Fresh
+ once
◇ twice
△ three times

### 1.4.2 Reaction Kinetics

In this study $H_2$ was used as the carrier gas and was in large excess. The partial pressure of the sample employed for all the temperature studies was 21 torr, where the product yield is dependent on the 1,2-dichloroethane partial pressure. It is reasonable to assume the reaction process would be pesudo first order because of the use of excess hydrogen. By using the integral method to fit data, we obtain the performance equation

$$\ln(1/(1-x)) = \tau * k$$

where x is the conversion of 1,2-dichloroethane, k is the rate constant, and $\tau$ is defined as $W/V_o$. W is the weight of catalyst and $V_o$ is the volume flow rate. Figure 1-8 and Table 1-4 shows kinetic parameters for this reaction.

The Arrhenius plot is shown in Figure 1-9, and the apparent activation energy is 13 kcal/mole. The straight line in Arrhenius plot indicates no diffusion limitation.

Figure 1-10 is a plot of formation rate of products verus 1/T, and from the slope of this plot it is concluded that the formation of ethylene is more difficult (high activation energy).

Table 1-4 Kinetic Parameters for Reaction 1,2-dichloroethane with Hydrogen over Rhodium on Silica Gel Catalyst.

| T($^{o}$C) | k(liter/kg-hr) |
|---|---|
| 200 | 2351 |
| 240 | 6063 |
| 260 | 11394 |
| 280 | 14341 |

### 1.4.3 Residence Effect on Products distribution

Figure 1-11 and Table 1-5 show the residence time effect on the selectivity at temperature 240°C. It indicates that the residence time has little effect on the products distribution. It also means that no secondary reactions are occurring.

### 1.4.4 Support and Catalyst Effects on selectivity

Table 1-6 compares the selectivity of different catalysts and the support effect on the reaction. From the data we see that $SiO_2$ is relatively inert in the reaction temperature range. This is good as it shows no necessity to consider support effects. At higher reaction temperatures $SiO_2$ promotes more ethylene formation. The selectivity for $C_2$ compounds in the hydrode-chlorination of 1,2-dichloroethane on $Rh/SiO_2$ catalyst is better than on the $Pd/Al_2O_3$ catalyst since $Rh/SiO_2$ catalyst yields more hydrocarbons (83%).

Figure 1-8

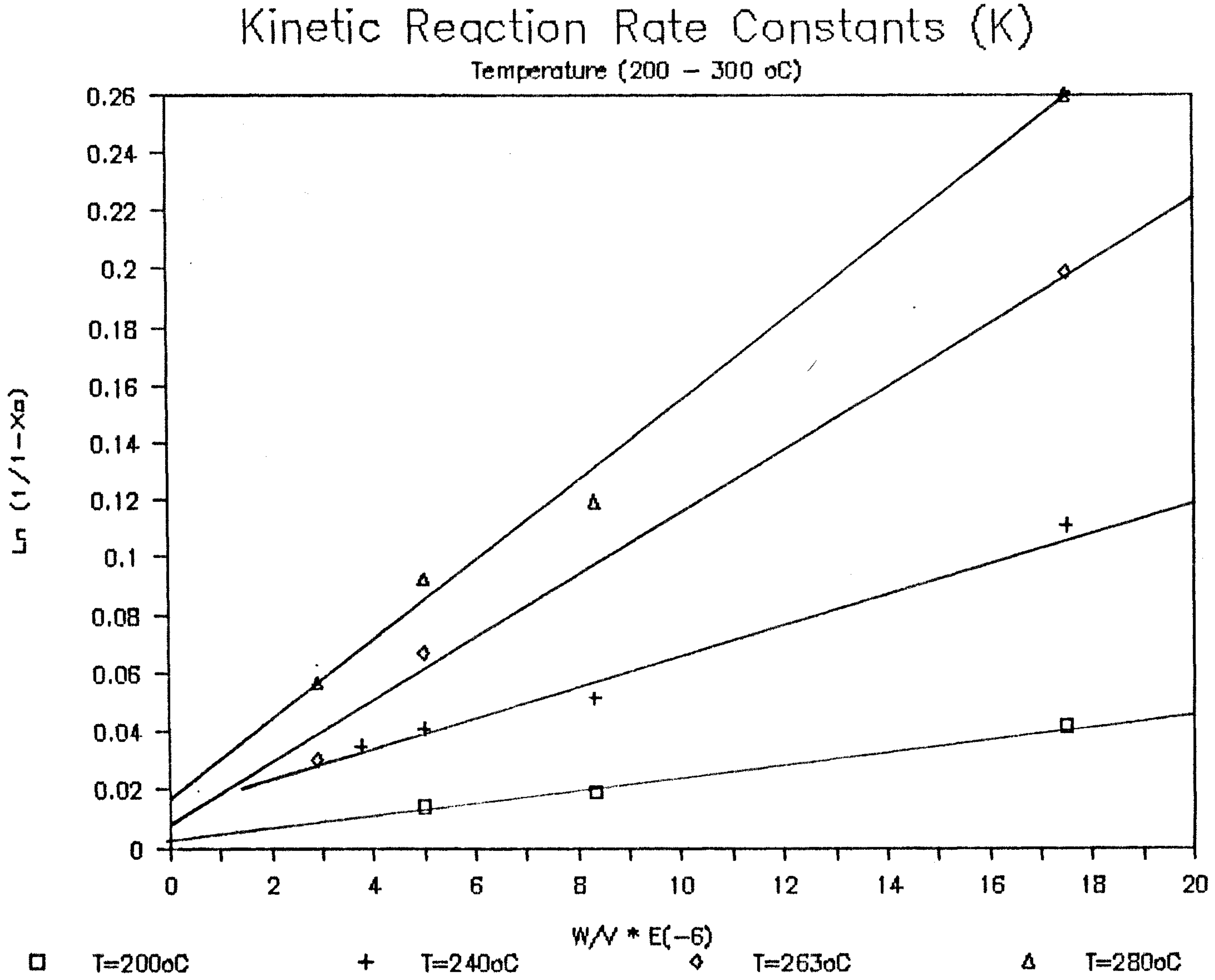

Kinetic Reaction Rate Constants (K)
Temperature (200 – 300 oC)
Ln (1/1–Xa)
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
2
4
6
8
10
12
14
16
18
20
W/V * E(–6)
□ T=200oC
+ T=240oC
◇ T=263oC
△ T=280oC

Figure 1-9

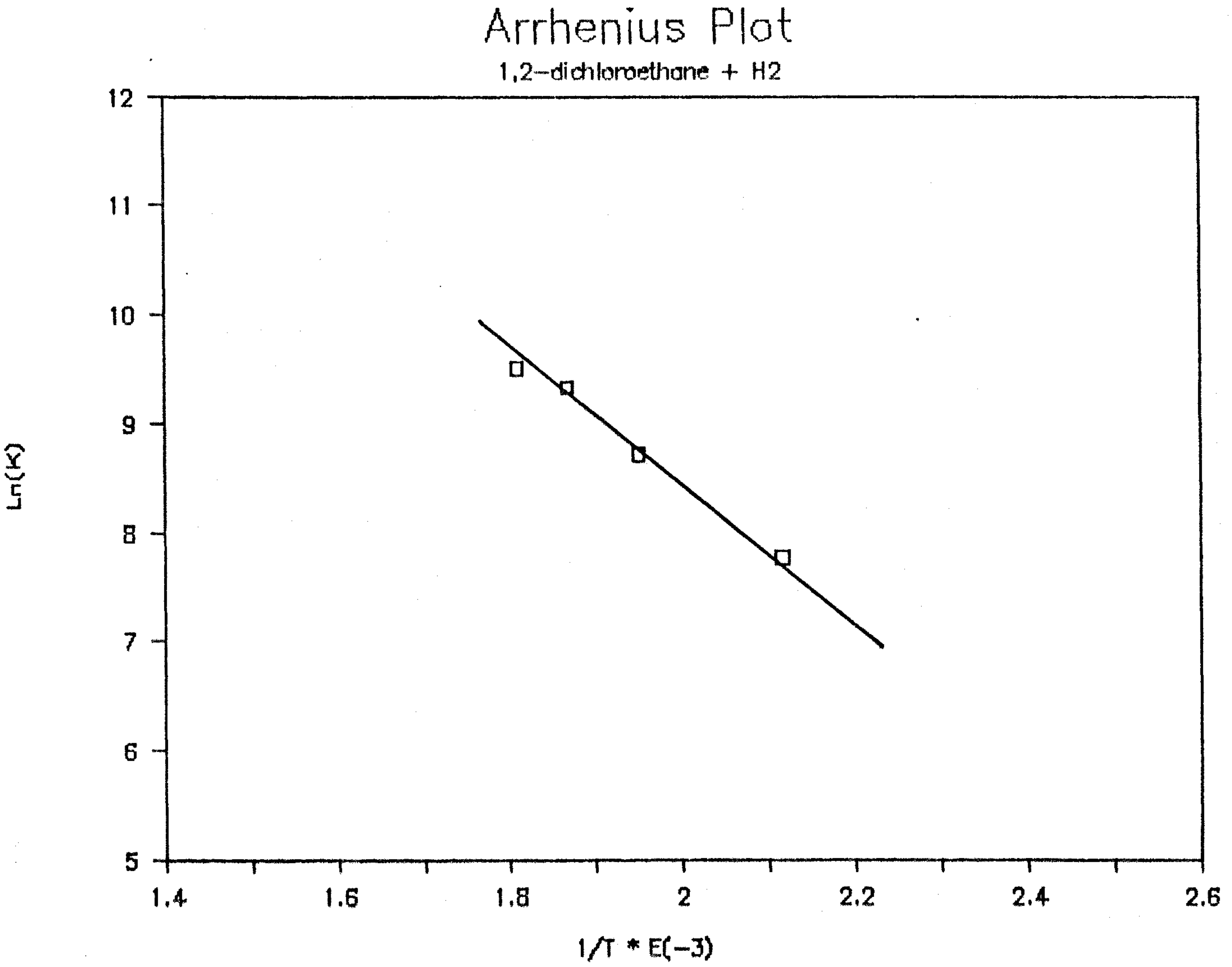

Arrhenius Plot
1,2-dichloroethane + H2
Ln(K)
12
11
10
9
8
7
6
5
1.4
1.6
1.8
2
2.2
2.4
2.6
1/T * E(-3)

Figure 1-10

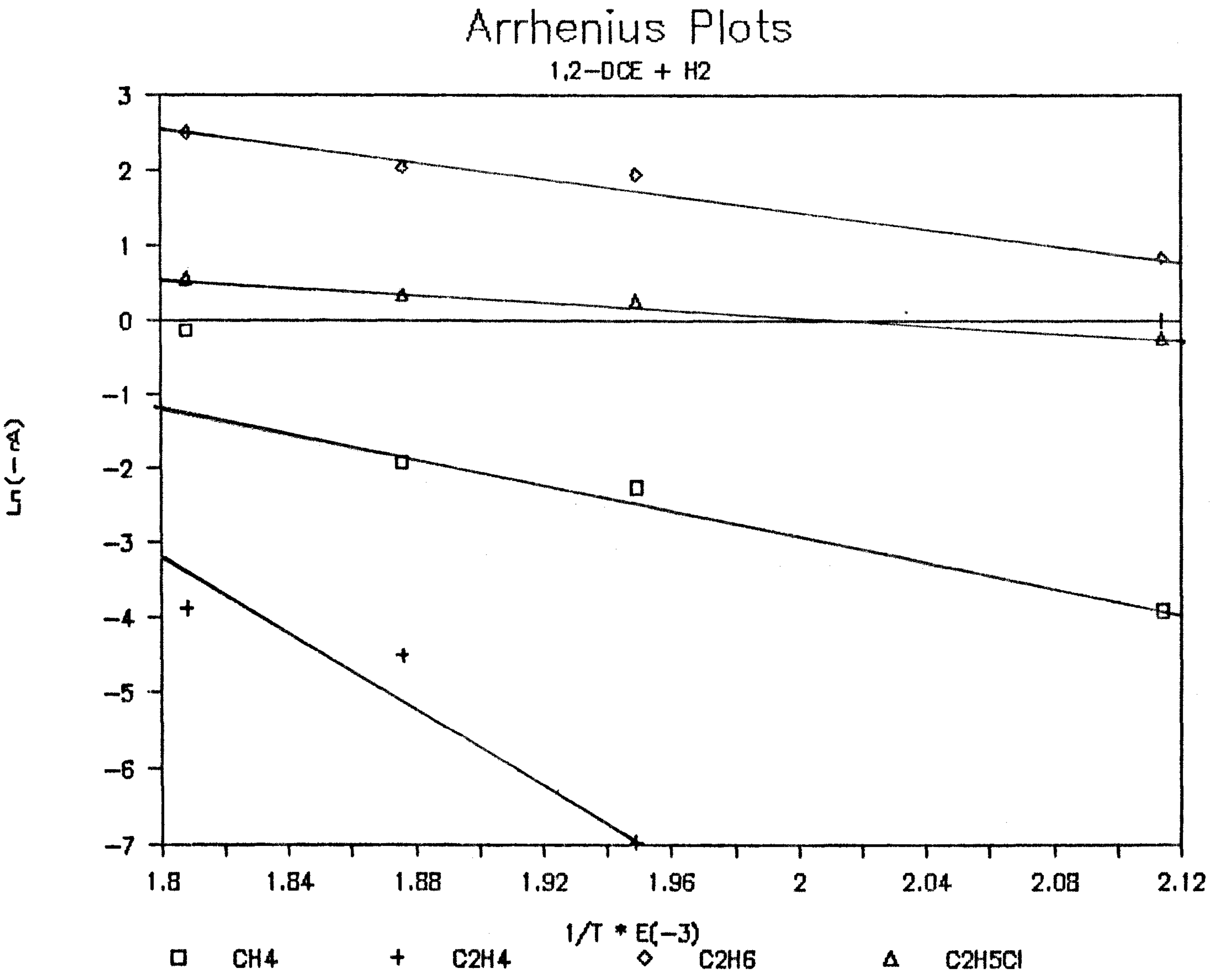
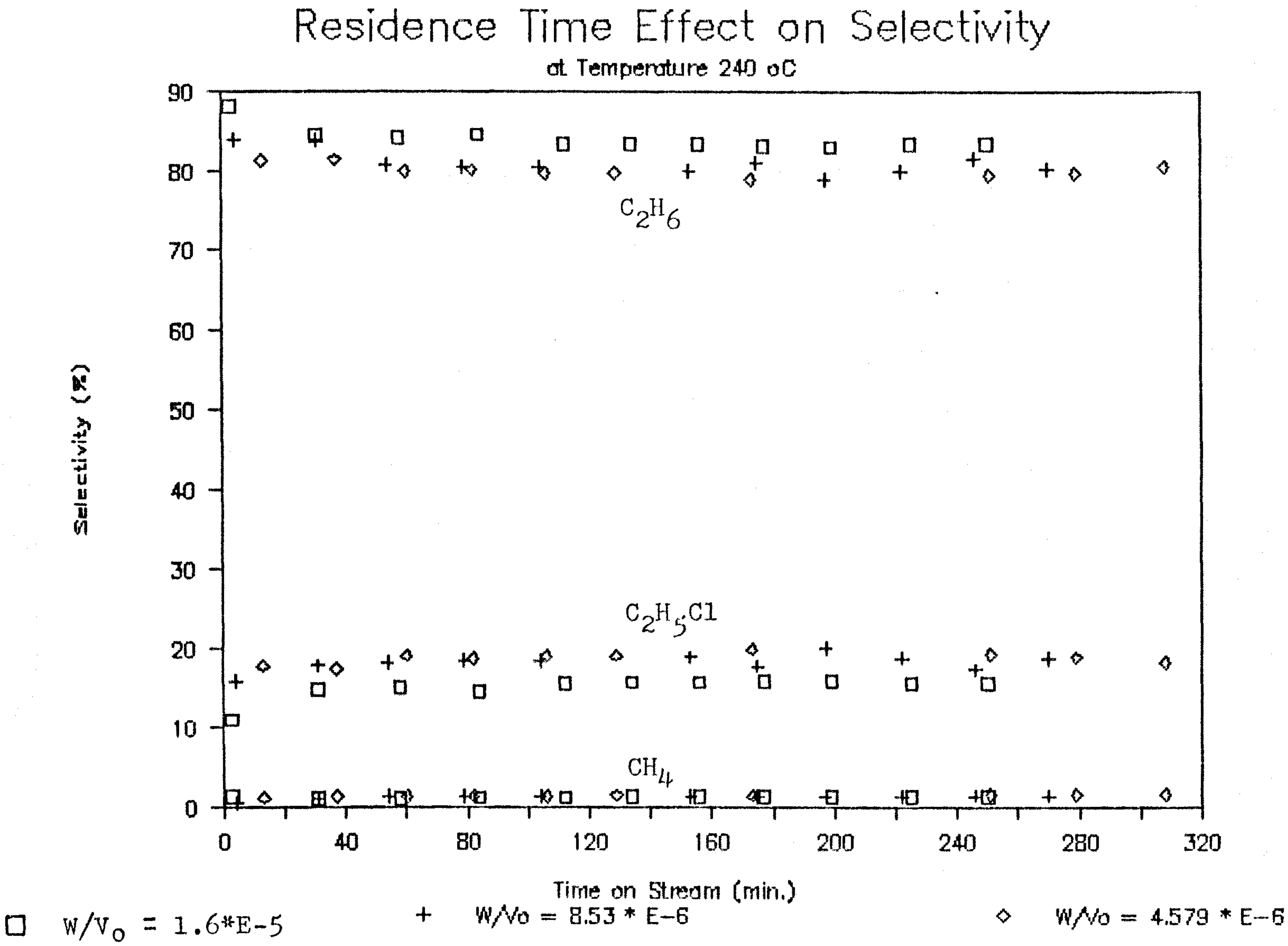

Arrhenius Plots
1,2-DCE + H2
Ln(-rA)
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
1.8
1.84
1.88
1.92
1.96
2
2.04
2.08
2.12
1/T * E(-3)
□ CH4
+ C2H4
◇ C2H6
△ C2H5Cl

Table 1-5 Selectivity of Hydrodechlorination of 1,2-Dichloroethane at Different Residence Time

| Time on stream (min) | Selectivity(%)<br>$CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_2H_5Cl$ |
|---|---|---|---|---|
| W/Vo = 1.60*E-5 (kg.hr/liter) | | | | |
| 3 | 1.11 | 0 | 88.05 | 10.84 |
| 31 | 0.90 | 0 | 84.51 | 14.59 |
| 58 | 1.01 | 0 | 84.09 | 14.90 |
| 84 | 1.04 | 0 | 84.56 | 14.40 |
| 112 | 1.07 | 0 | 83.45 | 15.48 |
| 134 | 1.11 | 0 | 83.29 | 15.60 |
| 156 | 1.10 | 0 | 83.31 | 15.59 |
| 177 | 1.16 | 0 | 83.03 | 15.81 |
| 199 | 1.25 | 0 | 82.99 | 15.76 |
| 225 | 1.15 | 0 | 83.35 | 15.50 |
| 250 | 1.20 | 0 | 83.31 | 15.49 |
| W/Vo = 8.53*E-6 (kg.hr/liter) | | | | |
| 4 | 0.45 | 0 | 83.89 | 15.76 |
| 31 | 1.04 | 0 | 83.89 | 17.75 |
| 54 | 1.09 | 0 | 80.82 | 18.18 |
| 79 | 1.10 | 0 | 80.54 | 18.36 |
| 104 | 1.16 | 0 | 80.49 | 18.35 |
| 153 | 1.20 | 0 | 80.01 | 18.79 |
| 175 | 1.23 | 0 | 81.06 | 17.71 |
| 197 | 1.24 | 0 | 78.77 | 19.91 |
| 222 | 1.28 | 0 | 79.98 | 18.74 |
| 246 | 1.31 | 0 | 81.48 | 17.21 |
| 270 | 1.29 | 0 | 80.12 | 18.59 |
| W/Vo = 4.579*E-6 (kg.hr/liter) | | | | |
| 13 | 1.06 | 0 | 81.23 | 17.71 |
| 37 | 1.19 | 0 | 81.38 | 17.35 |
| 60 | 1.15 | 0 | 79.85 | 19.00 |
| 82 | 1.21 | 0 | 80.10 | 18.69 |
| 106 | 1.24 | 0 | 79.76 | 19.00 |
| 129 | 1.35 | 0 | 79.66 | 18.99 |
| 173 | 1.33 | 0 | 78.87 | 19.80 |
| 251 | 1.43 | 0 | 79.36 | 19.21 |
| 279 | 1.49 | 0 | 79.70 | 18.81 |
| 308 | 1.52 | 0 | 80.41 | 18.07 |

Figure 1-11



Residence Time Effect on Selectivity

at Temperature 240 oC

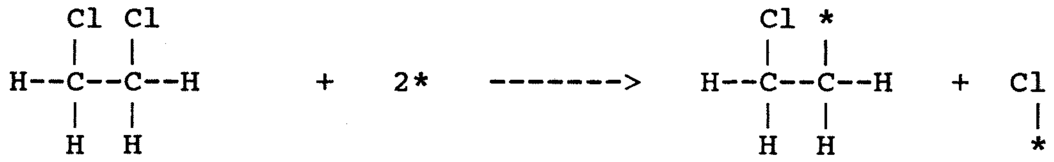
Table 1-6 $SiO_2$ Support and Catalyst Effects on the Selectivity of 1,2-dichloroethane Hydrodechlorination

| catalyst | $Rh/SiO_2$ (3 %) | $Pd/Al_2O_3$[9] (0.5 %) | thermal decompose | $SiO_2$ | |
|---|---|---|---|---|---|
| temperature (°C) | 240 | 245 | 240 | 245 | 300 |
| $W/V_o$ | 1.6*E-5 | 1.6*E-5 | | 1.6*E-5 | |
| total conversion(%) | 11 | 29 | 0 | <0.3 | 0.35 |
| selectivity(%) : | | | | | |
| $CH_4$ | 1.26 | 0 | 0 | 13.50 | 1.70 |
| $C_2H_4$ | 0 | 55.86 ($C_1$ & $C_2$) | 0 | 34.23 | 77.42 |
| $C_2H_6$ | 82.99 | | 0 | 32.43 | 16.00 |
| $C_2H_5Cl$ | 15.75 | 44.14 | 0 | 19.84 | 4.88 |

### 1.4.5 Mechanisms

In the study of C-Cl hydrogenolysis of aliphatic chloride on supported metal catalyst, Lapierre et al. [16] have proposed a free radical mechaism. Yang, Y.D. and Bozzelli, J. W. [9] suggested similar steps in the reaction of 1,2-dichloroethane with hydrogen over palladium supported on alumina. We also propose similar mechanisms involving the formation of both hydrogen and 1,2-dichloroethane radical intermediates to account for the production of $C_2H_6$, $C_2H_5Cl$, and $C_2H_4$. 1,2-dichloroethane and molecular hydrogen undergo dissociative adsortion.

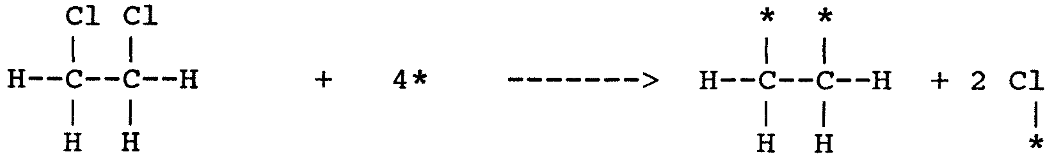
$$H_2 + 2* \text{-------}> 2\,H*$$



$$\mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{Cl}{C}}{-}H} + 2* \text{-------}> \mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{*}{C}}{-}H} + \underset{*}{\mathrm{Cl}}$$

(I)

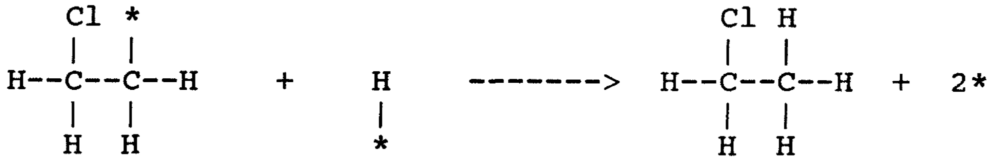
or



$$\mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{Cl}{C}}{-}H} + 4* \text{-------}> \mathrm{H{-}\underset{H}{\overset{*}{C}}{-}\underset{H}{\overset{*}{C}}{-}H} + 2\,\underset{*}{\mathrm{Cl}}$$

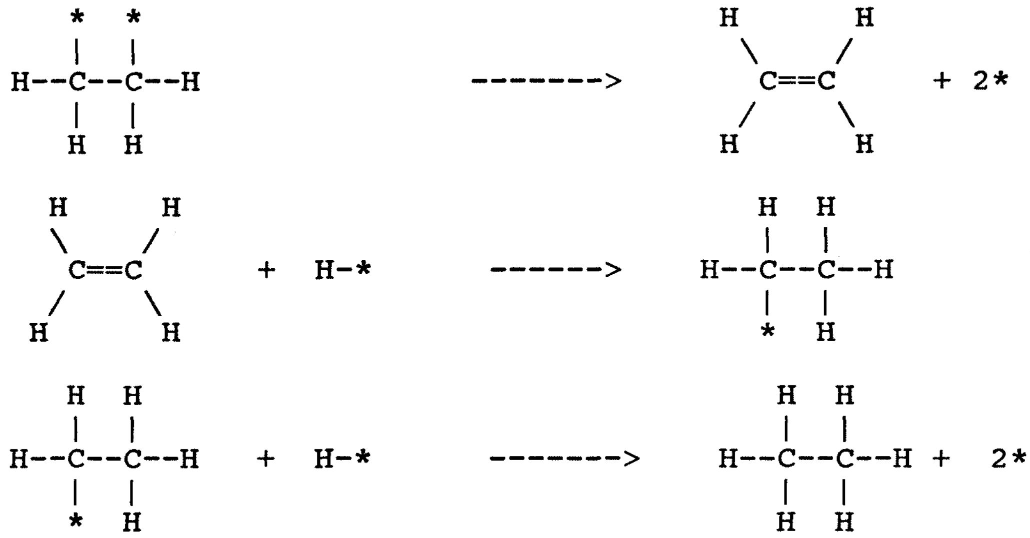
(II)

The intermediate(I) is then attacked by an adsorbed hydrogen on the catalyst surface to produce ethyl chloride.



$$\mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{*}{C}}{-}H} + \underset{*}{\mathrm{H}} \text{-------}> \mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + 2* \quad (A)$$

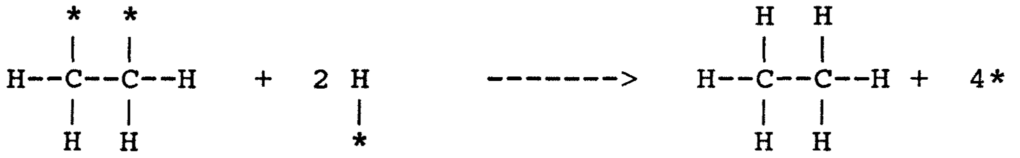
Multiple bond intermediates (II) on the surface have been considered by Sinfelt [17] as intermediates for the hydrogenolysis. Methane is a minor product in this study suggesting that (II) is not an important intermediate in this reaction. There are two possible reaction paths for intermediate (II): The first is production of ethylene.



(B)

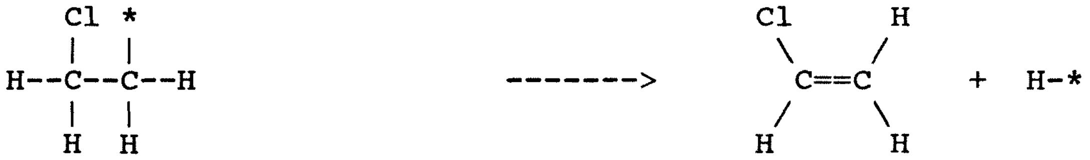
(C)

The second is the intermediate(II) reacts with two hydrogen atoms on the catalyst surface to produce ethane.



(D)

The reaction rate of vinyl chloride formation should be low because of the hydrogen atmosphere,



and vinyl chloride will be quickly converted to ethane because of a stable resonance intermediate being produced.

The secondary reaction of chloroethane to ethane was not observed in this study as indicated by the constant selectivity to chloroethane over the wide range of space residence time.

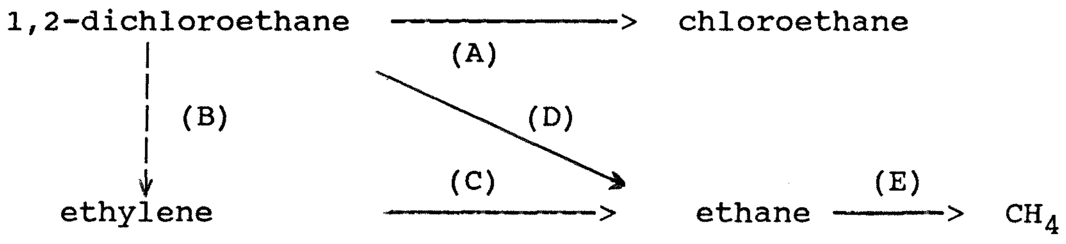
The formation of $CH_4$ could be due to the catalytic activity of Rhodium on the hydrogenolysis of ethane. In the analysis of ethane hydrogenolysis kinetics [5,17], the following sequence of reaction steps were proposed:

$$C_2H_6 \quad ==== \quad C_2H_5(ads) \quad + \quad H(ads)$$

$$C_2H_5(ads) \quad + \quad H(ads) \quad ==== \quad C_2H_x(ads) \quad + \quad a\ H_2 \qquad (E)$$

$$C_2H_x \quad + \quad H_2 \quad ---> \quad CH_y(ads) \quad + \quad CH_z(ads) ---> CH_4$$

Here the quantity a is equal to (6-x)/2. The initial chemisorption step involves the rupture of a carbon-hydrogen bond to form adsorbed $C_2H_5$, which undergoes further rapid dehydrogenation to the species $C_2H_x$, such that an equilibrium is effectively maintained between $C_2H_5$ and $C_2H_x$ on the surface. In this reaction scheme the species $C_2H_5$ and H are each singly bonded to the surface, whereas the species $C_2H_x$, $CH_y$ and $CH_z$ are in general multiply bonded. According to the above mechanisms, we propose the following reaction paths:



# CHAPTER 2: HYDRODECHLORINATION OF TRICHLOROETHYLENE OVER Rh/SiO$_2$ CATALYST

## 2.1 INTRODUCTION

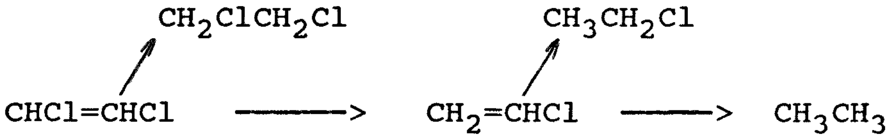
In the hydrogen atmosphere, chlorine in a chlorocarbon specie can be replaced by a hydrogen atom from $H_2$ in an exothemic reaction, where the chlorine is eliminated as HCl. Several catalytic liquid phase dehydrochlorination reactions on olefinic species have been reported [13,14,19,22]. The reactivity of olefinic chlorides relative to the number of halo atoms attached to each carbon influences the hydrogenolysis of carbon-halogen bond was reported by Witt et al. [12]. They showed that C-F hydrogenolysis took place more readily for compounds with no more than one F atom attached to each carbon and much less readily for compounds with two or more F atoms attached to the same carbon.

We have used a Rh/SiO$_2$ catalyst to facilitate the hydrodechlorination of olefinic compounds and to develop means to convert toxic chlorocarbons into HCl and hydrocarbons. We have also obtained insights on the reaction process and catalyst deactivation. We studied trichloroethylene which is widely used in metal degreasing and dry cleaning, applications accounting for 90% of the amount produced in the United States [18]. Discarding this spent solvent is a major problem. First to control trichloroethylene disposal was the city of Los Angeles in the historic Rule 66. More recently, other cities, and states have followed [39]. We report that a low and narrow temperature range is needed for this gas phase metal catalytic hydrodechlorination over rhodium catalysts in $H_2$ atmosphere.

## 2.2 LITERATURE SURVEY

Kammerer et al. [21] and Horner et al. [22] studied respectively the hydrogenative dehalogenation of aromatic and aliphatic halogen compounds in the presence of Raney nickel and alkali. They found that the primary and secondary monochloroalkanes did not react under their experimental conditions, but that a vinylic or allylic chloride would undergo hydrogenolysis as the double bond was reduced, and compounds with chlorine atoms adjacent (allylic) to a double or triple bond reacted readily.

It was found by Weiss et al. [20] that hydrodechlorinated vinyl chloride (cis- and trans-dichloroethylenes) reacted readily with $H_2$; they were simultaneously hydrogenated and hydrodechlorinated in the presence of platinum on alumina catalyst according to the following scheme.



$$\begin{tikzcd} & CH_2ClCH_2Cl & & CH_3CH_2Cl & \\ CHCl{=}CHCl \arrow[ur] \arrow[rr] & & CH_2{=}CHCl \arrow[ur] \arrow[rr] & & CH_3CH_3 \end{tikzcd}$$

They report that dichloroethylene hydrodechlorination is a consecutive reaction in which vinyl chloride is produced as a reactive intermediate. No isomerization of cis- and trans-dichloroethylenes was detected. Hydrogenation reactions are first order and hydrodechlorination reactions are half-order [20] with respect to hydrogen partial pressure; and at conversion levels below 1%, all reactions are zero order with respect to hydrogen partial pressures. The kinetic data were fitted to an Arrhenius curve showing an activation energy of 27.5 kcal/mole. The order of relative product mole fractions is: $C_2H_6$ > $C_2H_3Cl$ > $C_2H_5Cl$ > 1,2-$C_2H_4Cl_2$, which is in reverse relation to increasing boiling points. Since carbon-chlorine bond energies of aliphatic [BE($Csp^3$-Cl)=84.2 kcal/mole] and olefinic chlorides [BE($Csp^2$-Cl)=104.7 Kcal/mole] are opposite the observed trend, they do not offer a satisfactory approach to explain the large reactivity difference between the two species. Weiss proposes that a resonating olefinic chloride is stabilized as a tautomer (structures containing either -C=C- or $-C^{-}-C=Cl^{+}-$ bonds) on the catalyst surface, to account for production of both hydrogenation and hydrodechlorination products. He proposes that hydrogenation proceeds by molecular hydrogen addition to the carbon-carbon double of the tautomeric form; hydrodechlorination by proton addition to the carbon-chlorine double bond of the other form. From the fact that dichloroethane hydrodechlorinates at twice the rate of vinyl chloride, Weiss suggests that adsorption take place at both chloride atom sites rather than at a single atom.

In the study of the hydrogenation and hydrogenolysis of various $C_1$-$C_3$ fluorocarbons on palladium-on-carbon catalyst, some interesting results were found by Lacher et al. [23]. They are:

(1) The lower members of a homologous series are more difficult to hydrogenate than the members of higher molecular weight.

(2) The hydrogenolysis of C-Cl bonds occurs more readily than the hydrogenation of the C=C bonds, which in turn occurs more easily than the hydrogenolysis of the C-F bonds.

(3) The relative inertness of C-F bonds persists in fluoro-olefins as well as in fluoro-chloro-olefins.

On the other hand , Witt et al. [12] in work on heterogenous hydrogenolysis of several fluorocarbons on active carbon-supported Pd catalyst, observed that C=C hydrogenation is much faster than C-F hydrogenolysis. The principal support for this view is derived from observation that at low temperatures C=C hydrogenation is quantitative, while the C-F hydrogenolysis is still not observed. Their observed results [12] show that $CH_3CH_2F$ was a product via the catalytic hydrogenation and hydrogenolysis of CHF=CHF but not from the $CH_2=CF_2$. They proposed that when the carbon is chemisorbed on Pd surface it is compulsory for all the C-F bonds of this carbon to undergo hydrogenolysis, but that it is not necessary for the F atom on the $\beta$ carbon to be affected, the $\beta$ carbon in some adsorbed molecules may be standing in a vertical position away from the Pd surface. Witt et al. [12] also concluded that C-F hydrogenolysis took place more readily for compounds with one F atom attached to each carbon and less reaily for compounds with more than two F atoms attached to the same carbon. The apparent activation energy values for one F atom on each carbon $CH_2$=CHF, $C_2H_5F$, and CHF=CHF are in the range of 12-17 kcal/mole. With two or more fluorines on one of the carbon; $CH_2$=$CF_2$, $CH_3CHF_2$, and $CH_3CF_3$, Ea values are in the range of 20-26 Kcal/mole, as shown in Table 2-1.

Rhodium on alumina has been described as a good catalyst for the hydrogenation of vinylic or allylic halogen-substituted olefins to haloalkanes [14]. Ham and Coker, in this study, observed the superior selectivity of rhodium in the hydrogenation of 1,3-dichloropropene; the rhodium catalyst afforded higher yield of 1,3-dichloropropane and propyl chloride. The major products they observed [14] using palladium, platinum, and platium oxide catalysts were propane and hydrogen chloride. No hydrogenolysis of the chloroalkanes occured. In this study they also found that temperature had only a slight effect on the selectivity and the yield of chloroalkanes. The rate of hydrogenation, was affected by the catalyst support as follows: 5% rhodium on alumina powder > 5% rhodium on charcoal powder >> 0.5% rhodium on 1/8 in. alumina pellets. Table 2-2 shows their results hydrogenating several chloro-substituted olefins using 5% rhodium-on-alumina catalyst [14].

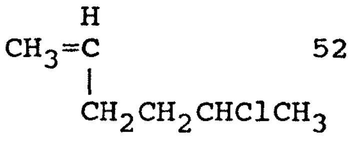
In the reaction of chlorobenzene with hydrogen over palladium catalyst supported on alumina [9], Yang and

Bozzelli pointed out the reaction occurred readily at low temperature (50-100°C) and with low activation energy (Ea=13 kcal/mole). The products were benzene and biphenyl. Comparsion of this catalytic reaction with thermal decomposition in the presence of hydrogen [24], one observes that it is difficult to get rid of chlorine from chlorobenzene, where the observed apparent activation is around 61 kcal/mole, and temperatures were in the range of 850 to 950°C.

Table 2-1 Apparent Ea and A Factor Values for the Complete C-F Hydrogenolysis Fluorocarbons[12]

| Compound | Slope(-Ea/R) | Apparent Ea (kcal/mol) | A factor ($sec^{-1}$) |
|---|---|---|---|
| $CH_2{=}CHF$ | -7685 | 15 | $3.7 * 10^7$ |
| $CH_3CH_2F$ | -6154 | 12 | $5.8 * 10^5$ |
| $CHF{=}CHF$ | -8774 | 17 | $7.3 * 10^7$ |
| $CH_2{=}CF_2$ | -10176 | 20 | $1.6 * 10^8$ |
| $CH_3CHF_2$ | -12964 | 26 | $2.4 * 10^{10}$ |
| $CH_3CF_3$ | -12854 | 26 | $9.6 * 10^8$ |

TABLE 2-2 Hydrogenation of Chloro-Substituted Olefins with 5% Rhodium-on-Alumina Catalyst[14]

| olefin | T(°C) | $H_2$ pressure (psi) | products | yield(%) |
|---|---|---|---|---|
| $ClCH{=}CHCH_3$ | 100 | 620 | $CH_3CH_2CH_2Cl$ | 42.4 |
| $CH_3{=}CHCH_2C$ | 100 | 580 | $CH_3CH_2CH_2Cl$ | 57.8 |
| $ClHC{=}CHCH_2Cl$ (cis) | 100 | 710 | $Cl(CH_2)_3Cl$ | 42.9 |
|  |  |  | $CH_2CH_2CH_2Cl$ | 31.4 |
| $ClHC{=}CHCH_2Cl$ (trans) | 100 | 680 | $Cl(CH_2)_3Cl$ | 47.0 |
|  |  |  | $CH_3CH_2CH_2Cl$ | 33.5 |
|  $CH_3{=}\overset{H}{\underset{CH_2CH_2CHClCH_3}{C}}$ | 52 | 500 | $CH_3(CH_2)_3CHClCH_3$ | 96.9 |

## 2.3 EXPERIMENTAL

### 2.3.1 Materials

All gases used for this study were obtained from Airco Inc., N.J. and had purities greater than 99.5%. Trichloroethylene was purchased from Fisher Scientific Company, and it was 99.9 % pure and purity was verified by GC analysis. The catalyst used in this study was prepared as mentioned in chapter 1.

### 2.3.2 Apparatus and Methods

The experimental set up of the system used for this study was that described in chapter 1. The reaction temperature range was 90-120°C. The reactant partial pressure was 20-170 torr. The reactor effluent stream was analyzed by FID GC after the system reached steady state (usually 4 to 5 hr) and then passed through a sample loop and then to a vent (exhausted hood). The product or feed gas sample was trapped in the loop by a nylon sampling valve, and then passed into a Perkin Elmer Model 900 Gas Chromatograph equipped with a flame ionization detector. Separation was effected by a 12 ft by 1/8 inch OD stainless steel tubular column packed with Porapak Q and operated from 50°C-190°C at a programming rate of 16°C/min. Nitrogen was used as a carrier gas. A GC/MS spectrometer was used to help identify the sample products through batch analysis. The hydrodechlorination reaction is extremely exothermic, and a differential reactor was used to avoid temperature gradients in the catalyst bed. Conversions were confined in the range 0.01 to 0.17.

## 2.4 RESULTS AND DISCUSSION

### 2.4.1 Arrhenius Plot and Apparent Activation Energy

It is found that this relatively low (90 - 120°C) temperature range was needed for the trichloethylene hydrodechlorination to achieve the same conversion that we observed for 1,2-dichloroethane.

The constant temperature at the inlet and outlet of the fixed catalyst bed and the small diameter of the reactor, allowed us to assume that there were no concentration or temperature gradients inside the reaction bed. Use of a rather inert support $SiO_2$ (see Table 1-6) to dilute a catalyst also permitted reducing these effects [2].

The rate contants and Arrhenius plots for trichloroethylene hydrodechlorination are shown in Figure 2-1, 2-2 respectively, and the apparent activation energy is 13.9 Kcal/mole.

Table 2-3 Kinetic Parameters for Reaction Trichloroethylene with Hydrogen over Rhodium on Silica Gel Catalyst

| T(°C) | k(liter/kg-hr) |
|---|---|
| 92 | 2996 |
| 102 | 6461 |
| 112 | 8278 |
| 122 | 13946 |

Figure 2-1

Kinetic Reaction Rate Constant (K)

Trichloroethylene + H2

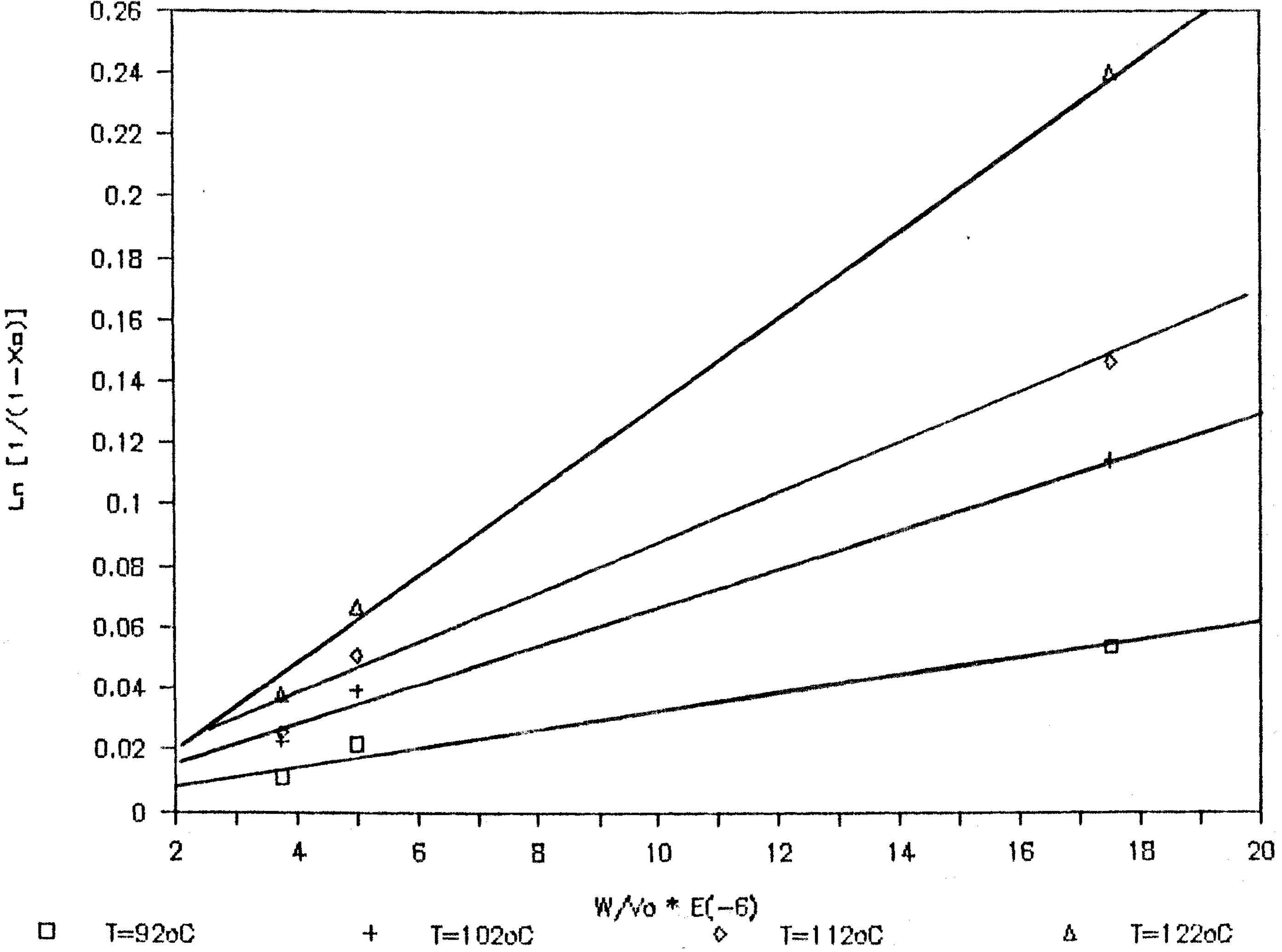
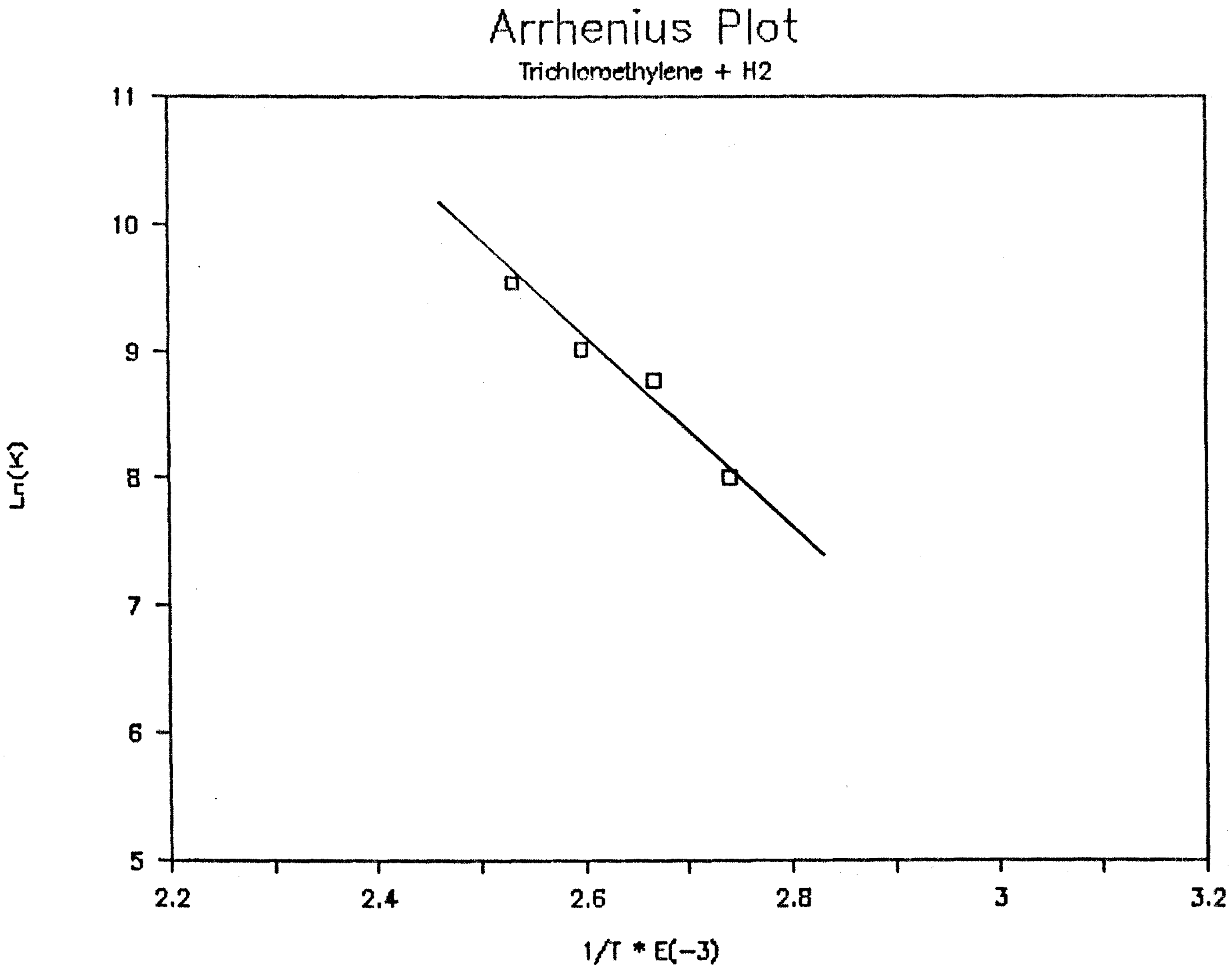


Figure 2-2


Arrhenius Plot
Trichloroethylene + H2
Ln(K)
11
10
9
8
7
6
5
2.2
2.4
2.6
2.8
3
3.2
1/T * E(-3)

### 2.4.2 Some Effects on Products Distribution

#### 2.4.2.1 Temperature Effect

Figure 2-3 and Table 2-4 show the effect of temperature on the major products distribution. $C_1$ to $C_4$ hydrocarbon formation increases as reaction temperature increases, while the partial hydrogenolysis products ($C_2H_3Cl$, $C_2H_2Cl_2$, $C_2H_5Cl$ and $C_2H_4Cl_2$) selectivity decreases as the temperature increases. From the products distribution, it shows that $Rh/SiO_2$ catalyst undergoes the hydrodechlorination (or hydrogenolysis) reaction more easily than the hydrogenation reaction, since no measurable trichloroethane was detected in the study. The inference is that the reagent species are chemisorbed on the Rh surface, and will remove until all the C-Cl bonds undergo hydrogenolysis. It is, in addition, not necessary for all the Cl atoms on the $\alpha$ carbon to be removed from the catalyst surface at the same time (i.e. as HCl). This is a difference in the hydrodechlorination on $Rh/SiO_2$ catalyst as compared to data reported by Witt et al. [12] on Pd catalyst. At higher reaction temperatures more hydrodechlorination (or hydrogenolysis) products are produced.

#### 2.4.2.2 Residence Time Effect

Tables 2-5 and Figures 2-4-1 to 2-4-4 show that total conversion increases with residence time at the different temperatures. The selectivity to ethane also decreases as residence time decreases with selectivity to $C_2H_2Cl_2$,

$C_2H_5Cl$, and $C_2H_4Cl_2$ decreasing as residence time increases. This suggests that $C_2H_2Cl_2$, $C_2H_5Cl$ and $C_2H_4Cl_2$ are secondary products, where at the longer contact time the initial hydrogenolysis products may undergo further reaction to ethane.

### 2.4.2.3 Reactant Partial Pressure

Table 2-6 shows that at constant temperature, higher reactant partial pressure yields lower conversion. The major products distribution is shown in Figure 2-5. At higher reactant concentrations less $C_2H_6$ and more $C_2H_2Cl_2$ is produced. This implies that the trichloroethylene hydrodechlorination undergoes consecutive reactions on the $Rh/SiO_2$. A higher hydrogen pressure will provide more secondary reaction to the final product $C_2H_6$. $CH_4$ formation may be ascribed to the hydrogenolysis activity of ethane on rhodium catalyst (d character) as discussed in chapter 1, while $C_4$ formation may occur via dimerization of intermediate product, ethylene, as dicussed in Chapter 3.

### 2.4.2.4 Regeneration Effect on Conversion

Table 3-1 shows the particle size of Rh before and after reaction. Sintering does not occur to a significant extent during reaction. The deactivation appears to result from poisoning, as shown by an increase in the Cl content on the catalyst, and fouling as shown by the coke formation on the upstream particules. Figure 2-6 shows that the catalyst deactivates rapidly during the first few minutes then reaches steady state. Regeneration only affects the initial rate, i.e. the steady state reaction rate is not affected by regeneration.

Table 2-4 Temperature Effect on Trichloroethylene Hydrodechlorination Selectivity

| Temperature ($^oC$) | 92 | 102 | 112 | 122 |
|---|---|---|---|---|
| Reaction rate (mole/kg/hr) | 3.36 | 7.03 | 9.17 | 12.8 |
| Total conversion(%) | 4.50 | 9.43 | 12.30 | 17.18 |
| Selectivity(%) : | | | | |
| $CH_4$ | 1.91 | 2.31 | 3.04 | 2.20 |
| $C_2H$ | 0 | 0 | 0.33 | 0.40 |
| $C_2H_6$ | 73.5 | 74.32 | 75.20 | 80.29 |
| $C_3$ | 1.02 | 1.48 | 1.79 | 1.12 |
| $C_2H_3Cl$ | 1.68 | 1.29 | 1.00 | 1.05 |
| $C_4$ | 3.38 | 3.15 | 4.28 | 5.39 |
| $C_2H_2Cl_2$* | 5.58 | 5.32 | 4.38 | 3.90 |
| $C_2H_5Cl$ | 8.52 | 7.53 | 6.98 | 3.69 |
| $C_2H_4Cl_2$ | 4.32 | 5.30 | 3.00 | 1.95 |

* mixture of 1,1-dichloethylene and 1,2-dichloethylene

Figure 2-3

Temperature Effect on Selectivity

Trichloroethylene + H2

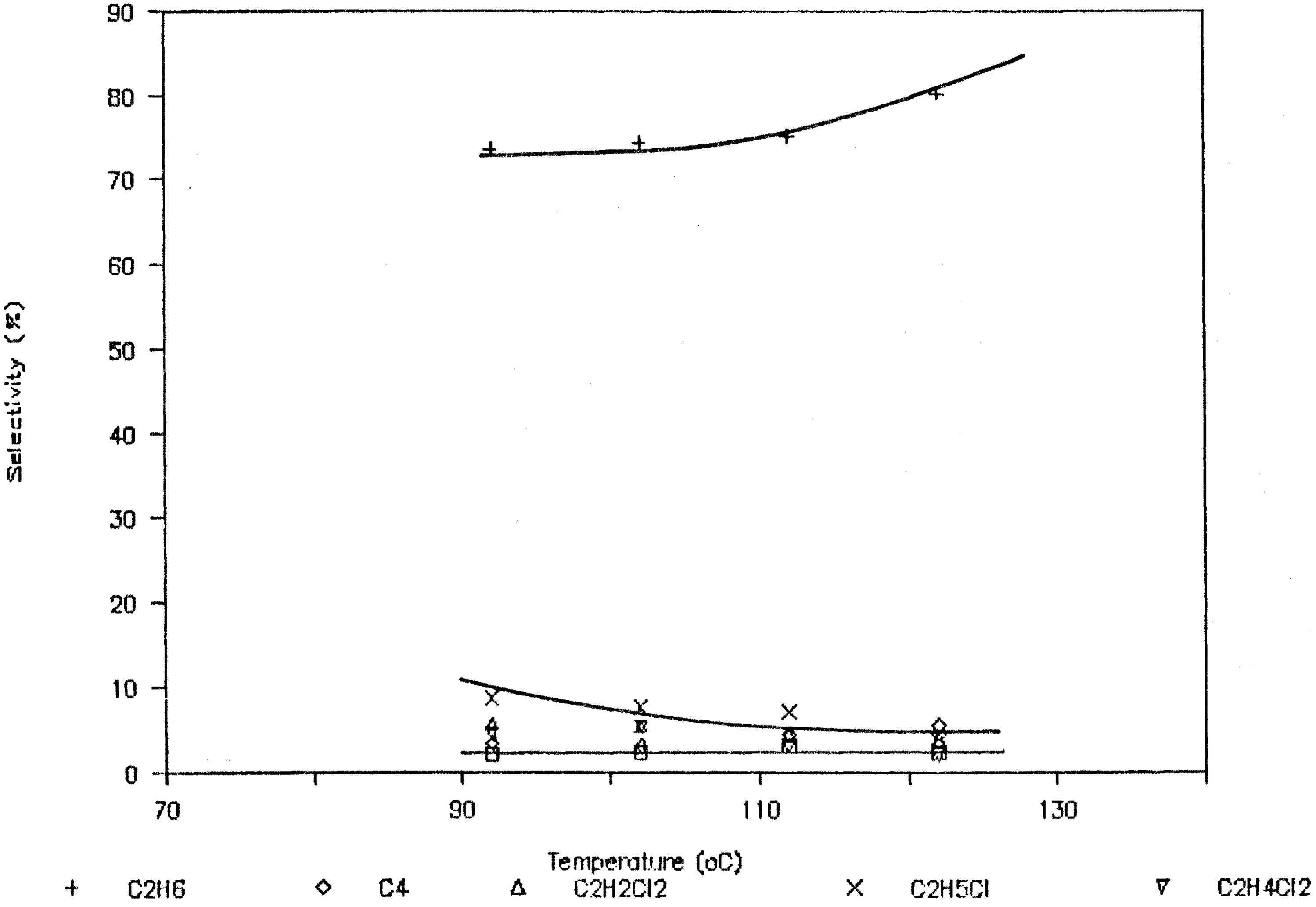


Table 2-5 Selectivity of Hydrodechlorination of Trichloroethylene at Different Temperature and Residence Times

T=92°C

| $W/V_o$ | 1.6*E-5 | 5.95*E-6 | 4.85*E-6 |
|---|---|---|---|
| Reaction rate (mole/kg/hr) | 3.36 | 3.06 | 2.79 |
| Total conversion(%) | 4.50 | 1.87 | 1.17 |
| Selectivity(%) : | | | |
| $CH_4$ | 1.91 | 1.81 | 1.21 |
| $C_2H_4$ | 0 | 0 | 0 |
| $C_2H_6$ | 73.59 | 70.81 | 63.73 |
| $C_3$ | 1.02 | 1.12 | 0.66 |
| $C_2H_3Cl$ | 1.68 | 1.30 | 1.45 |
| $C_4$ | 3.38 | 3.48 | 3.15 |
| $C_2H_5Cl$ | 8.52 | 8.58 | 13.45 |
| $C_2H_2Cl_2$* | 5.58 | 7.20 | 10.80 |
| $C_2H_4Cl_2$ | 4.32 | 5.70 | 5.55 |

* : 1,1-dichloroethylene and 1,2-dichloroethylene
W : weight of catalyst, 1.5*E(-4) kg
$V_o$: volume flow rate, liter/hr

Figure 2-4-1

Residence Time Effect on Selectivity

Trichloroethylene + H2 (T=92oC)

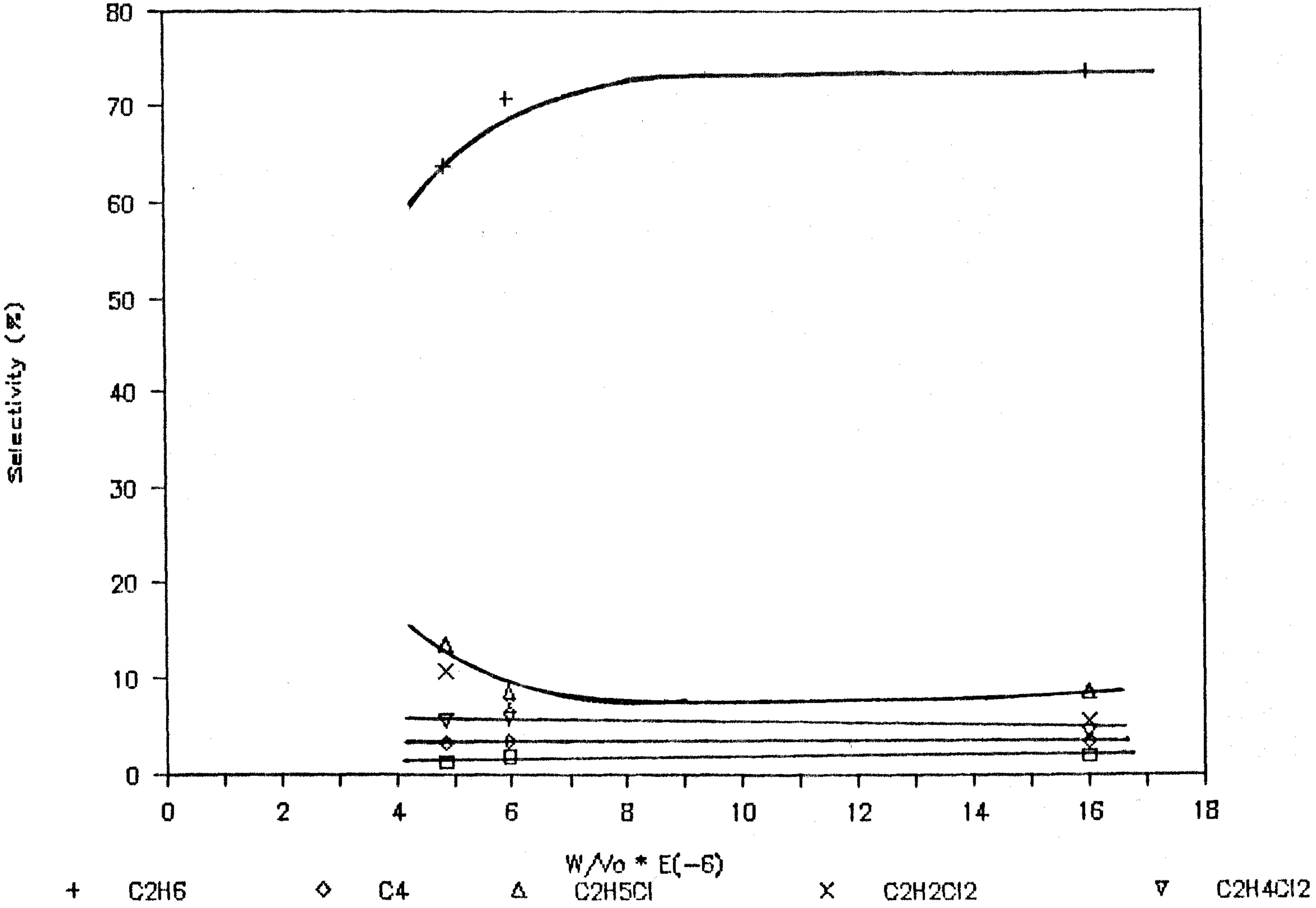


Table 2-5 (a)

T=102$^oC$

| $W/V_o$ | 1.6*E-5 | 5.95*E-6 | 4.85*E-6 |
|---|---|---|---|
| Reaction rate (mole/kg/hr) | 7.03 | 6.78 | 5.04 |
| Total conversion(%) | 9.43 | 3.37 | 1.93 |
| Selectivity(%) : | | | |
| $CH_4$ | 1.91 | 1.93 | 1.60 |
| $C_2H_4$ | 0 | 0 | 0 |
| $C_2H_6$ | 74.32 | 71.05 | 64.91 |
| $C_3$ | 1.48 | 1.10 | 1.45 |
| $C_2H_3Cl$ | 1.29 | 1.60 | 1.00 |
| $C_4$ | 3.15 | 3.34 | 3.66 |
| $C_2H_5Cl$ | 7.53 | 10.15 | 11.25 |
| $C_2H_2Cl_2$ | 5.32 | 5.33 | 10.03 |
| $C_2H_4Cl_2$ | 5.00 | 5.50 | 6.16 |

Figure 2-4-2

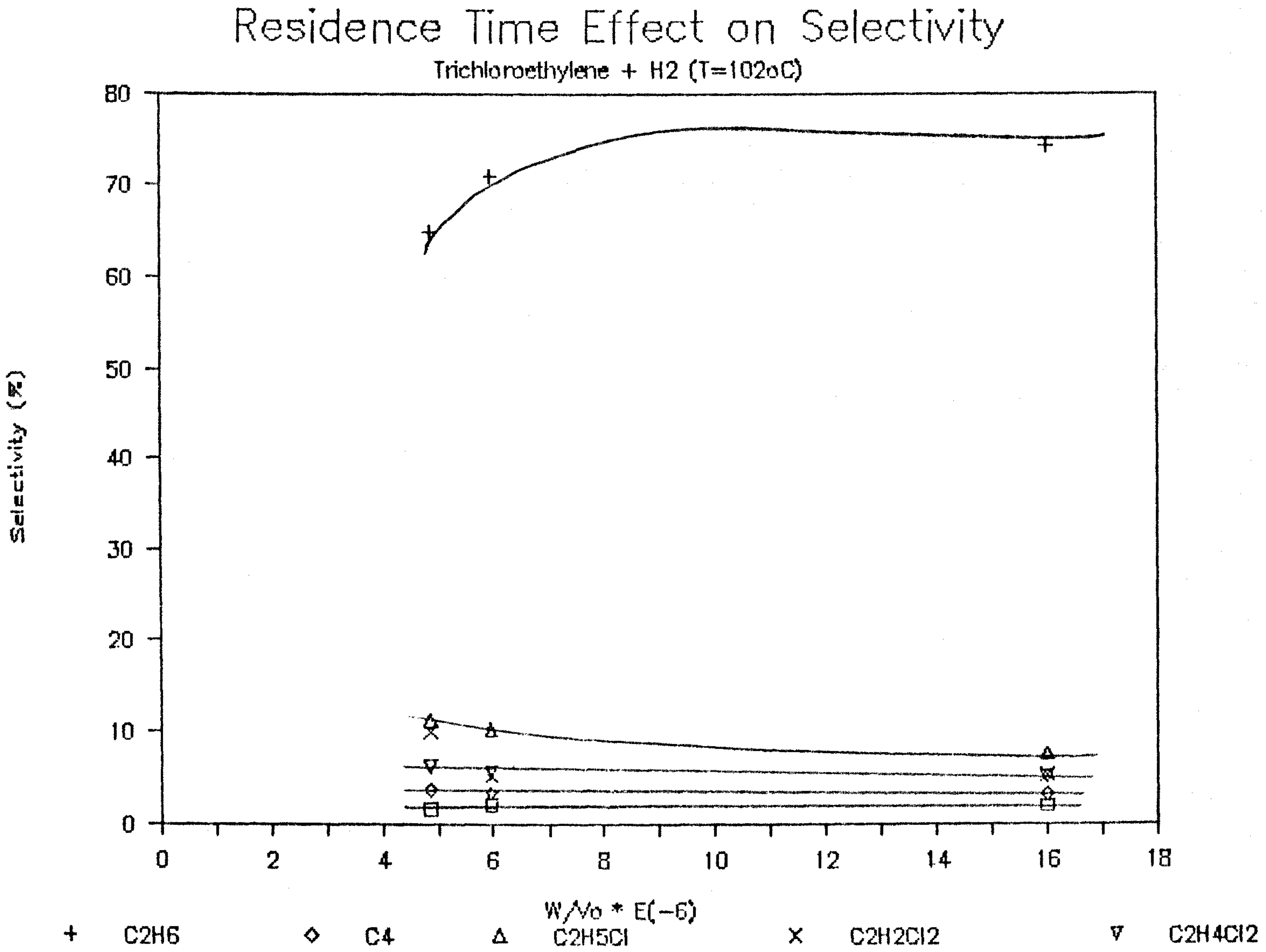
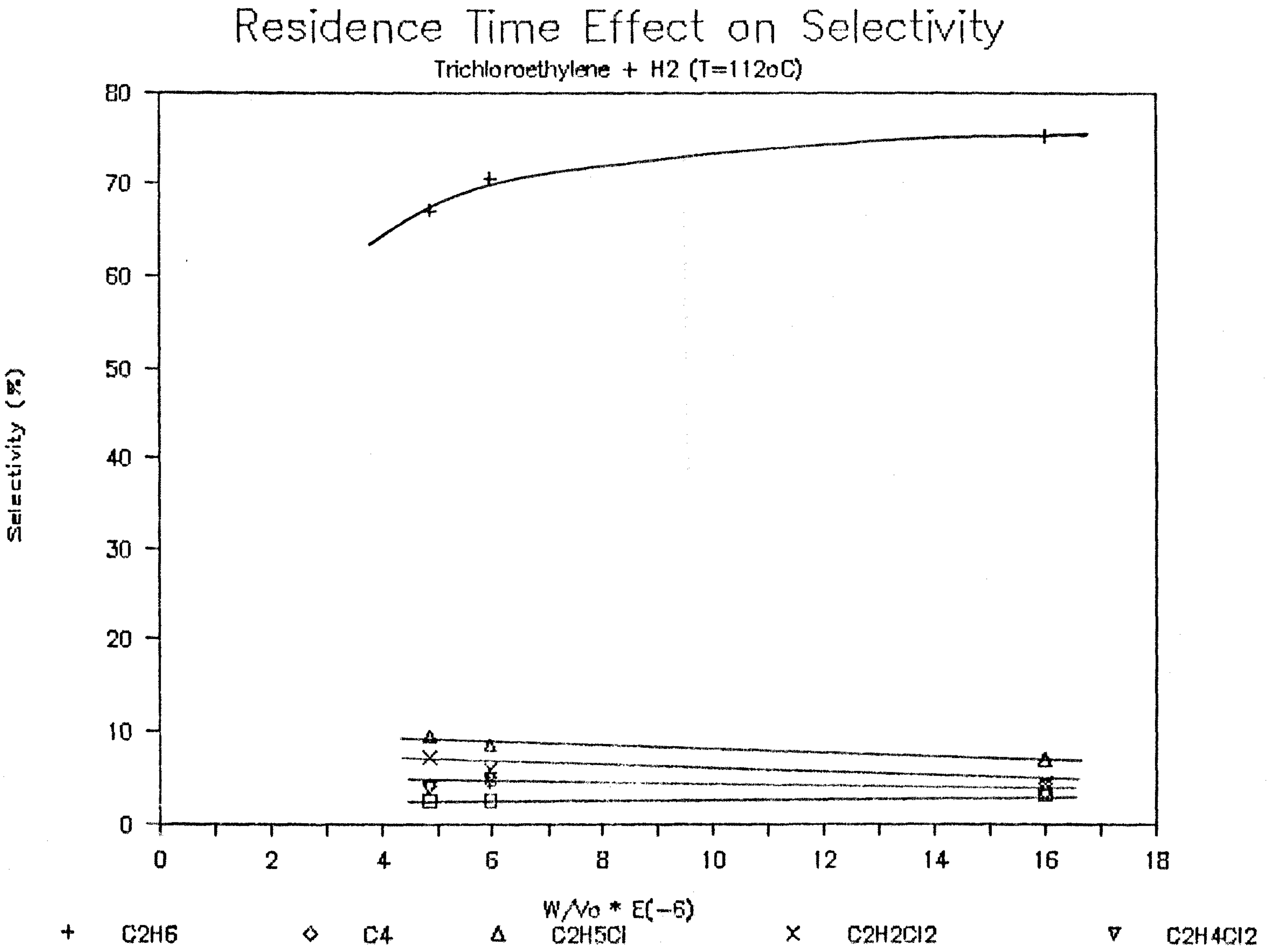

Residence Time Effect on Selectivity
Trichloroethylene + H2 (T=102oC)
Selectivity (%)
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
W/Vo * E(-6)
+ C2H6
◇ C4
△ C2H5Cl
× C2H2Cl2
▽ C2H4Cl2

Table 2-5 (b)

T=112°C

| $W/V_o$ | 1.6*E-5 | 5.95*E-6 | 4.85*E-6 |
|---|---|---|---|
| Reaction rate (mole/kg/hr) | 9.17 | 7.30 | 4.56 |
| Total conversion(%) | 12.30 | 3.63 | 1.75 |
| Selectivity(%) : | | | |
| $CH_4$ | 3.04 | 2.50 | 2.57 |
| $C_2H_4$ | 0.33 | 0.69 | 3.00 |
| $C_2H_6$ | 75.20 | 70.67 | 67.16 |
| $C_3$ | 1.79 | 1.48 | 1.49 |
| $C_2H_3Cl$ | 1.00 | 1.2 | 1.15 |
| $C_4$ | 4.28 | 4.46 | 4.16 |
| $C_2H_5Cl$ | 6.98 | 8.48 | 9.46 |
| $C_2H_2Cl_2$ | 4.33 | 5.72 | 7.16 |
| $C_2H_4Cl_2$ | 3.05 | 4.80 | 3.85 |

Figure 2-4-3

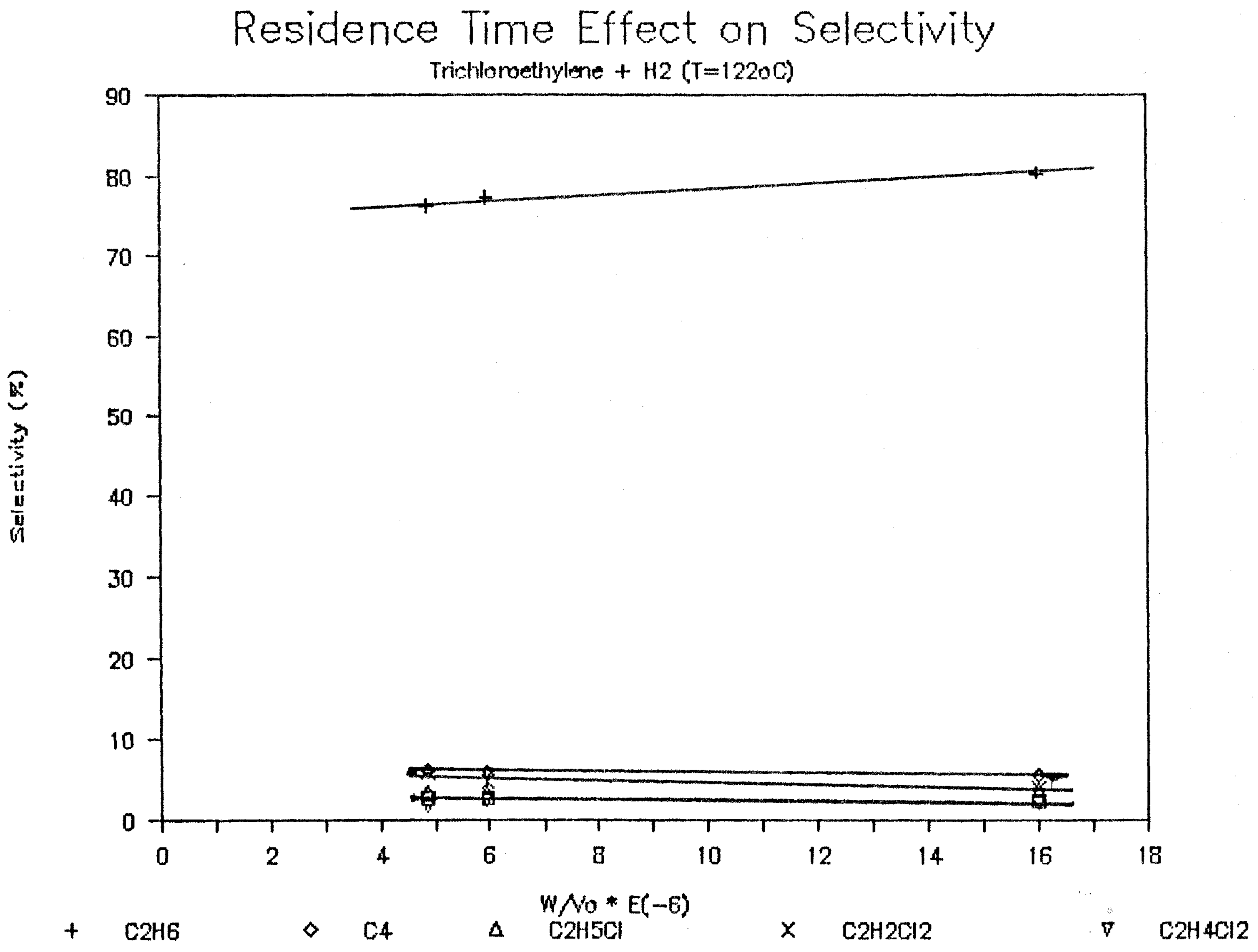

Residence Time Effect on Selectivity
Trichloroethylene + H2 (T=112oC)
Selectivity (%)
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10
12
14
16
18
W/Vo * E(-6)
+ C2H6
◇ C4
△ C2H5Cl
× C2H2Cl2
▽ C2H4Cl2

### Table 2-5 (c)

T=122°C

| $W/V_o$ | 1.6*E-5 | 5.95*E-6 | 4.85*E-6 |
|---|---|---|---|
| Reaction rate (mole/kg/hr) | 12.80 | 11.64 | 8.77 |
| Total conversion(%) | 17.18 | 5.80 | 3.36 |
| Selectivity(%) | | | |
| $CH_4$ | 2.20 | 2.48 | 2.53 |
| $C_2H_4$ | 0.40 | 0.74 | 1.61 |
| $C_2H_6$ | 80.29 | 77.34 | 76.25 |
| $C_3$ | 1.13 | 1.93 | 1.94 |
| $C_2H_3Cl$ | 1.05 | 2.30 | 1.60 |
| $C_4$ | 5.39 | 5.85 | 5.98 |
| $C_2H_5Cl$ | 3.69 | 3.35 | 3.32 |
| $C_2H_2Cl_2$ | 3.90 | 4.55 | 5.57 |
| $C_2H_4Cl_2$ | 1.95 | 2.30 | 1.60 |

Figure 2-4-4



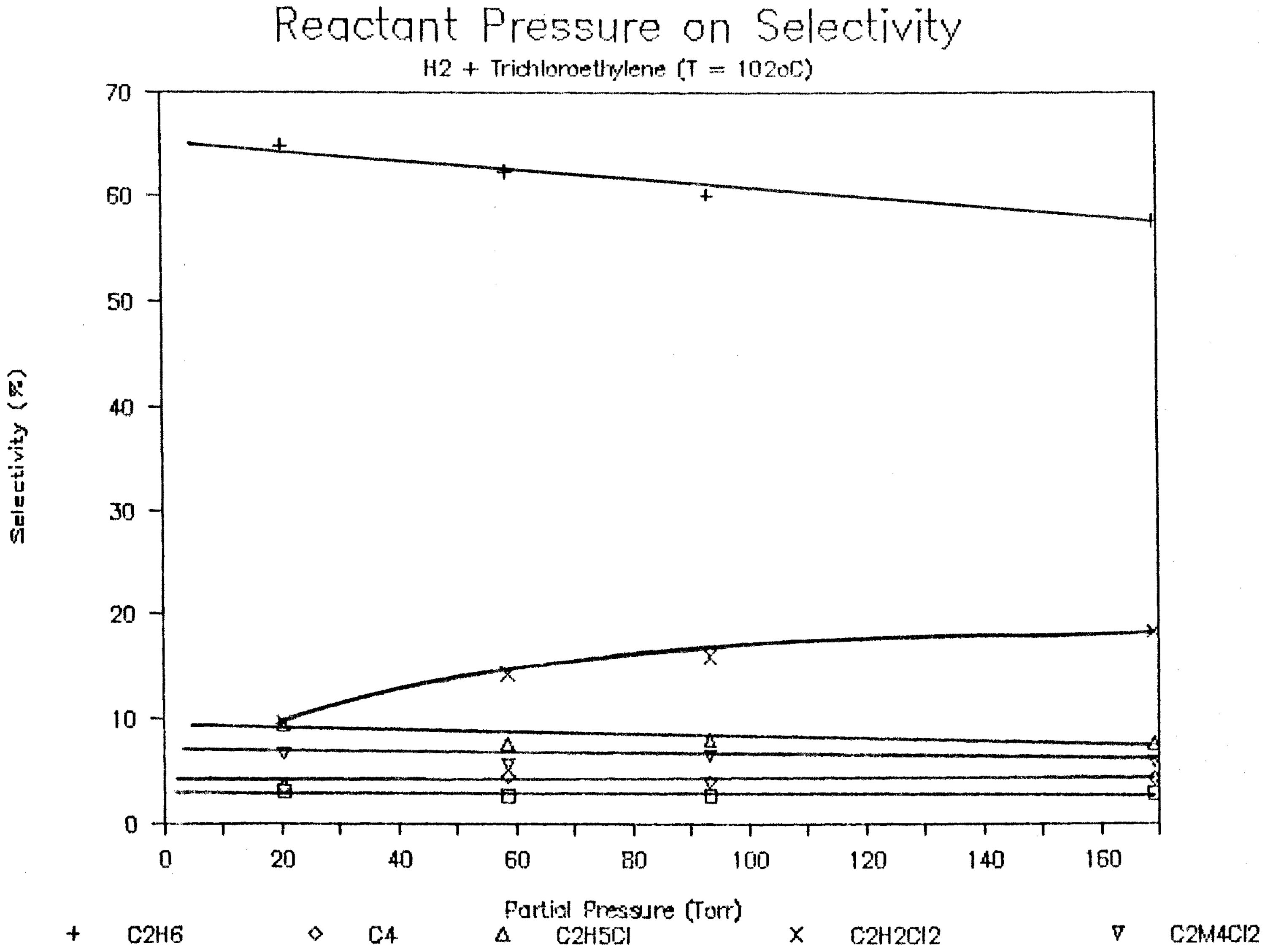
Residence Time Effect on Selectivity
Trichloroethylene + H2 (T=122oC)
Selectivity (%)
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
W/Vo * E(-6)
+ C2H6
◇ C4
△ C2H5Cl
× C2H2Cl2
▽ C2H4Cl2

## Table 2-6 Effect of Reactant Partial Pressure on Selectivity

| Temperature (°C) | 102 | | | |
|---|---|---|---|---|
| Reactant Partial Pressure (Torr) | 20.45 | 58.62 | 92.40 | 169.18 |
| Reaction Rate (mole/kg/hr) | 3.77 | 2.26 | 2.07 | 1.35 |
| Total Conversion(%) | 5.06 | 3.04 | 2.77 | 1.81 |
| Selectivity(%) : | | | | |
| $CH_4$ | 2.94 | 2.57 | 2.53 | 2.82 |
| $C_2H_4$ | 0.17 | 0.30 | 0.18 | 0.50 |
| $C_2H_6$ | 64.87 | 62.34 | 60.21 | 57.62 |
| $C_3$ | 1.78 | 1.97 | 2.13 | 2.04 |
| $C_2H_3Cl$ | 1.24 | 1.15 | 0.61 | 1.16 |
| $C_4$ | 3.48 | 4.41 | 3.93 | 4.20 |
| $C_2H_5Cl$ | 9.37 | 7.47 | 8.0 | 7.51 |
| $C_2H_2Cl_2$* | 9.60 | 14.25 | 16.02 | 18.34 |
| $C_2H_4Cl_2$ (1,2) | 6.55 | 5.54 | 6.39 | 5.80 |

* products of 1,1-dichloroethylene and 1,2-dichloroethylene (cis- and trans-)

Figure 2-5

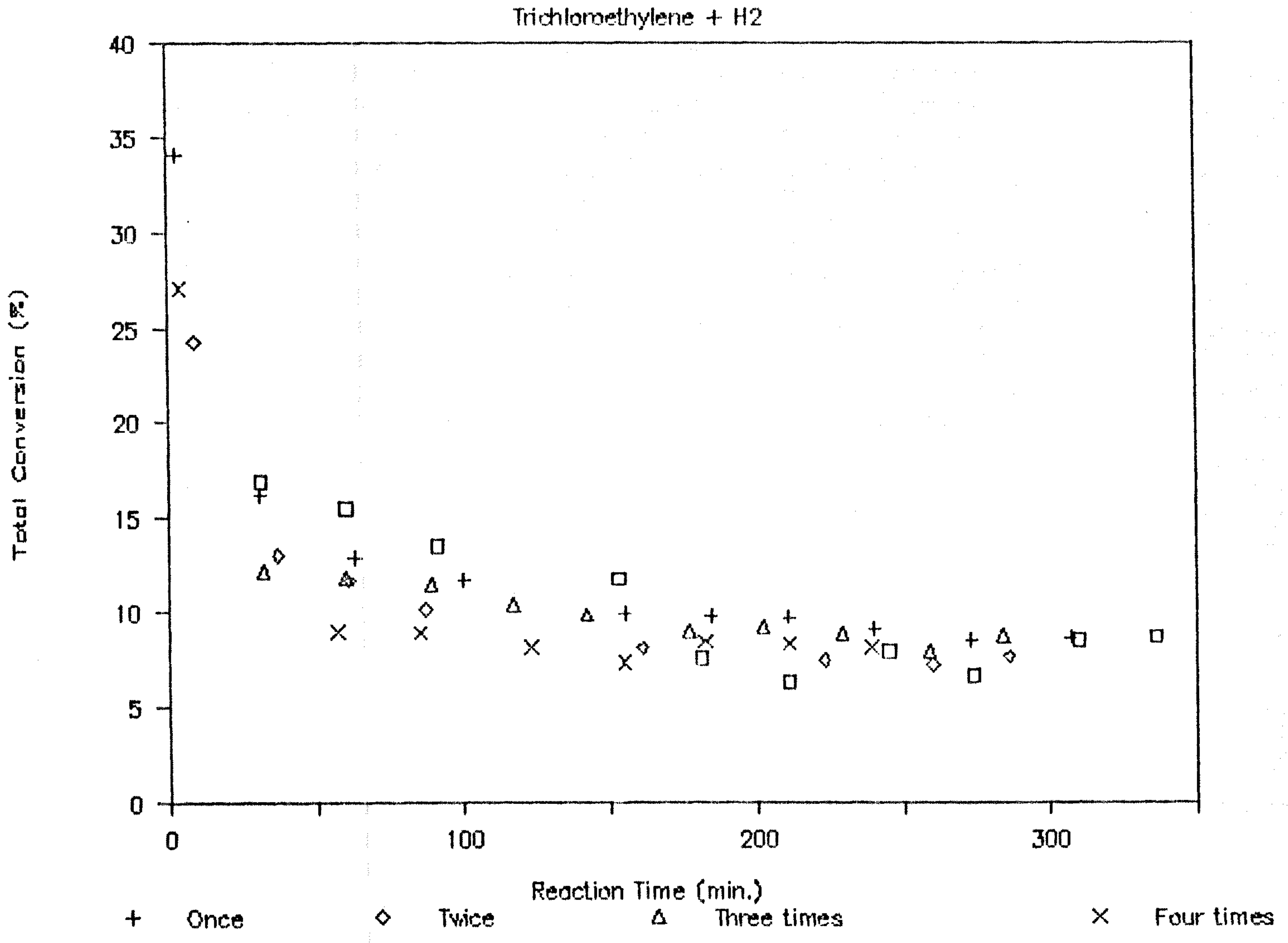


Reactant Pressure on Selectivity

H2 + Trichloroethylene (T = 102oC)

Figure 2-6

Regeneration Effect on Conversion



# CHAPTER 3 : ETHYLENE HYDROGENATION ON DEACTIVATED $Rh/SiO_2$ CATALYSTS

## 3.1 INTRODUCTION

The activity of most catalysts declines sharply with initial use and then reaches a state where the decrease is slower with time. The selectivity associated with this activity change may improve or become worse. General reviews of catalyst deactivation given by Butt [25] and by Levenspiel [26] indicate a better method to characterize the catalyst deactivation. Basically, three kinds of deactivation may occur: (1) sintering or thermal deactivation of the catalyst; (2) poisoning; and (3) fouling.

Sintering is an irreversible physical process associated with loss in area of the catalyst which occurs when the catalyst is operated above the normal range of temperature. For a high surface area support material such as $SiO_2$, the various forms of $Al_2O_3$ or silica-alumina cracking catalysts, operation at high temperatures will cause a loss of specific surface plus associated change in the pore structure, giving a corrresponding loss in activity. For the metal/support type catalyst such as Ni, Pd, and Rh supported on alumina or silica, sintering can occur not only by reduction of the support area but by a coalesence or loss of dispersion of the metal crystallites. This loss of area by the active constituent in the catalyst causes a drop in activity.

The deactivation of catalyst by poisoning is due to small amounts of material, specific to a given catalyst and associated with the adsorption of the poison on active sites in the catalyst and reduced activity.

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. The most typical fouling process is carbonaceous deposit or coke formation. In many processes fouling, especially coking, will occur simultaneously with poisoning and possibly with some sintering of the catalyst.

A study of the ethylene hydrogenation on fresh and contaminated (after reaction with 1,1-dichloroethane) Rh-$SiO_2$ catalyst showed the deactived Rh-$SiO_2$ catalysts had a negative effect on the product selectivity.

## 3.2 LITERATURE SURVEY

Halogen-containing compounds have been studied for their effect on Raney nickel catalyst by Pattison and Degering [27]. They first added a specific amount of anhydrous hydrogen chloride to a Raney nickel catalyzed reduction of styrene. They found that a sharp break in the hydrogen uptake curve, and pointed out that Taylor [28] had already shown that some catalysts have more than one active surface. They assumed Raney nickel has at least two types of active surface, and that HCl is preferentially attached to the most active one, thus causing inhibition. They also extended their study [27] to the effect of organic halides including alkyl, aryl halides, some polychlorides, and a few miscellaneous chloro-compounds on the reduction of styrene. Among the alkyl chlorides, there was a relationship between chain length and poisoning, the shortest chain having the greatest inhibiting power. They suggested that the poisoning power of these compounds is due to the reactive chlorine that each contains. Freifelder [18] suggested that it might be more to the point to attribute poisoning to the release of hydrogen halide. This could explain why short chain alkyl chlorides were stronger inhibitors than the long chain alkyl chlorides which are dehalogenated less readily. Figure 3-1 illustrates results of their data, where it is demonstrated that HCl inhibits the reaction more strongly than alkylhalides by comparing the inhibition of each. The rate of the ethylene hydrogenation over evaporated metal films of the transition elements has also been studied [29,30,31,32]. Beeck [29] concluded the rate is strongly depending on the heat of adsorption of ethylene. The greater the d-character, the lower are the heats of adsorption, the less strongly the atom is bound on the surface, and the higher the rates. The results of his investigation showed rhodium with the highest activity. It is of particular interest that the rate over Rh (apparent activation energy 10.7 Kcal) was faster than over nickel and more active than tungsten. In the study of hydrogen reaction with pre-adsorbed ethylene on nickel at $23^{o}C$, 20 % of the adsorbed residue can be reacted off in one hour and the product is about 90 % saturated polymers ($C_4$ to $C_8$ and higher) plus 10 % ethane. Similar experiments with rhodium yield 60% of the adsorbate in one minute and nearly 100% with long contact times, but the major product is ethane, with only a few percent polymer.

Campbell and Kemball [7] investigated the gas-phase dehalogenation of ethyl chloride and ethyl bromide on evaporated metal films of palladium, platium, and nickel and to a lesser extent on those of iron, tungsten, and rhodium. The major products are ethane and hydrogen halide but ethylene was also formed over nickel and iron catalysts. Fe and Ni catalyzed the decomposition of the ethyl halides only at higher temperature. The reduction in rate for ethyl chloride reaction by adding hydrogen chloride was studied on palladium [7]. Campbell and Kemball pointed out the inhibition was substantial and approximately proportional to the pressure of the hydrogen chloride. They reasoned that the reduction in rate was due to hydrogen halide except when nickel was used. In the reactions the high percentages of ethylene formed over Ni provide evidence that the secondary reaction: $C_2H_4 + H_2 \text{--->} C_2H_6$ is strongly poisoned by either the ethyl halides or the hydrogen halides. In their other study [7] of hydrogenation of ethylene over nickel they also reported the reaction was strongly inhibited by hydrogen chloride, where the reaction was extremely rapid at much lower temperature in the absence of added hydrogen chloride.

In the hydrodechlorination of 1,2-Dichloroethane over palladium on alumina catalyst, Yang and Bozzelli [9] indicated that the catalyst underwent sintering and some fraction of the surface was covered by carbonaceous material. Regeneration of the catalyst for 12 hr (after reaction proceeded 36.8 hr) returned the activity to only 56% of initial value.

In a model reaction, hydrodechlorination of cis- and trans- dichloethylene on 0.5% Pt peripherally deposited on alumina catalyst, Gambhir and Weiss [20,33] observed the depletion of reactants on a catalytic surface. The observation of depletion of the amounts of reactants on the surface as a function of conversion at constant partial pressure is a consequence of a required surface diffusion process from the inert alumina surface to the active Pt sites, and product species ($C_2H_6$, $C_2H_3Cl$, $C_2H_5Cl$, and 1-2 $C_2H_4Cl_2$) on the catalyst were found to be present in only minute quantities. The quantities of each product on the catalyst were proportional to increasing boiling points.

The relation between catalytic properties and the microstructures of a metal has been studied by several research groups. The effect of particle size (or dispersion) on the specific activity of ethane hydrogenolysis for a series of $Rh/SiO_2$ catalysts has been reported by Yates and Sinfelt as mentioned in chapter 1. Martin and Dalmon [34] studied ethane hydrogenolysis over silica-supported nickel catalysts and showed that increasing nickel particle size by thermal sintering in hydrogen leads to a large decrease of specific activity. A maximum in specific activity was observed with an average Ni particle size around 50$^{o}$A.

Based on the data presented in the study of sintering of supported metal catalysts, Wanke and Flynn [35] reported the most important factors affecting the sintering phenomenon are temperature, and atmosphere. The nature of the support and the degree of metal loading appear to be of secondary importance. They mentioned that the loss of dispersion increases with increasing temperature for a non-oxygen-containing sintering atmosphere. Redispersion in an oxygen-containing atmosphere and temperature range of 400 to 620 $^{o}$C was also observed. They [35] also did a stability comparison on the resistance of the various metals toward sintering in non-oxidizing atmospheres, and showed Ni least stable: i.e. Ni < Pd < Pt < Rh.

In a study on structure effects in ethane hydrogenolysis by $H_2$ chemisorption with $Rh/SiO_2$ catalysts, Lee, C. and Schmidt, L. D. [36] examined effects of repeated oxidation-reduction on the morphology, surface composition, metal surface area, and kinetics. They showed, using TEM, that particle morphology is dramatically changed by different gas environments, and this is likely important in determining the performance of a catalyst. They reported that solid-state redispersion causes the particle surface to be very irregular upon low-temperature reduction, but high-temperature reduction transforms the morphology back to the initial shape. Their hydrogen uptake results showed some sintering upon higher temperature reduction, as the temperature of $H_2$ treatment increased the $CH_4$ formation rate decreased dramatically, and Rh metal redispersed under the oxidation-reduction atmosphere.

Figure 3-1

Hydrogen Chloride Effect on the Hydrogen Uptake [8]

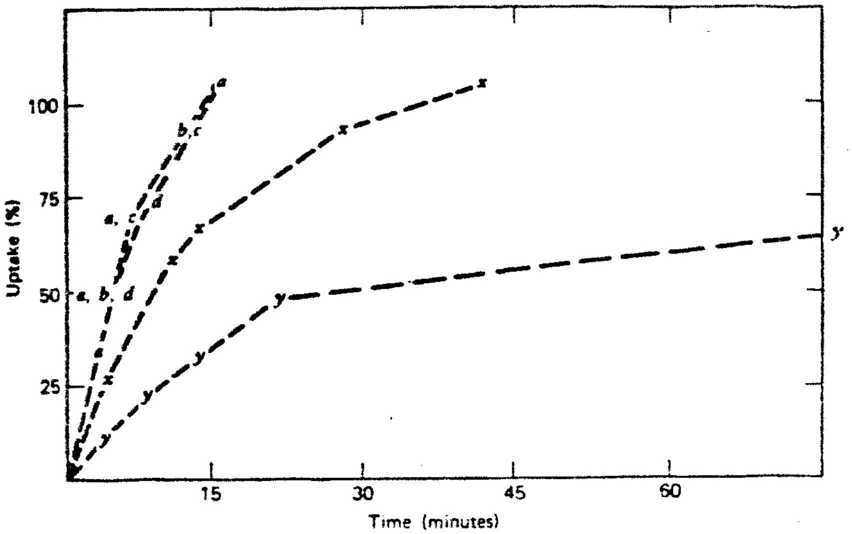


Figure 3-1-1
(a) Hydrogenation of cyclohexene in abs EtOH with PtO2
(b) with 0.025 mole propyl chloride
(c) with 0.05 mole propyl chloride
(d) with 0.2 mole propyl chloride
(x) with 0.125 mole dry HCl
(y) with 0.25 mole dry HCl

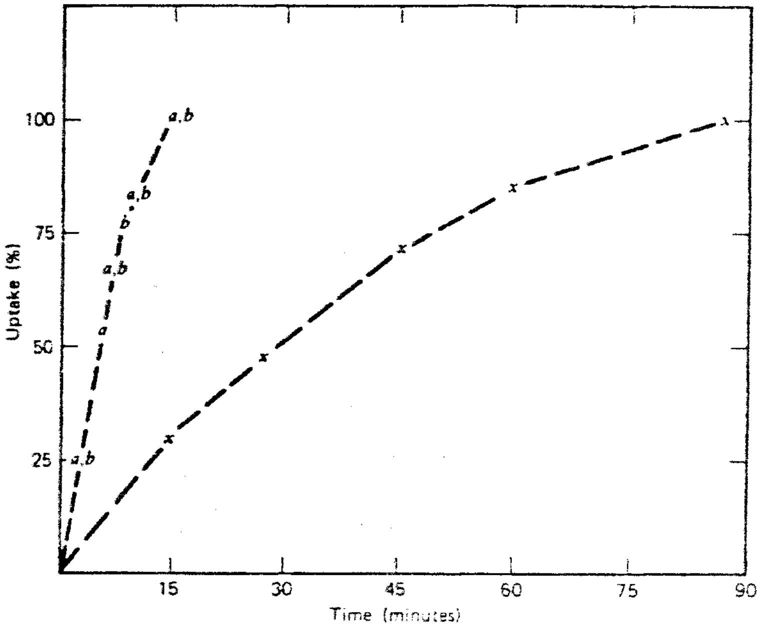


Figure 3-1-2
(a) Hydrogenation of cyclohexene in abs EtOH with 5% Pd on C
(b) with 0.15 mole propyl chloride
(x) with 0.25 mole dry HCl

## 3.3 EXPERIMENTAL

**Apparatus and methods:** The general apparatus and reaction procedure have been described in chapters 1 and 2. The principal feature in this study is that the catalyst was deactivated first. The effect of the deactivation on the catalyst selectivity was investigated.

**Materials:** The preparation of 3% Rh silica catalyst has been described in chapters 1 and 2, and the deactivated catalyst used in this study was that used in reaction of hydrodechlorination of 1,1-dichloroethane. Cylinder ethylene from Matheson Gas Products (purity 99.9%) was used as one of the reactant streams.

## 3.4 RESULTS AND DISCUSSION

Table 3-1 shows that the particle size of Rh both before and after reaction is around 50-62 $A^o$, indicating that sintering does not occur to a significant extent during reaction.

We observed a marked decrease in rate with time on $Rh/SiO_2$ catalyst for the hydrodechlorination of 1,2-dichloroethane (Figure 1-6) and trichloroethylene (Figure 2-4). This may be attributed to poisoning by the hydrogen chloride produced in the reaction and accumulation of carbonaceous deposits on the catalyst surface. An analysis of chlorine content between the fresh and contaminated catalysts is given in Table 3-2. It shows that after the reduction for 5 hr (under the hydrogen flow, 300°C) little of the $Rh/SiO_2$ catalyst exists in metal chloride form. After the reaction the chlorine content on the catalyst surface increased to 0.35 wt%, indicating that some chloride indeed deposited on the catalyst surface. The chlorine content of regenerated catalyst was also higher than initial. As many reports show [2] metal chlorides are slighty easier to reduce back to the metal, than the oxides. Hydrogen chloride formed is highly corrosive if water is present, so care should be taken to keep the system dry. The regeneration effect on the total conversion is also shown in Figure 1-7 and Figure 2-4. The steady state reaction rate is not affected by regeneration.

It is easy to achieve metal-catalysed olefin hydrogenation at low temperature and pressure. Table 3-4 and Figure 3-3 show the Rh catalyst even in metal chloride form is still very effective in hydrogenation of ethylene reaction but with a different selectivity, more $C_1$ formation. As the reaction proceeds the rate of the major product $C_2H_6$ increases. We believe this is due to further reduction of catalyst since in the hydrogen atmosphere the unreduced catalyst undergoes reduction gradually.

In general, the conversion of simple olefinic compounds to saturated ones occurs readily in the presence of any typical hydrogenation catalyst. Table 3-3 shows that the only product of ethylene hydrogenation over reduced $Rh/SiO_2$ catalyst is ethane at 26°C. At higher temperature some methane was formed and a trace amount of polymer ($C_4$ hydrocarbon) was also observed. The $C_4$ hydrocarbons formation may be attributed to the dimerization of ethylene [37,38]. In this temperature range, there is little temperature effect on the selectivity of secondary reaction (Fig 3-2), ethane hydrogenolysis to methane. The hydrogenation rate of ethylene is more rapid than the hydrogenolysis of ethane.

Table 3-5 and Figure 3-4 illustrate the selectivity of ethylene hydrogenation over the contaminated $Rh/SiO_2$ catalyst. The deactivated catalyst clearly has a different selectivity and reactivity. As reaction time increased, selectivity of $C_2H_6$ increases and this may be attributed to the contaminated catalyst being regenerated simultaneously. From Table 3-2 to Table 3-5 we can observe the effect of poisoning and fouling on the selectivity of $CH_4$ formation. We also see that there are at least two distinct types of active sites present in the catalyst surface via the selectivity of $CH_4$ and $C_2H_6$.

Comparison of Table 3-4 and Table 3-5 illustrates that the required time for regenerating the contaminated $Rh/SiO_2$ catalyst is longer than the time for reduction of the fresh metal chloride catalyst, and that the higher the metal forms in the catalyst, the higher the yield to ethane.

In this study some carbonaceous (or coke deposit) was observed. The coke deposit originates from the reaction and it is not an impurity. It deposits first on the upstream portions of the catalyst, and with time it distributes progressively downstream in the bed.

Table 3-1 The Average Particle Size of $Rh/SiO_2$ Catalysts*

| Rh catalyst | Crystallite Size ($A^o$) |
|---|---|
| S-1 | 62 |
| S-2 | 61 |
| S-3 | 50 |

*: determined by X-ray diffraction
S-1: the reduced catalyst
S-2:sample taken after the reaction: $H_2$ + 1,2-dichloroethane for 4 hours
S-3: sample taken after the reaction: $H_2$ + trichloroethylene for 4 hours

Table 3-2 Chlorine Analysis of the $Rh/SiO_2$ Catalysts*

| sample # | catalysts | chlorine (wt%) |
|---|---|---|
| Q-20 | fresh $Rh/SiO_2$** (3 wt%) | 0.11 |
| Q-21 | sample Q-20 hydrodeclorination with 1,2-dichloroethane for 5hr | 0.46 |
| Q-22 | sample Q-21 being regenerated for 5 hr | 0.17 |

* Galbraith Laboratories, Inc. Knoxville, TN. 37921.

** Catalyst was prepared by impregnating silica gel ($350\ m^2/g$) with solution of $RhCl_3\ 3H_2O$ at PH 2. The catalyst was dried 24 hr.at $100^oC$ and then reduced in flowing hydrogen at $400^oC$ for 24 hr.

Table 3-3 Temperature Effect on Selectivity of Ethylene Hydrogenation over Reduced $Rh/SiO_2$ Catalyst

| Temperature ($^oC$) | Total Conversion (%) | Selectivity(%) | | | |
|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_6$ | $C_3$ | $C_4$ |
| 26 | 100 | 0 | 100 | 0 | 0 |
| 60 | 100 | 0.04 | 99.91 | 0 | 0.05 |
| 85 | 100 | 0.15 | 99.68 | 0 | 0.17 |
| 125 | 100 | 0.13 | 99.66 | 0 | 0.21 |

Table 3-4 Selectivity of Ethylene Hydrogenation over Unreduced $RhCl_3/SiO_2$ Catalyst($T=260^oC$)

| Time (min.) | Total Covversion (%) | Selectivity(%) | | | |
|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_6$ | $C_3$ | $C_4$ |
| 5 | 100 | 62.62 | 37.34 | 0.04 | 0 |
| 19 | 100 | 6.85 | 92.79 | 0.03 | 0.33 |
| 32 | 100 | 2.46 | 96.87 | 0.02 | 0.55 |
| 55 | 100 | 0.82 | 98.58 | 0.02 | 0.58 |
| 100 | 100 | 0.16 | 99.30 | 0.02 | 0.52 |

Figure 3-2

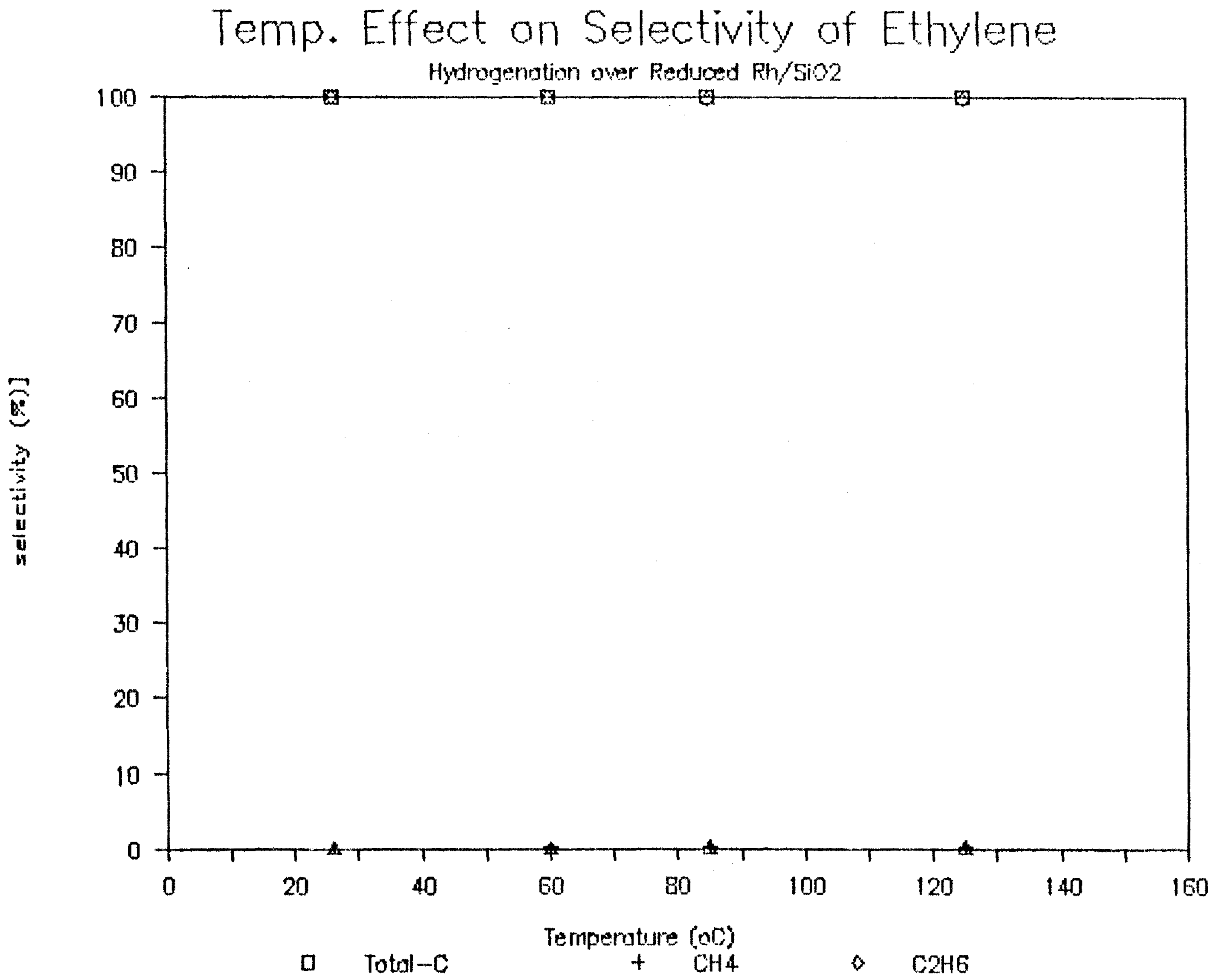

Temp. Effect on Selectivity of Ethylene
Hydrogenation over Reduced Rh/SiO2
selectivity (%)]
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
Temperature (oC)
□ Total-C
+ CH4
◇ C2H6

Figure 3-3

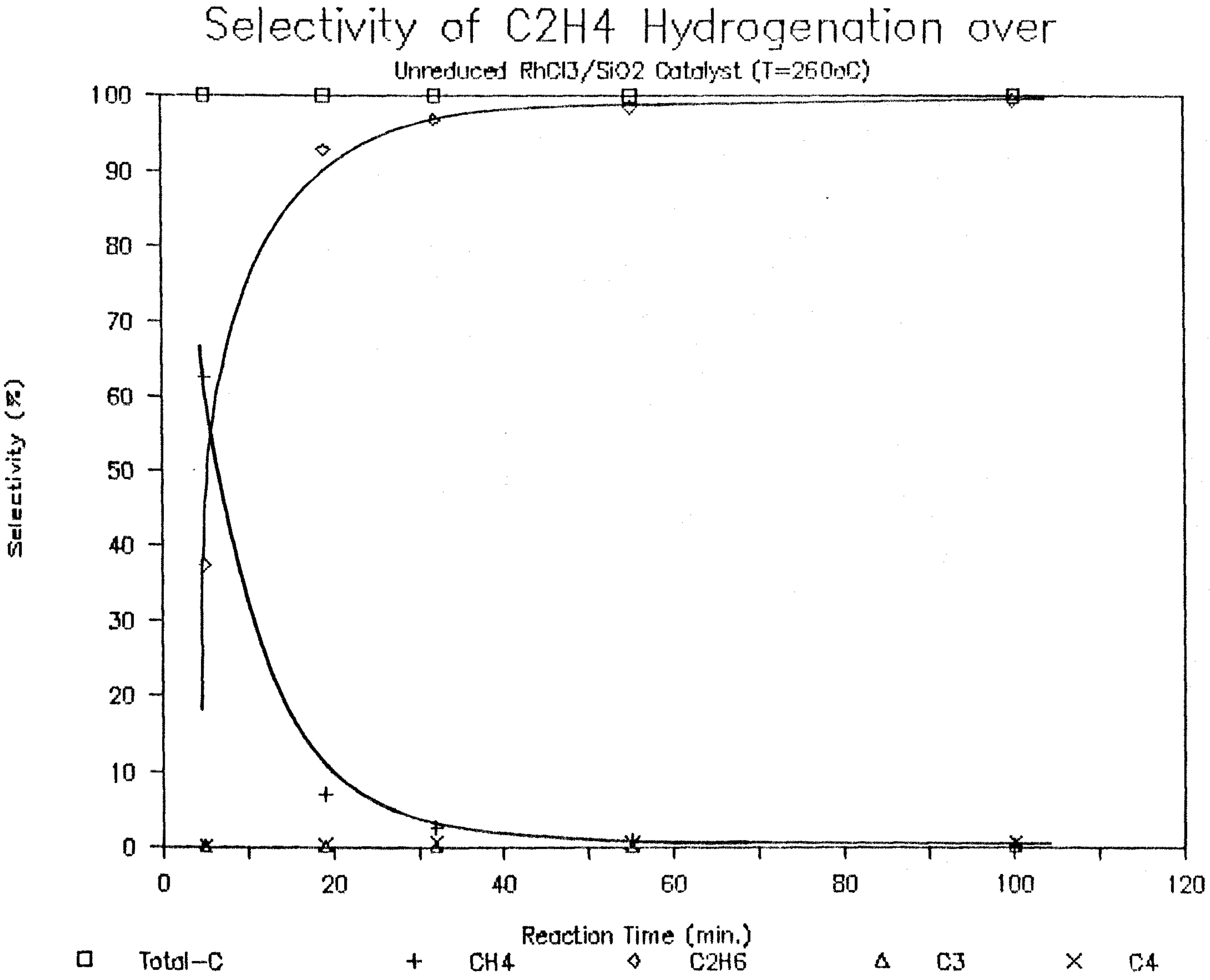
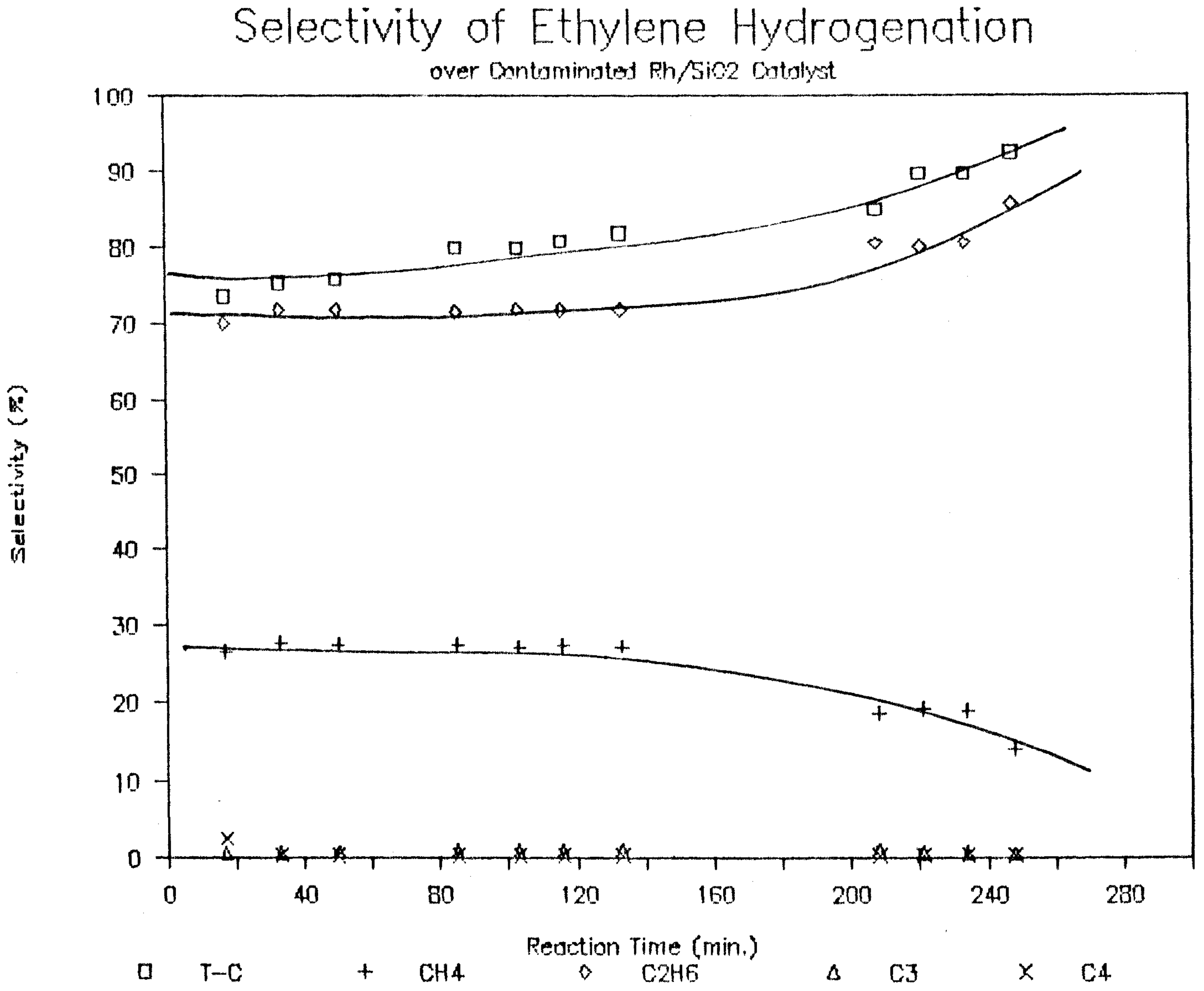

Selectivity of C2H4 Hydrogenation over
Unreduced RhCl3/SiO2 Catalyst (T=260oC)
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Reaction Time (min.)
□ Total-C
+ CH4
◇ C2H6
△ C3
× C4

Table 3-5 Selectivity of Ethylene Hydrogenation over Contaminated Rh/$SiO_2$ Catalyst* (T=260°C)

| Time (min) | Total Conversion (%) | Selectivity(%) | | | |
|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_6$ | $C_3$ | $C_4$ |
| 17 | 73.50 | 26.59 | 70.11 | 0.53 | 2.37 |
| 33 | 75.25 | 27.73 | 71.72 | 0.44 | 0.11 |
| 50 | 75.74 | 27.53 | 71.68 | 0.60 | 0.19 |
| 85 | 79.83 | 27.61 | 71.58 | 0.65 | 0.16 |
| 103 | 79.86 | 27.27 | 71.89 | 0.68 | 0.16 |
| 116 | 80.72 | 27.42 | 71.69 | 0.69 | 0.20 |
| 133 | 81.86 | 27.30 | 71.82 | 0.70 | 0.18 |
| 208 | 84.82 | 18.71 | 80.45 | 0.65 | 0.19 |
| 221 | 89.53 | 19.31 | 79.95 | 0.58 | 0.16 |
| 234 | 89.55 | 18.85 | 80.43 | 0.56 | 0.16 |
| 248 | 92.37 | 13.95 | 85.59 | 0.34 | 0.12 |

* The catalyst was taken from the hydrodechlorination of 1,1-dichloroethane after reaction proceeding 5hr.

Figure 3-4


Selectivity of Ethylene Hydrogenation
over Contaminated Rh/SiO2 Catalyst
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
0
40
80
120
160
200
240
280
Reaction Time (min.)
□ T-C
+ CH4
◇ C2H6
△ C3
× C4

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