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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

QUARTERLY REPORT

October 10, 1979

CONTRACT NO. 955382

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ABSTRACT

A laboratory stainless steel reactor has been constructed and installed to study the hydrogenation of SiCl_4 ,

The pressure reactor is designed to operate at pressures up to 500 psig and at temperatures up to 600°C. After pressure and leak tests, the apparatus was started-up for the hydrogenation experiments. Temperature and flowrate measurements were calibrated. A safety review showed that the apparatus functioned smoothly and satisfactorily as designed. Experiments on the hydrogenation of SiCl_4 were carried out during the last two weeks of September.

A series of experiments on the hydrogenation of SiCl_4 was carried out at reactor pressure of 300 psig and 500 psig. Reaction temperature varies from 450°C to 550°C. Some preliminary reaction kinetic data and equilibrium data were collected. More hydrogenation experiments are in progress.

INTRODUCTION

Work on the JPL Government Contract no. 955 382 began in April of this year to study the hydrogenation of SiCl_4 to SiHCl_3 . This report is the second Quarterly Report. Activities during this quarter include the completion of the hydrogenation apparatus, calibration of instruments, safety review and carrying out preliminary hydrogenation experiments.

DISCUSSION

A. The Hydrogenation Apparatus

The laboratory stainless steel reactor for the hydrogenation of SiCl_4 is schematically shown in Figure 1. The design and function of the hydrogenation apparatus was reported in details in the first Quarterly Report (DOE/JPL 955 382 - 79/1). Construction and installation of the hydrogenation apparatus were completed in late August. Then, the apparatus was leak tested and pressure tested. Instruments were calibrated. The temperature controller for the hydrogenation reactor was calibrated with a standardized mercury-filled thermometer. The mass flowmeter readings for the hydrogen gas flowrate were standardized with an independent method of measurement by water displacement. Variable transformer settings for the electrical heaters were calibrated against the selected temperatures. The in-line gas chromatograph was conditioned and calibrated. Finally, a safety review was conducted. The hydrogenation apparatus functions satisfactorily as designed.

B. Preliminary Experiments on the Hydrogenation of SiCl_4

After a thorough shake-down of the hydrogenation apparatus, the reactor was started-up for some hydrogenation experiments.

Initially, the experiments were carried out at 300 psig. Then, the reactor pressure was raised to the designed pressure of 500 psig.

The first attempt was to measure the equilibrium constant at 300 psig as a function of reactor temperature.

Long residence time (about 3 minutes) was allowed for the hydrogenation reaction to equilibrate. Results of this experiment are given in Table I. The chlorosilane product compositions in Table I show a steady rise of SiH_2Cl_2 and SiHCl_3 conversions with respect to rising reactor temperatures. However, later experiments at 500 psig showed that the hydrogenation reaction(1) approaches equilibrium very slowly. This is shown in the following series of experiments carried out at 500 psig and at 500°C with a H_2/SiCl_4 ratio of 2.8. Result of this experiment is summarized in Table II. Data in Table II showed that the SiH_2Cl_2 and SiHCl_3 conversions raise steadily with respect to increasing residence time. The reaction has not yet reached equilibrium as shown by the varying chlorosilane product compositions between 117 seconds and at 215 seconds residence time. At 500 psig, the hydrogenation reaction approaches equilibrium very slowly. For example, at 215 seconds residence time, the SiHCl_3 conversion (35.62%) increases only a few percent from the value obtained at 65 seconds residence time (32.19%).

SUMMARY OF PROGRESS

Experimental work on the hydrogenation studies has progressed on schedule according to the attached Program Plan. After carrying

out these preliminary hydrogenation experiments, the apparatus has been fine-tuned to operate smoothly and satisfactorily. Reproducibility of the in-line gas chromatographic analysis is excellent. More experiments are in progress.

PROJECTED THIRD QUARTER ACTIVITIES

Planned activities for the third quarter (October-December) include:

- continue experiments on the hydrogenation of SiCl_4 to SiHCl_3
- collect reaction kinetic data as functions of T, P, H_2/SiCl_4 ratio
- collect equilibrium data as functions of T

TABLE I Hydrogenation of SiCl_4 at 300 psig with H_2/SiCl_4 1.4 Ratio

Reactor Temperature °C	Residence Time Second	Chlorosilane SiH_2Cl_2	Product mole % SiHCl_3	Composition SiCl_4
450	196	0.74	29.82	69.45
475	205	0.92	31.85	67.23
500	190	1.04	32.91	66.06
525	188	1.17	33.88	64.97
550	208	1.27	34.16	64.57

TABLE II Hydrogenation of SiCl_4 at 500 psig, 500°C and
 H_2/SiCl_4 2.8 Ratio

Hydrogen Gas Feedrate SCCM ⁽¹⁾	Residence Time Second	Chlorosilane SiH_2Cl_2	Product mole % SiHCl_3	Composition SiCl_4
1290	65	1.19	32.19	66.63
925	91	1.29	33.36	65.36
720	117	1.39	34.04	64.57
393	215	1.40	35.62	62.94

(1) Standard c.c. per minute

FIGURE 1 Apparatus For The Hydrogenation Of SiCl_4 To SiHCl_3

PROGRAM PLANInvestigation of the Hydrogenation of SiCl_4

(JPL Contract No. 955382)

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	4	5	6
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27

- I Program Plan, Laboratory Site Preparation
 II Finalize Reactor Design, Order Equipment
 III Construct Hydrogenation Apparatus
 IV Safety Review, Start-Up, Standardization

+		
+		
+		
+		

V Process Studies**A. Reaction Kinetics**

- (1) Function of $\text{T, P, H}_2/\text{SiCl}_4$ with no Catalyst
- (2) Establish Rate Equation, Reaction Order
- (3) Copper Catalyst Studies: $\text{T, P, H}_2/\text{SiCl}_4$
- (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

▲	▲	▲	
± ± ± ± ± ± ± ±			
5 6 7 8			
8 9	10 11 12 13		
± ± ± ± ± ± ± ±			
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		
8 9	10 11 12 13 14 15		
8 9	10 11 12 13 14 15		
8 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