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LOW-COST SOLAR ARRAY PROJECT, TASK I SILICON MATERIAL

Investigation of the Hydrogenation of SiCl_4

Fifth Quarterly Report

By
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July 3, 1980

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

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U.S. Department of Energy

Solar Energy

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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

FIFTH QUARTERLY REPORT

July 3, 1980

CONTRACT NO. 955382

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The JPL Low-Cost Silicon Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photo-voltaic 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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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

Massachusetts Institute of Technology
Office of Sponsored Programs
Department of Chemistry
Cambridge, Massachusetts

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ABSTRACT

Reaction kinetic measurements on the hydrochlorination of SiCl_4 and m.g. silicon metal in the presence of a copper catalyst were last reported as a function of reaction temperature, reactor pressure and H_2/SiCl_4 ratio,

The same reaction was repeated at a lower catalyst loading of 2 wt%. In the presence of 2 wt% cuprous chloride (based on silicon metal), the hydrochlorination reaction rate is doubled to give about the same performance as those obtained at a higher copper catalyst loading.

The effect of particle size distribution of the m.g. silicon metal on the hydrochlorination reaction rate was studied. Reaction kinetic measurements were made on 150 x 400 mesh Si and on 32 x 65 mesh Si in addition to the standard 65 x 150 mesh Si used in previous studies. Results of these experiments show that the reaction rate is essentially independent of the silicon metal particle size. Thus, the reaction occurring on the Si metal surface is the rate-determining step. Mass transfer via diffusion of reactants and product is not rate-limiting. A plausible mechanism of the hydrochlorination reaction is discussed.

INTRODUCTION

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 fifth in the series. Reaction kinetic measurements in the presence of a copper catalyst were last reported. Activities during this quarter included reaction rate studies in the presence of a lower level of 2 wt% cuprous chloride catalyst. The effect of particle size distribution of the m.g. silicon metal on the rate of the hydrochlorination of SiCl_4 to SiHCl_3 was studied.

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 5 wt% copper catalyst (cement copper and CuCl) were last reported. Cuprous chloride was found to be a more effective catalyst than cement copper. The same experiment has been repeated at a lower catalyst loading to study the effect of copper catalyst concentration on the rate of the hydrochlorination reaction.

A. Reaction Kinetic Measurements with 2% Cuprous Chloride

A series of experiments were carried out to study the hydrochlorination of SiCl_4 and silicon metal to SiHCl_3 in the presence of 2 wt% CuCl . A mixture of 180 g. 65 x 150 mesh m.g. Si and 36 g -400 mesh cuprous chloride powder was prepared and carefully charged into the reactor tube. The reactor was sealed and pressurized with

hydrogen gas. It was brought up to reaction conditions in the usual manner at 300 psig, 500°C and H_2/SiCl_4 feed ratio of 1.0. As previously observed, there was no induction period with CuCl as shown in Figure II in which the reaction rate is plotted as a function of reaction time. Also plotted in Figure II are reaction kinetic data obtained under similar reaction conditions but with no copper added (dotted line). As the graphs in Figure II show, the presence of 2% CuCl results in a significantly higher reaction rate at the start of the reaction (0% conversion) in comparison with the same reaction with no copper added (dotted line). After a few hours of reaction, the activity of the Cu/Si mass bed stabilized. Reaction kinetic measurements were made. Results are summarized in Table I. Data in Table I are presented in Figure III by plotting the SiHCl_3 and SiH_2Cl_2 conversion versus residence time. Also plotted in the same graph are reaction rate data previously obtained from the same reaction with 5 wt% CuCl added and from the same reaction with no copper added. As data in Figure III show, the reaction rate in the presence of CuCl (solid line) increases by approximately 100% in comparison with that obtained without copper added (dotted line). Other than a slightly slower initial reaction rate (see Figure II), the performance of 2 wt% CuCl in the hydrochlorination reaction is essentially the same as that of a 5 wt% CuCl/silicon mass. A lower catalyst level of 2% CuCl for the hydrochlorination reaction is advantageous from a process and an economics point of view.

Since the copper-catalyzed hydrochlorination reaction is a gas-solid reaction, the absolute amount of copper in the bulk of the silicon mass bed is not important. Rather, the distribution of copper and the number of active sites on the Si metal surface are

important variables for the catalytic activity. As the hydrochlorination reaction proceeds, migration of copper on the Si metal surface can spread the copper concentrations over the entire solid surface. This phenomenon explains why 2% CuCl can provide the same catalytic activity as 5% CuCl. Since a gas-solid reaction normally does not involve surface atoms more than 10 to 20 atomic layers deep, the 2 wt% CuCl still represents a large excess of copper, much more than what is actually needed for the active Cu/Si catalytic sites. The question of copper transport from one silicon particle to another will be the subject of investigations later on in the Program Plan on Mass Life Studies. If such a copper transport mechanism occurs rapidly, one conceivably may need to use only one initial charge of copper catalyst for as long as the production process lasts.

B. Effect of Particle Size Distribution on Reaction Rates

Two particle size distributions of m.g. silicon, 150 x 400 mesh and 32 x 65 mesh, were evaluated in the hydrochlorination reaction of SiCl_4 to SiHCl_3 . In previous experiments, the 65 x 150 mesh m.g. silicon was used as a standard. The 150 x 400 mesh Si and the 32 x 65 mesh Si are sieved from the same lot of metallurgical grade silicon metal supplied by Union Carbide Corporation. The effect of particle size distribution (total surface area) on the rate of the hydrochlorination reaction was studied as a function of reactor pressure, reaction temperature and H_2/SiCl_4 feed ratio. Reaction kinetic measurements were made on these two particle size distributions (150 x 400 and 32 x 65 mesh) under the same reaction conditions as used in the experiments previously carried out with the standard 65 x 150 mesh Si. Results are summarized below.

A series of experiments was carried out with 180 g. 32 x 65 mesh m.g. silicon at a reactor pressure of 500 psig, reaction

temperature of 500°C and H_2/SiCl_4 feed ratio of 2.8. After several hours of reaction, the Si mass bed stabilized. Reaction kinetic data were collected by measuring the chlorosilane product composition as a function of residence time. Results are summarized in Table II. Another series of experiments was carried out with 180 g of a finer 150 x 400 mesh silicon under the same reaction conditions. Results of this series of experiments are given in Table III. Data in Table II and Table III are presented in Figure IV by plotting the SiHCl_3 conversion versus residence time. Also plotted in the same graph are reaction rate data previously obtained from the standard 65 x 150 mesh silicon under the same reaction conditions. As the results in Figure IV show, the effect of Si particle size distribution on the hydrochlorination reaction rate is very small. A close examination of the data points in Figure IV shows that the 32 x 65 mesh Si (circular points) appears to give a slightly slower reaction rate than that obtained with the much finer 150 x 400 mesh Si (square points). However, the difference of reaction rate is not much greater than the range of standard deviations from the scattering of data points from one experiment to another.

Reaction rate measurements on the 150 x 400 mesh Si were repeated at 500 psig and a H_2/SiCl_4 feed ratio of 2.8 but at a lower reaction temperature of 450°C. Results of this experiment are summarized in Table IV. The data in Table IV are presented in Figure V by plotting the SiHCl_3 conversion versus residence time. Also plotted in Figure V are reaction rate data previously obtained from the same reaction with the standard 65 x 150 mesh Si. As the results in Figure V show, the finer 150 x 400 mesh Si appears to give a somewhat faster reaction rate. Again, the difference is small.

The above experiments were repeated at a lower reactor pressure of 300 psig. A series of experiments was carried out with the 150 x 400 mesh Si at reactor pressure of 300 psig, reaction temperature of 450°C and $H_2/SiCl_4$ feed ratio of 1.0. Results are summarized in Table V. Data in Table V are presented in Figure VI by plotting the $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are reaction rate data previously obtained from the standard 65 x 150 mesh Si under the same experimental conditions. As the data in Figure VI show, there is essentially no difference in the reaction rate between these two Si particle size distributions.

Another series of experiments was carried out with the 150 x 400 mesh Si and the 32 x 65 mesh Si at a reactor pressure of 300 psig, reaction temperature of 500°C and a $H_2/SiCl_4$ feed ratio of 1.0. Results of these two series of experiments are summarized in Table VI and Table VII, respectively. Data in Table VI and Table VII are also presented in Figure VII by plotting the $SiHCl_3$ conversion versus residence time. As results in Figure VII show, there is essentially no difference of reaction rate between the 150 x 400 mesh Si and the 32 x 65 mesh Si.

In conclusion, the above experimental results show that the hydrochlorination reaction rate is essentially independent of the silicon particle size distributions. Table VIII summarizes the physical properties of these fractions of Si particle size distributions. The total surface area per unit weight of the standard 65 x 150 mesh Si is about 2.2 times larger than that of the coarser 32 x 65 mesh Si. On the other hand, the finer 150 x 400 mesh Si has a total surface area about 5 times larger than that of the 32 x 65 mesh Si. Despite the large differences in total solid

surface area, the reaction rate remains about the same for these different particle size distributions of silicon metal. Thus, the chemical reactions occurring on the silicon solid surfaces is the rate-determining step. Mass transfer via diffusion of reactants and products is not rate-limiting. The constant reaction rate with respect to particle size distribution is advantageous from a process point of view. It provides a broader operating latitude for the hydrochlorination reactor. For example, one can conveniently increase the output of product SiHCl_3 by operating the reactor at a higher reaction temperature to provide a higher reaction rate. The increase in linear gas velocity due to the higher H_2/SiCl_4 feedrate can be compensated for by simply increasing the particle size distribution of the m.g. silicon metal.

C. Summary of Progress

Work on the JPL Government Contract No. 955 382 has progressed on schedule as outlined in the attached Program Plan. The effect of copper catalyst concentration on the rate of the hydrochlorination reaction was studied. Cuprous chloride is an effective catalyst for this reaction at concentrations as low as 2 wt% based on Si metal. The effect of Si particle size distribution on the reaction rate also was studied. The rate of the hydrochlorination of SiCl_4 to SiHCl_3 is essentially independent of the Si particle size.

PROJECTED SIXTH QUARTER ACTIVITIES

Planned activities for the sixth quarter (July - September) include,

- Effect of impurities in the m.g. silicon metal on the hydrochlorination reaction rate
- Mass life studies with respect to reaction rate, copper catalyst distribution, etc.
- Equilibrium data as a function of reaction temperature

TABLE I Hydrochlorination of SiCl_4 and m.g. Silicon at 300 psig,
 500°C and $\text{H}_2/\text{SiCl}_4 = 1.0$ with 2% CuCl

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition		
			mole%		
			<u>SiH_2Cl_2</u>	<u>SiHCl_3</u>	<u>SiCl_4</u>
1	1350	21.5	0.4644	21.98	77.56
2	940	30.9	0.5206	23.58	75.91
3	620	46.8	0.7516	27.05	72.21
4	220	132	1.040	30.25	68.71

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

TABLE II Hydrochlorination of SiCl_4 and 32 x 65 mesh m.g. Si
at 500 psig, 500°C and $\text{H}_2/\text{SiCl}_4 = 2.8$

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole%		
			<u>SiH_2Cl_2</u>	<u>SiHCl_3</u>	<u>SiCl_4</u>
1	1767	28.8	0.615	25.16	74.23
2	1186	42.9	0.786	27.88	71.34
3	618	82.3	1.004	31.44	67.56
4	328	155	1.273	33.30	65.43
5	175	290	1.162	35.09	63.75

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

TABLE III Hydrochlorination of SiCl_4 and 150 x 400 mesh m.g. Si at 500 psig, 500°C and $\text{H}_2/\text{SiCl}_4 = 2.8$

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole%		
			<u>SiH_2Cl_2</u>	<u>SiHCl_3</u>	<u>SiCl_4</u>
1	1489	50.9	1.086	31.18	67.74
2	1015	75.2	1.190	33.52	65.29
3	649	118	1.218	34.20	64.59
4	347	220	1.564	36.20	62.24
5	191	400	1.723	37.84	60.44

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

TABLE IV Hydrochlorination of SiCl_4 and 150 x 400 mesh m.g. Si.
at 500 psig, 450°C and $\text{H}_2/\text{SiCl}_4 = 2.8$

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole%		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1554	50.3	0.5388	24.49	74.98
2	1150	68.0	0.7547	27.72	71.53
3	656	119	0.8805	30.16	68.96
4	427	183	0.9271	31.34	67.74

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

TABLE V Hydrochlorination of SiCl_4 and 150 x 400 mesh m.g. Si
at 300 psig, 450°C and $\text{H}_2/\text{SiCl}_4 = 1.0$

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole%		
			<u>SiH_2Cl_2</u>	<u>SiHCl_3</u>	<u>SiCl_4</u>
1	1082	32.7	0.1972	15.39	84.42
2	740	47.8	0.2711	17.84	81.89
3	424	83.4	0.3851	20.80	78.82
4	184	192	0.4702	23.30	76.23

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

TABLE VI Hydrochlorination of SiCl_4 and 150 x 400 mesh m.g. Si
at 300 psig, 500°C and $\text{H}_2/\text{SiCl}_4 = 1.0$

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole%		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1058	32.7	0.3501	20.52	79.13
2	716	48.3	0.4318	21.79	77.79
3	425	81.3	0.5152	24.62	74.86
4	168	206	0.6550	25.76	73.59

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

TABLE VII Hydrochlorination of SiCl_4 and 32 x 65 Mesh m.g. Si
at 300 psig, 500°C and $\text{H}_2/\text{SiCl}_4 = 1.0$

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole%		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1760	12.9	0.1527	14.55	85.30
2	1230	18.5	0.2137	17.00	82.78
3	626	36.4	0.2784	20.50	79.23
4	315	72.3	0.4356	23.19	76.38
5	158	144	0.5277	24.63	74.84

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

TABLE VIII Particle Size Distribution of m.g. Silicon Metal for the Hydrochlorination Studies

Tyler Mesh No.	Particle Size Range (1) μm	Mean Particle Size μm	Relative Surface Area 65 x 150 = 1.0	Bulk Density		Average Density g./c.c.	% Void Space
				Compact g./c.c.	Loose g./c.c.		
32 x 65	500 x 210	355	0.45	1.39	1.29	1.34	43
65 x 150	210 x 105	158	1.00	1.24	1.14	1.19	49
150 x 400	105 x 37	71	2.23	1.24	1.07	1.16	50

(1) μm , micrometer = microns

FIGURE 1 Apparatus For The Hydrogenation Of SiCl_4 To SiHCl_3

FIGURE II HYDROCHLORINATION OF SiCl_4 AT 300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$ WITH 2% CuCl INITIALLY ADDED

FIGURE III HYDROCHLORINATION OF SiCl_4 AT
300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$
WITH 2% AND 5% CuCl CATALYST

FIGURE IV

PARTICLE SIZE DISTRIBUTION STUDIES:
THE HYDROCHLORINATION OF SiCl_4 AND M.G. Si
AT 500 PSIG, 500°C AND H_2/SiCl_4 RATIO OF 2.8

FIGURE V

PARTICLE SIZE DISTRIBUTION STUDIES :
THE HYDROCHLORINATION OF SiCl_4 AND M.G. Si
AT 500 PSIG, 450°C AND H_2/SiCl_4 RATIO OF 2.8

FIGURE VI

PARTICLE SIZE DISTRIBUTION STUDIES:
THE HYDROCHLORINATION OF SiCl_4 AND M.G. Si
AT 300 PSIG, 450°C AND H_2/SiCl_4 RATIO OF 1.0

FIGURE VII

PARTICLE SIZE DISTRIBUTION STUDIES :
THE HYDROCHLORINATION OF SiCl_4 AND M.G. Si
AT 300 PSIG, 500°C AND H_2/SiCl_4 RATIO OF 1.0

Year
Month of Year
Month of Contract

1979												1980												1981		
4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3			
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
II	Finalize Reactor Design, Order Equipment
III	Construct Hydrogenation Apparatus
IV	Safety Review, Start-Up, Standardization

+		
1 2		
2 3 4 5		
5		

V Process Studies

A. Reaction Kinetics

- (1) Function of $T, P, H_2/SiCl_4$: with no Catalyst
- (2) Establish Rate Equation, Reaction Order
- (3) Copper Catalyst Studies: $T, P, H_2/SiCl_4$
- (4) Particle Size Distribution, Surface Area
- (5) Different Grade of MG Si

B. Mass Life Studies

- (1) With no Catalyst Added
- (2) With Cu Catalyst Added
- (3) Different Grade of MG Si

5 6 7 8			
8 9			
8 9 10 11 12 13			
	13 14 15		
	14 15 16		
		16 17 18	
		18 19 20	
		20 21	22

VI Research and Development

A. Method of Preparing Cu/Si Mass

- (1) Literature Studies
- (2) Prepare Cu/Si Mass
- (3) Evaluation and Optimization

B. Reaction Mechanism Studies

- (1) Literature Studies
- (2) Identify Reaction Intermediates: HCl, etc.
- (3) Identify Intermediate Reaction Steps
- (4) Nature of the Equilibrium Reactions
- (5) The Role of Copper Catalyst
 - a. Nature of the Catalytic Sites
 - b. Copper Transport Mechanism
 - c. Copper Distribution on Solid Si Surfaces
- (6) Kinetic Isotope Effect

C. Other Hydrogenation Catalysts

	▲		▲		▲	
1 2 3 4 5 6 7 8						
5 6 7 8						
0 9 10 11 12 13						
1 2 3 4 5 6 7 8						
6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21						
6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21						
6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21						
0 9 10 11 12 13 14 15						
0 9 10 11 12 13 14 15						
0 9 10 11 12 13 14 15						
	▲					22 23
	▲					22 23

VII Reports

- A. Recommendation on Optimum Reaction Conditions
- B. Recommendation for Additional Development Work
- C. Final Report

9	14	19	23
9	14		23
			23 24

▲ Milestone Check Points