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LOW-COST SOLAR ARRAY PROJECT. TASK I: SILICON MATERIAL

Investigation of the Hydrogenation of $SiCl_4$

Sixth Quarterly Report

By
Jeffrey Y. P. Mui
Dietmar Seyferth

October 7, 1980

Work Performed Under Contract No. NAS-7-100-955382

Massachusetts Institute of Technology
Cambridge, Massachusetts

U.S. Department of Energy

Solar Energy

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CONTRACT NO. 955382

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The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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ABSTRACT

Reaction kinetic measurements on the hydrochlorination of $SiCl_4$ and m.g. silicon metal were last reported as a function of reaction temperature, reactor pressure, $H_2/SiCl_4$ ratio and silicon metal particle size distribution,

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftarrows 4\ SiHCl_3$$

The effect of impurities in the m.g. silicon metal on the rate of this reaction has been investigated in this quarter. The m.g. silicon was replaced with high purity, electronic grade silicon metal in the hydrochlorination reaction. With electronic grade Si, the reaction rate was found to be about one order of magnitude slower than those obtained with m.g. silicon metal. These metallic impurities in the m.g. silicon appear to have a catalytic effect. Addition of 5 wt% cuprous chloride to the electronic grade Si mass bed increased the reaction rate to the same level as those obtained with m.g. silicon with 5% CuCl added.

The effect of prolonged reaction time on the hydrochlorination reaction was studied. The plan is to run the reaction for long periods of time with the object of studying the life of the Si mass bed. No significant change in the reaction rate was observed after about 80 hours of reaction.

INTRODUCTION

Experimental work on the JPL Government Contract No. 955 382 began in April of 1979 to study the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$. This Quarterly Report is the sixth in the series. Activities during this quarter included the studies on the effect of impurities in the m.g. silicon metal on the reaction rate. The effect of prolonged reaction time on the hydrochlorination reaction also was investigated.

DISCUSSION

The laboratory scale stainless steel reactor for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$ is schematically shown in Figure I. The design and function of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 955 382 - 79/1). Reaction kinetic measurements in the presence of a copper catalyst and the effect of Si metal particle size distribution on the hydrochlorination reaction were last reported. During this quarter, the effect of impurities in m.g. Si metal on the reaction rate was studied. The effect of prolonged reaction times on the hydrochlorination reaction was also investigated. Results are discussed in the following.

A. Effect of Impurities in the M.G. Silicon Metal on Reaction Rate

A series of experiments was carried out to study the effect of impurities in the m.g. silicon on the hydrochlorination reaction. Table I lists the common metallic impurities present in the metallurgical grade silicon metal. The major contaminants are iron and aluminum which account for 80% to 90% of the total impurities in m.g. Si metal. A convenient method to study the overall effects of these impurities on the hydrochlorination reaction is to measure the reaction rates in comparison with those obtained with a high purity, electronic grade silicon metal. This electronic grade, polycrystalline silicon metal contains no impurities from a chemical reaction point of view. The common impurities listed in Table I are reduced to the less than parts per billion range in electronic grade Si metal. Sample of an electronic grade Si was ground and sieved to 32 x 400 mesh (500 x 37 micrometers). The experiment was carried out with 180 g. of this high purity silicon metal at a reactor pressure 500 psig, a reaction temperature 500°C and a $H_2/SiCl_4$ feed ratio of 2.8. The results of this experiment are summarized in Table II. Data in Table II is presented in Figure II by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are reaction kinetic data previously obtained with m.g. Si metal under the same reaction conditions. The shaded curve in Figure II represents the combined results obtained from the same reaction with 32 x 65 mesh, 65 x 150 mesh and 150 x 400 mesh m.g. Si metal. As results in Figure II show, the reaction rate is about one order of magnitude slower with electronic grade Si in comparison with those obtained from the 98.5% m.g. silicon. Thus, the presence of metallic impurities in m.g. Si metal appears to greatly increase the rate of the hydrochlorination reaction with $SiCl_4$ and hydrogen.

The catalytic effect of copper also was studied. The high purity Si mass bed was taken out of the reactor and thoroughly mixed with 9 g (5 wt%) of -400 mesh cuprous chloride powder. The mixture was carefully charged back into the reactor tube. The experiment was repeated under the same reaction condition. The results of this experiment are summarized in Table III. Data in Table III also are plotted in Figure III together with the experimental results shown in Figure II. As the results in Figure III show, the presence of a copper catalyst greatly increases the hydrochlorination reaction rate to a level above that of m.g. silicon metal. Hence, the copper catalyst provides a convenient means to recycle off-specification solar-grade silicon metal. In Figure IV, the reaction kinetic data obtained from the electronic grade Si + 5% CuCl experiment are plotted in comparison with those collected from the m.g. Si + 5% CuCl experiment under the same reaction conditions. Interestingly, both experiments show essentially the same reaction rates. These experimental results appear to show that the metallic impurities in m.g. Si metal function like a catalyst. The presence of these metallic impurities in m.g. Si metal does not appear to product harmful effects. In fact, they are beneficial to the hydrochlorination reaction.

The above experimental results show that the metallic impurities in m.g. Si appear to function equally effectively as the copper catalyst. With no other elements present, the high purity, polycrystalline silicon metal produces a much slower reaction rate. Thus, crystal defects caused by the presence of copper or other metallic elements on the silicon metal surface provide a plausible explanation for the observed catalytic activities. However, there are some fundamental differences between copper and the metallic impurities in m.g. Si metal. Iron and aluminum which account for 80% to 90% of the total impurities in m.g. Si are actually consumed in the hydrochlorination reaciton to produce ferric chloride and aluminum chloride. The volatile $FeCl_3$ (b.p. 315°C) and $AlCl_3$ (b.p. 183°C) are readily removed from the reactor along with the reaction product stream. In this respect, they are not true catalysts.

B. Corrosion Studies

After the experiments on impurities study, the reactor was taken apart and cut up for corrosion measurements. During the course of this investigation, extensive atmospheric corrosion of the reactor wall was noted. A dense "coating" was first observed on the wall of the reactor parts which have been exposed to the hydrochlorination environment. The coating has a physical appearance similar to the layer of silicon produced by a vapor phase deposition process. However, on standing in the atmosphere for extended periods of time, this dense coating produces creeps, cracks and it eventually flakes off. Slowly, some greenish material appears and the surface becomes wet. The green color is most likely due to salts of nickel and chromium. Ferric chloride, chromium chloride and nickel chloride are deliquescent solids which absorb moisture from the atmosphere to cause wetting of the exposed reactor surface. These observations point to the effect of atmospheric corrosion. The effect of atmospheric corrosion complicates the previous study on the material of construction for the hydrochlorination reactor. The corrosion measurements made in the past are combined results of atmospheric corrosion and the corrosion due to the hydrochlorination reaction itself. Since atmospheric corrosion is normally not a problem for a production hydrochlorination reactor in an integrated plant (except for service or repair), one needs to separate the effect of atmospheric corrosion from the corrosoin due to the hydrochlorination reaction environment. Presently, corrosion studies are in progress for type 304 stainless steel and Incolloy 800.

C. Mass Life Studies

A new hydrochlorination reactor was built to replace the old reactor. The new reactor is also made of type 304 stainless steel and it has the same physical dimension as the old reactor tube. Modifications were made on the electrical heaters to provide a better temperature control on the Si mass bed. A strip of Incolloy 800 sample is afixed to the side wall of the reactor tube for corrosion studies. A charging port is provided at the top of the reactor so that fresh Si metal can be charged into the reactor. A series of experiments was carried out with the object of studying the life of the Si mass bed. In practice, the hydrochlorination reactor must be able to sustain sufficiently long periods of operation before it has to be shut down for service. Thus, the longevity of the silicon mass bed is an important factor in operating the hydrochlorination process efficiently and economically. The object of this experiment is to study the effect of prolonged reaction time on the hydrochlorination reaction. The rate of the hydrochlorination reaction is measured as a function of total reaction time. The experiment is carried out at a reactor pressure 300 psig, a reaction temperature 500°C and a H_2/-$SiCl_4$ feed ratio of 2.0. Fresh Si metal is intermittently added to replenish the silicon metal consumed in the reaction. The reaction rate is continuously monitored by analyzing the composition of the reaction product mixtures. About 80 hours of reaction time have been accumulated so far. No significant changes in the hydrocholorination reaction rate were observed. More work is in progress.

D. Summary of Progress

Experimental work on the JPL Government Contract No. 955 382 has progressed on schedule as outlined in the attached Program Plan. The effect of impurities in the m.g. Si metal on the hydrochlorination reaction was studied. The metallic impurities in the m.g. Si act like a catalyst to greatly increase the reaction rate. These measurements provide some evidence on the mechanism of the hydrochlorination reaction. Corrosion studies are in progress on selected material of construction for the hydrochlorination reactor. Extensive atmospheric corrosion was noted when reactor parts were exposed to air and moisture. This points to the need of re-examining some corrosion measurements previously made on certain selected materials of construction for the hydrochlorination reactor. Experiments on the effect of prolonged reaction time on the hydrochlorination reaction were carried out. The plan is to run the reaction for long periods of time for one or two mass turn-over of the Si mass bed.

PROJECTED SEVENTH QUARTER ACTIVITIES

Planned activities for the seventh quarter (October - December) include,

Corrosion studies

Mass life studies

Mass life studies with copper catalyst added

LSA PROJECT
SILICON MATERIAL

PROBLEMS - CONCERNS

TABLE I METALLIC IMPURITIES IN METALLURGICAL GRADE SILICON

Fe	~	0.5-0.9%
Al	~	0.3-0.6%
Mn	~	0.06%
Ca	~	0.05%
Cu	~	0.01%
Ni	~	0.01%
Cr	~	0.01%
Ti	~	0.01%

TABLE II Hydrochlorination of $SiCl_4$ and Electronic Grade Si to $SiHCl_3$ at 500 PSIG, 500°C and $H_2/SiCl_4$ Ratio of 2.8

Experiment No.	Hydrogen Feedrate SCCM[(1)]	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	1200	71.3	0.2982	10.19	89.51
2	800	107	0.3507	12.71	86.94
3	415	207	0.2990	16.86	82.84
4	205	419	0.6389	25.70	73.66

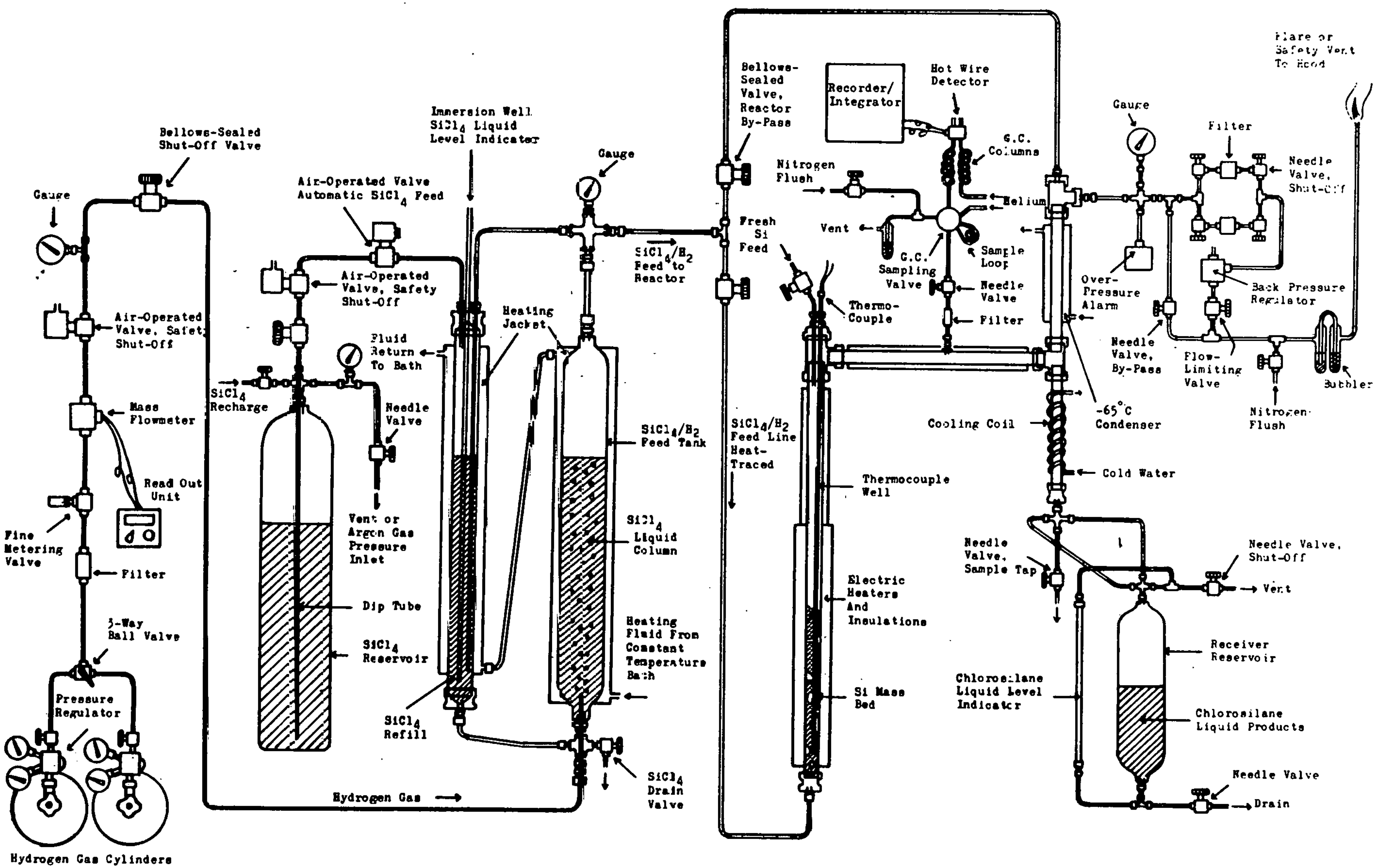
(1) SCCM, Standard c.c. per minute

TABLE III Hydrochlorination of $SiCl_4$ and Electronic Grade Si metal with 5% CuCl added at 500 PSIG, 500°C and $H_2/SiCl_4 = 2.8$

Experiment No.	Hydrogen Feedrate SCCM(1)	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	1417	50.1	1.756	34.58	63.67
2	1009	70.4	1.652	36.32	62.03
3	542	131	1.817	38.40	59.78
4	309	231	1.704	40.08	58.21

(1) SCCM, Standard c.c. per minute

FIGURE 1 Apparatus For The Hydrogenation Of $SiCl_4$ To $SiHCl_3$



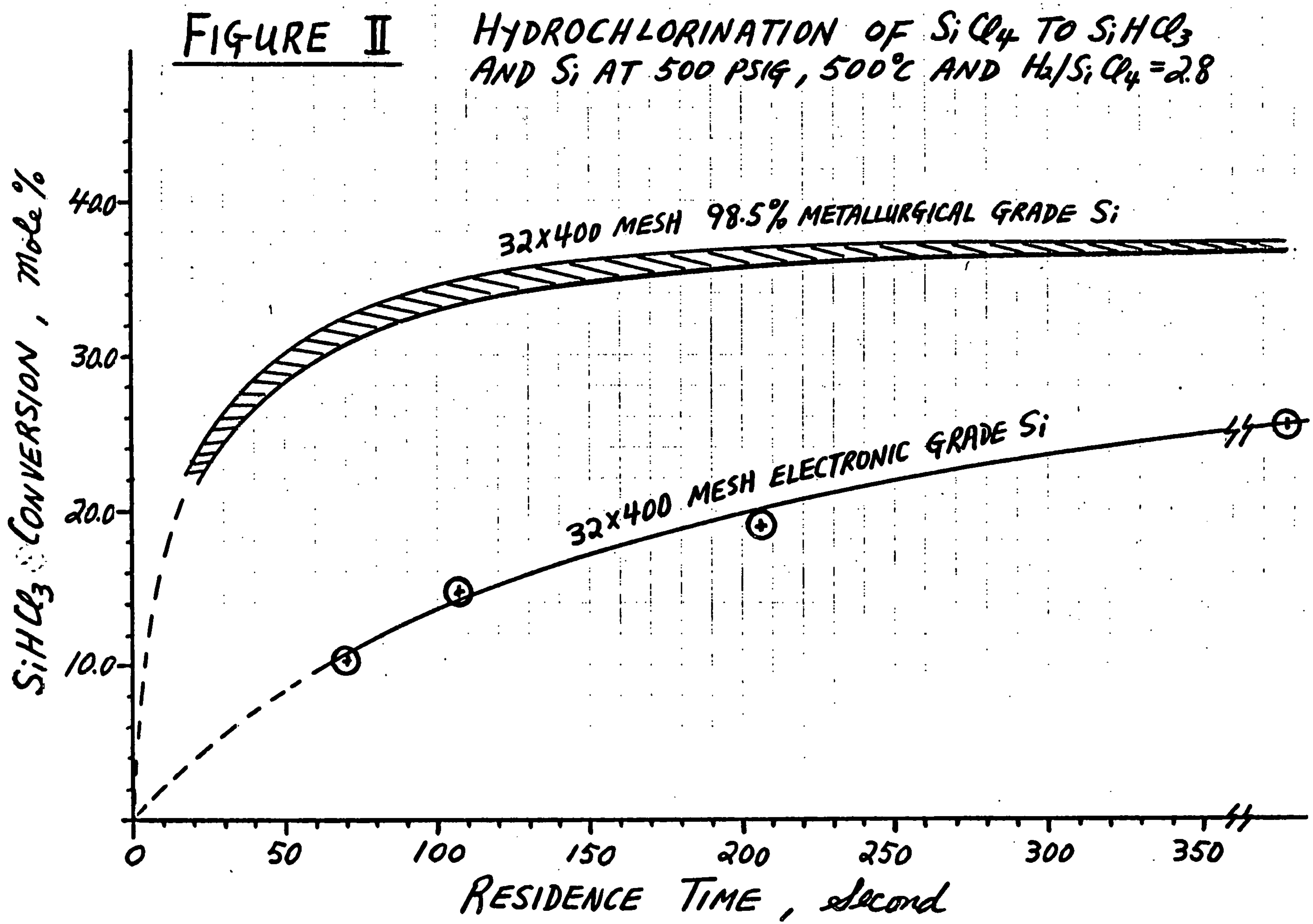


FIGURE II
HYDROCHLORINATION OF $SiCl_4$ TO $SiHCl_3$
AND Si AT 500 PSIG, 500°C AND $H_2/SiCl_4$=2.8
32X400 MESH 98.5% METALLURGICAL GRADE Si
32X400 MESH ELECTRONIC GRADE Si
$SiHCl_3$ CONVERSION, Mole %
40.0
30.0
20.0
10.0
0
50
100
150
200
250
300
350
RESIDENCE TIME, Second

FIGURE III HYDROCHLORINATION OF $SiCl_4$ TO $SiHCl_3$ AND Si AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8

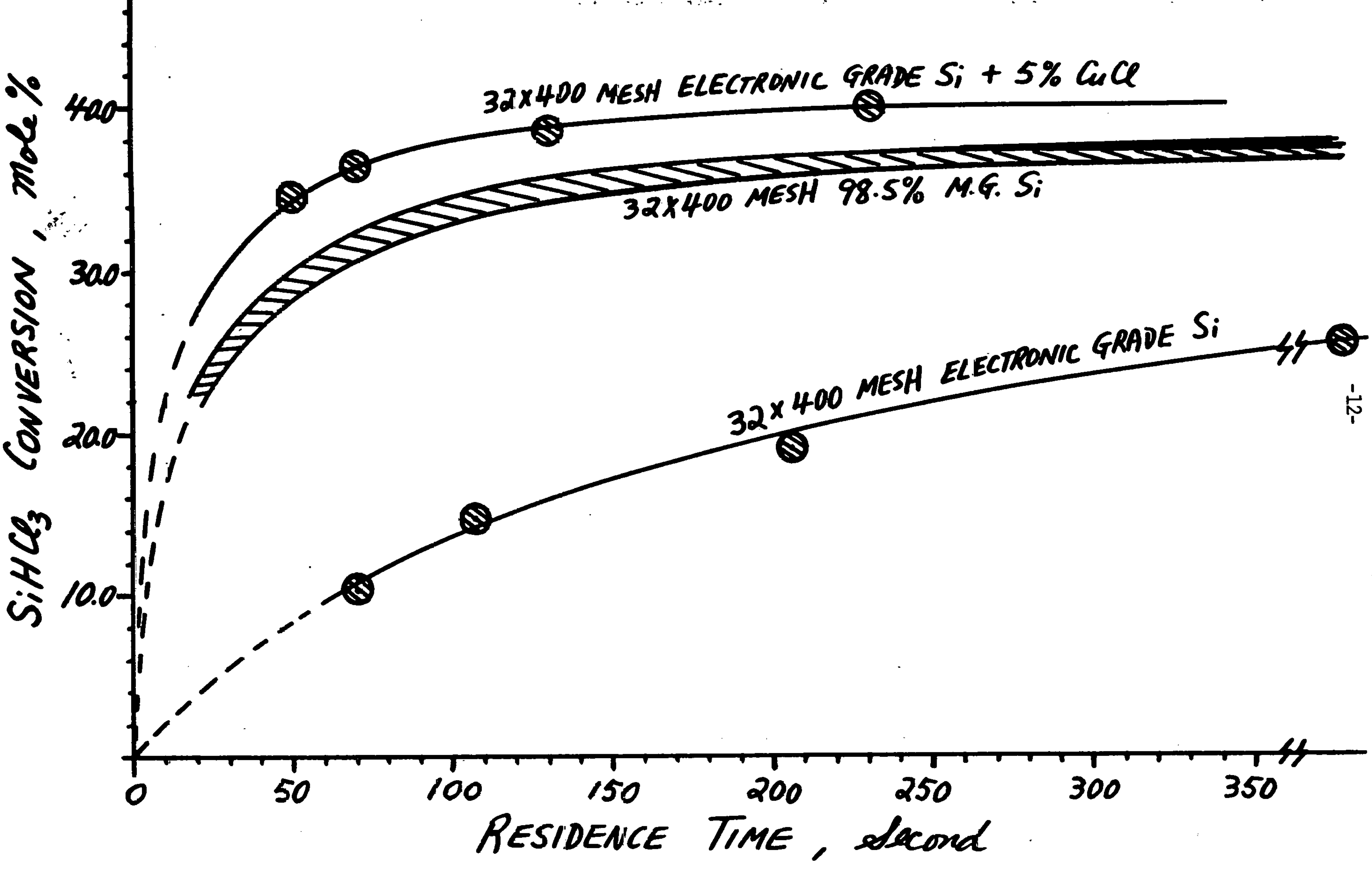
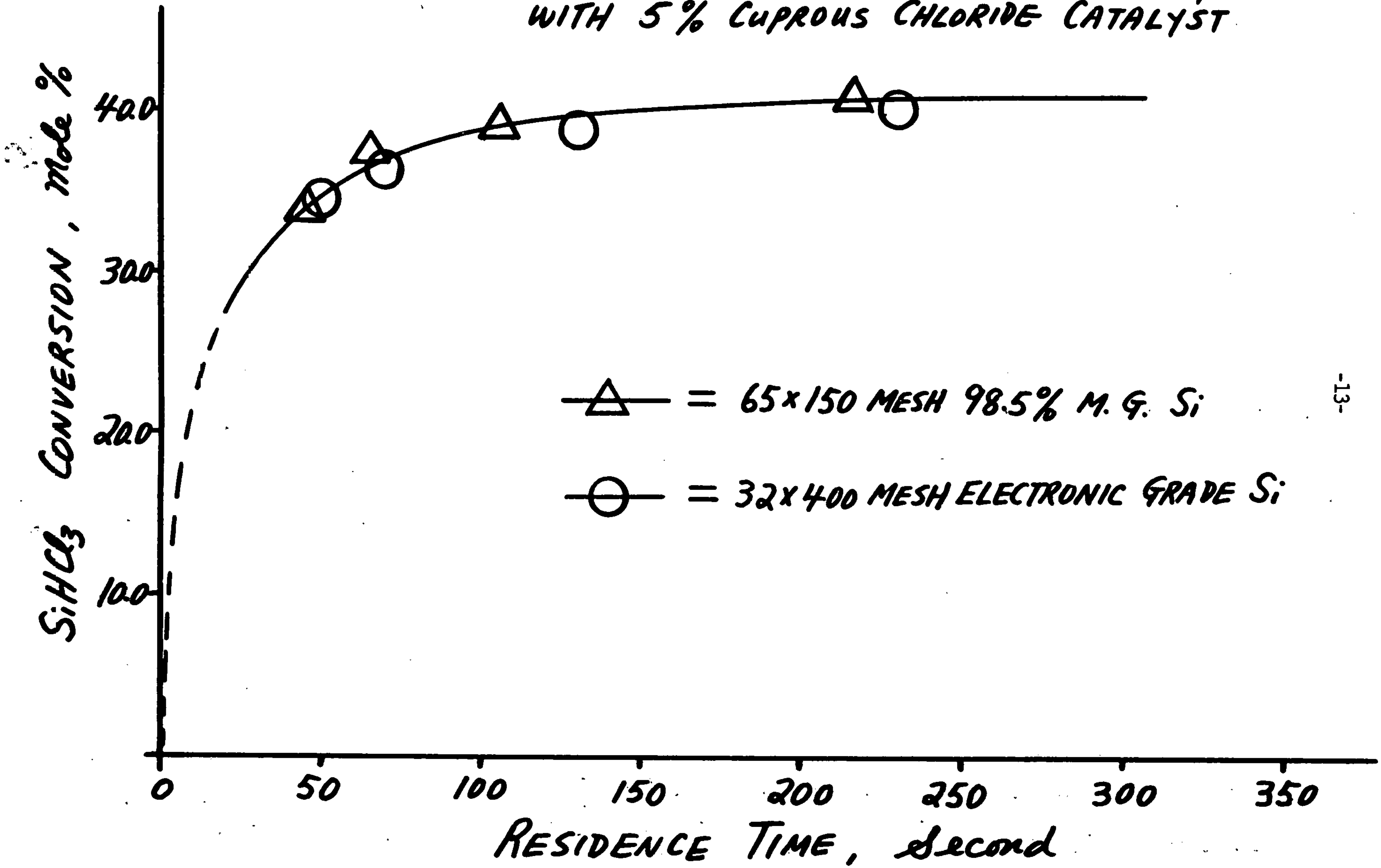


FIGURE IV HYDROCHLORINATION OF $SiCl_4$ TO $SiHCl_3$ AND Si AT 500 PSIG, 500°C AND $H_2/SiCl_4 = 2.8$ WITH 5% CUPROUS CHLORIDE CATALYST



PROGRAM PLAN Investigation of the Hydrogenation of $SiCl_4$ (JPL Contract No. 955382)

Year	1979									1980												1981		
Month of Year	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Month of Contract	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
I Program Plan, Laboratory Site Preparation	~~1~~																							
II Finalize Reactor Design, Order Equipment	~~1~~	~~2~~																						
III Construct Hydrogenation Apparatus		~~2~~	~~3~~	~~4~~	~~5~~																			
IV Safety Review, Start-Up, Standardization					~~5~~																			
V Process Studies								▲					▲					▲						
A. Reaction Kinetics																								
(1) Function of T,P,$H_2/SiCl_4$: with no Catalyst					~~5~~	~~6~~	~~7~~	~~8~~																
(2) Establish Rate Equation, Reaction Order								~~8~~	~~9~~															
(3) Copper Catalyst Studies: T,P,$H_2/SiCl_4$								~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~											
(4) Particle Size Distribution, Surface Area													~~13~~	~~14~~	~~15~~									
(5) Different Grade of MG Si														~~14~~	~~15~~	~~16~~								
B. Mass Life Studies																								
(1) With no Catalyst Added																~~16~~	~~17~~	~~18~~						
(2) With Cu Catalyst Added																		~~18~~	19	20				
(3) Different Grade of MG Si																				20	21	22		
VI Research and Development								▲					▲					▲						
A. Method of Preparing Cu/Si Mass																								
(1) Literature Studies	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	~~7~~	~~8~~																
(2) Prepare Cu/Si Mass					~~5~~	~~6~~	~~7~~	~~8~~																
(3) Evaluation and Optimization								~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~											
B. Reaction Mechanism Studies																								
(1) Literature Studies	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	~~7~~	~~8~~																
(2) Identify Reaction Intermediates: HCl, etc.						~~6~~	~~7~~	~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~	~~14~~	~~15~~	~~16~~	~~17~~	~~18~~	19	20	21			
(3) Identify Intermediate Reaction Steps						~~6~~	~~7~~	~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~	~~14~~	~~15~~	~~16~~	~~17~~	~~18~~	19	20	21			
(4) Nature of the Equilibrium Reactions						~~6~~	~~7~~	~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~	~~14~~	~~15~~	~~16~~	~~17~~	~~18~~	19	20	21			
(5) The Role of Copper Catalyst																								
a. Nature of the Catalytic Sites								~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~	~~14~~	~~15~~									
b. Copper Transport Mechanism								~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~	~~14~~	~~15~~									
c. Copper Distribution on Solid Si Surfaces								~~8~~	~~9~~	~~10~~	~~11~~	~~12~~	~~13~~	~~14~~	~~15~~									
(6) Kinetic Isotope Effect													▲									22	23	
C. Other Hydrogenation Catalysts													▲									22	23	
VII Reports																								
A. Recomendation on Optimun Reaction Conditions									~~9~~					~~14~~					19				23	
B. Recomendation for Additional Development Work									~~9~~					~~14~~									23	
C. Final Report																							23	24

▲ Milestone Check Points