Reaction of Magnesium Silicide & Silicon Tetrachloride/Trichlorosilane in Presence of Hydrogen†

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Received 3 December 1987; revised and accepted 12 February 1988

The formation of silane (SiH₄) has been observed during the reaction of silicon tetrachloride and hydrogen (SiCl₄ + H₂) with magnesium silicide (Mg₂Si) at 400-500°C. The silane formed decomposes to give silicon in the vicinity of Mg₂Si charge. A mixture of trichlorosilane + H₂ reacts with Mg₂Si at 250°C to afford silane which has been separated and decomposed to high purity silicon. The reaction of SiHCl₃ + H₂ with Mg₂Si gives optimum conversion when SiHCl₃:H₂ ratio is 1:4 at the reaction temperature of 250°C.

A major proportion of high purity silicon used in semiconductor industry is produced by the Siemen's process¹ which involves chemical vapour deposition of trichlorosilane (TCS) onto hot silicon filament. However, the process has some basic disadvantages such as low conversion efficiency of TCS to Si, high energy requirements in the process and problems associated with separation and recycling of byproduct silicon tetrachloride (STC).

Recently SiH₄ (silane) as well as dichlorosilane (DCS), SiH₂Cl₂, have been tried² for the production of silicon on pilot plant scale. The advantage of using silane is that its boiling point is lower than that of TCS and it is easier to purify it to a higher level than any other chlorosilane. Union Carbide Corporation³ has developed a process for the preparation of SiH₄ by hydrogenation of SiCl₄ under high pressure and by successive disproportionation of intermediate chlorosilanes to SiH₄. Silane can also be generated by the reaction of Mg₂Si and NH₄Br at low temperature⁴. We have tried to prepare SiH₄ by hydrogenation of SiCl₄ (STC) as well as SiHCl₃ (TCS), using various hydrogenating catalysts. It has been observed by us that in the presence of Mg₂Si and H₂, TCS and STC can be converted into silane. The reaction of Mg₂Si, STC and TCS was studied in detail and the results are given in this paper.

Materials and Methods
The experimental set-up for the preparation of silane is shown in Fig. 1. A mixture of Mg powder (AR) and silicon (metallurgical grade) in the weight ratio of 64:36 (50 g) was heated in a previously weighed quartz tubular reactor (B) for 6 hr under H₂ atmosphere at 480-500°C. This treatment was found to be adequate to form Mg₂Si, as confirmed by X-ray diffraction. The temperature of the reactor tube was then reduced to the desired reaction temperature (250-500°C) and a mixture of H₂ and STC (300 g) was passed through it. The ratio of H₂/STC was maintained by (i) adjusting the bath temperature

![Fig. 1—Schematic diagram of experimental set-up](image-url)
of STC and (ii) the quantity of \( \text{H}_2 \) bubbled through STC.

The condensable portion of the exit gas was condensed using three liquid nitrogen traps successively. The condensed portion was first scrubbed through distilled deionized water to hydrolyse any chlorosilane which had escaped condensation and finally through silver nitrate solution to estimate silane, as silane reacts quantitatively with \( \text{AgNO}_3 \), reducing it to metallic silver and giving free silicon. The condensed gases were analysed by gas chromatography.

On completion of the experiment the reactor tube was cooled to room temperature and was weighed immediately to minimise any absorption of moisture. The powder was boiled with distilled deionized water to dissolve \( \text{MgCl}_2 \). The Mg and Cl in solution were estimated quantitatively. The unreacted \( \text{Mg}_2\text{Si} \) was decomposed by AR \( \text{HCl} \) (1:1) and Mg was again estimated quantitatively from the \( \text{MgCl}_2 \) solution. The silica was removed by reacting the residue with HF and subsequent evaporation in a platinum crucible and finally free silicon was weighed. The purity of Si was determined spectrographically.

The temperature of reactor was varied from 300 to 500°C and the effect of temperature on the efficiency of reduction (\( \text{SiCl}_4 \) to Si) was studied. Ratio of \( \text{H}/\text{SiCl}_4 \) was also varied at each temperature.

In another set of experiments, \( \text{Mg}_2\text{Si} \) was prepared as above, STC was passed over it in the absence of \( \text{H}_2 \). Here, pure \( \text{N}_2 \) was used as the carrier gas. In this case also the analytical processes were repeated as narrated above.

**Results and Discussion**

On cooling the reactor at the end of the experiment it was observed that a mirror like silicon deposition had occurred on the walls of the reactor tube away from the original \( \text{Mg}_2\text{Si} \) which was indicative of the formation of a volatile compound of silicon presumably \( \text{SiH}_4 \). The reactor tube was weighed immediately and the increase in weight was noted. \( \text{MgCl}_2 \) and unreacted \( \text{Mg}_2\text{Si} \) were removed as described earlier and finally free silicon was weighed. The reaction was poor below 400°C. At 500°C the amount of \( \text{Mg}_2\text{Si} \) remaining unreacted was less than 2%. STC and \( \text{H}_2 \) were kept in excess. The entire unreacted STC was collected in the traps.

The formation of silane, TCS, \( \text{SiH}_2\text{Cl}_2 \) (DCS), \( \text{SiH}_3\text{Cl} \) (MCS) is confirmed in all experiments by gas chromatographic analysis using Perkin-Elmer (Sigma 3B) gas chromatograph and Sigma 15 data station. An SE-52 column (length = 12 inches; int. diam. = 1/8 inch) was used for the analysis.

The various probable primary and secondary reactions alongwith thermodynamic parameters are listed in Table 1.

Amongst the various reactions given in Table 1, reaction (i) is thermodynamically highly favourable, still it does not appear to be occurring when the reaction is carried out in the absence of \( \text{H}_2 \) using \( \text{N}_2 \) as carrier gas. Neither mirror-like deposition on the walls of reactor tube nor formation of \( \text{MgCl}_2 \) was detected hence reaction is considered to take place as per Eq. (ii) or Eq. (iii) (see Table 1). The formations of TCS, DCS, MCS are due to the secondary reactions (iv) and (v) (Table 1) which are also thermodynamically favourable.

\( \text{Mg}_2\text{Si} \) contains small amounts of Mg and MgO as revealed by the X-ray diffraction pattern of \( \text{Mg}_2\text{Si} \), Mg, MgO,\( \text{Mg}_2\text{Si} \) is used for hydrogen storage and its adsorption-desorption property has been studied. The Mg-MgO and \( \text{Mg}_2\text{Si} \) adsorb hydrogen used for hydrogenation, the molecular hydrogen dissociates and reacts with STC (see reactions vi-viii) leading to reaction (iii) (Table 1).

<table>
<thead>
<tr>
<th>Probable reaction</th>
<th>( \Delta F ) (kcal mol(^{-1}))</th>
<th>( \Delta H ) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( (800 \text{ K}) )</td>
<td>( (600 \text{ K}) )</td>
</tr>
<tr>
<td>Primary reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) ( \text{Mg}_2\text{Si} + \text{SiCl}_4 = 2 \text{MgCl}_2 + 2 \text{Si} )</td>
<td>-92</td>
<td>-97</td>
</tr>
<tr>
<td>(ii) ( \text{Mg}_2\text{Si} + \text{SiCl}_4 + 2 \text{H}_2 = 2 \text{MgCl}_2 + \text{Si} + \text{SiH}_4 )</td>
<td>-71</td>
<td>-74</td>
</tr>
<tr>
<td>(iii) ( \text{Mg}_2\text{Si} + \text{SiCl}_4 + 4\text{H}_2 = 2 \text{MgCl}_2 + 2 \text{SiH}_4 )</td>
<td>-47</td>
<td>-56</td>
</tr>
<tr>
<td>Secondary reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iv) ( \text{SiH}_4 + \text{SiCl}_4 = \text{SiHCl}_4 + \text{SiH}_2\text{Cl}_3 )</td>
<td>-16.08</td>
<td>-14.85</td>
</tr>
<tr>
<td>(v) ( \text{SiCl}_4 + \text{SiH}_4 = 2 \text{SiH}_2\text{Cl}_3 )</td>
<td>-7.74</td>
<td>-6.06</td>
</tr>
</tbody>
</table>

*Free energy changes (\( \Delta F \)) and heat of formation (\( \Delta H \)) are calculated from thermodynamic values given in Janaf Thermochemical Table*.
2 Mg$_2$Si + H$_2$ → 2 Mg$_3$Si(−H)* ... (vi)
8 Mg$_2$Si − H + SiCl$_4$ → 8 Mg$_2$Si + SiH$_4$ + 4 HCl ... (vii)
Mg$_2$Si + 4 HCl → 2 MgCl$_2$ + SiH$_4$ ... (viii)

The HCl formed in the reaction (viii) reacts with Mg$_2$Si leading to the formation of silane which is one of the conventional methods for preparation of silane from Mg$_2$Si (see ref. 9).

From these observations it can be inferred that silane is formed during the hydrogenation of STC in the presence of Mg$_2$Si, which further decomposes to Si at the reaction temperature 500°C.

Experiments on the same lines were carried out to study the hydrogenation of trichlorosilane (TCS) using Mg$_2$Si and hydrogen. For this purpose a mixture of TCS and H in the molar ratio of 1:4 was preheated at 500°C and then passed over the Mg$_2$Si charge which was heated up to 220°C. A cracking sound was heard at 220°C which increased in its magnitude with increase in temperature up to 250°C. The reaction was carried out for 4 hr and the effluent gases were condensed in the liquid nitrogen traps and gases were analysed by the online gas chromatograph. The analysis showed presence of silane, lower chlorosilanes and unreacted TCS, STC and hydrochloric acid.

After completion of the reaction, the Mg$_2$Si charge was cooled to room temperature under H$_2$ atmosphere. A thin layer of shining silicon was deposited on the inner wall of the reactor in the vicinity of Mg$_2$Si, with marginal increase in the weight of the charge.

In another experiment the effluent gases of SiHCl$_3$ and H$_2$ reaction in the presence of Mg$_2$Si were passed through a separate silica tube reactor heated at 500°C. After completion of the reaction the reactor tube was cooled to room temperature under H$_2$ atmosphere. It was found that a thick coating of silicon was deposited in the separate tube. This is a clear indication of formation of silane in the hydrogenation of TCS in the presence of Mg$_2$Si at 250°C, which further decomposes to Si at 500°C in the second reactor.

There was a marginal increase in the weight of Mg$_2$Si charge after the reaction. The molecular hydrogen passing over hot Mg$_2$Si gets converted (dissociated) into atomic hydrogen which in turn reduces TCS to silane. The plausible chemical reactions can be written as follows:

Mg$_2$Si + 2 SiHCl$_3$ + 6 H$_2$ → 2 MgCl$_2$ + 3 SiH$_4$ + 2 HCl ... (ix)
3 Mg$_2$Si + 4 SiHCl$_3$ + 12 H$_2$ → 6 MgCl$_2$ + 7 SiH$_4$ ... (x)

The formation of silane from TCS and STC by hydrogenation in the presence of Mg$_2$Si is an interesting reaction and needs further investigation for its commercial exploitation.

References
6 Janaf Thermochemical Table, Aug. 1965.