Title: METHOD FOR PRODUCTION OF TRICHLOROSILANE AND SILICON FOR USE IN THE PRODUCTION OF TRICHLOROSILANE

Abstract: The present invention relates to a method for the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, and a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, where the silicon supplied to the reactor contains less than 50 ppmw manganese. The invention further relates to a method for producing silicon for use in the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, and a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, said silicon containing less than 50 ppmw manganese.
Title of Invention
Method for production of trichlorosilane and silicon for use in the production of trichlorosilane.

Field of Invention
The present invention relates to a method for the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas, and silicon for the use in production of trichlorosilane from silicon tetrachloride and hydrogen.

Background Art
In the method of production of trichlorosilane (TCS), metallurgical grade silicon is reacted with silicon tetrachloride (STC) gas and hydrogen gas in a fluidized bed reactor, solid bed reactor or in a stirred bed reactor (US patent 4676967). The process is generally carried out at a temperature between 400 and 600°C.

\[ Si + 3SiCl_4 + 2H_2 = 4HSiCl_3 \]

TCS can also be produced by reacting metallurgical grade with hydrogen chloride (HCl) gas in a fluidized bed reactor, solid bed reactor or in a stirred bed reactor. This process is generally carried out at a temperature between 250 and 1100°C. In the reaction, other volatile silanes than TCS are also formed, mainly STC. The amount of STC is typically about 10-85% depending on the reactor temperature, impurity content in the metallurgical silicon and any catalysts added to the reactor.

\[ Si + 3HCl = HSiCl_3 + H_2 \]
\[ Si + 4HCl = SiCl_4 + 2H_2 \]

STC is also produced in large amounts during decomposition of TCS to pure silicon and in the redistribution reactions to produce silane (SiH₄) from TCS.

\[ 4HSiCl_3 = Si + 3SiCl_4 + 2H_2 \]
\[ 4HSiCl_3 = SiH_4 + 3SiCl_4 \]
STC is mainly used to produce silicon dioxide (fume silica) by reacting STC with hydrogen and oxygen. Some STC is also used to produce optical fibres or sold to other applications. In general too much STC is available in the market and recycling is required to balance the production.

The advantage of reacting STC with metallurgical silicon and hydrogen is that the by-product from the decomposition or redistribution step is recycled to TCS. Recycling will reduce the amount of silicon required to produce polysilicon since the silicon that otherwise produces STC will be converted to polysilicon. Only part of the STC can be converted to TCS in one reactor pass and maximum conversion of STC is given by the equilibrium composition. Complete conversion of the STC requires multiple reactor passes and subsequent distillations to remove TCS. Normally, the conversion of STC in one reactor pass is lower than predicted from the equilibrium composition due to the fact that reaction kinetics are important at these temperatures.

Additions of catalysts to the reactor will increase the conversion (closer to the equilibrium composition), and well known catalysts for this process is copper (any copper source will work) and/or iron (any iron source will work). Iron is always present in metallurgical silicon and will act as a catalyst to increase conversion.

Increased temperature will reduce the effect of reaction kinetics, but also reduce the equilibrium composition of TCS. Higher pressure will favor a higher TCS formation. Diagrams showing the equilibrium conversion of STC as a function of temperature and pressure are shown in Figures 1 and 2.

Metallurgical grade silicon contains a number of contaminating elements like Fe, Ca, Al, Mn, Ni, Zr, O, C, Zn, Ti, B, P and others. Some contaminants will either be inert to STC, or, like Fe and Ca, form solid, stable chlorides. The stable metal chlorides will, depending on their size, either be blown out of the reactor with the silane or be accumulated in the reactor. Other contaminants like Al, Zn, Ti, B and P normally form volatile metal chlorides, which leave the reactor together with the silanes produced.
O and C are enriched in slag particles of the silicon that do not react or react very slowly with STC and tend to accumulate in the reactor. The smallest slag particles can be blown out of the reactor and trapped in the filter systems.

Many of the contaminants in metallurgical grade silicon influence the performance of the silicon in the process of producing trichlorosilane by reaction of silicon with STC and hydrogen.

Disclosure of Invention
It has now been found that the content of manganese in the silicon supplied to the reactor for production of STC and the total amount of manganese in the reactor are important in order to have a STC conversion in the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen.

The present invention thus relates to a method for the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C and a pressure of 0.1 - 30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, which method is characterised in that silicon containing less than 50 ppmw of manganese is added to the reactor.

Preferably the silicon supplied to the reactor contains less than 35 ppmw of manganese.

It has been found that by applying silicon containing less than 50 ppmw to the reactor a high STC conversion is obtained.

The present invention further relates to a method for production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 500°C and a pressure of 0.1 to 30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, which method is characterized in that the amount of manganese in the reactor is kept at a maximum level of 200 ppmw, based on the weight of the silicon in the reactor.

Preferably the amount of manganese in the reactor is kept at a maximum level of 150 ppmw based on the weight of the silicon in the reactor.
It has surprisingly been found that by keeping the manganese content in the reactor at a maximum level of 200 ppmw, conversion of silicon tetrachloride, and thereby also the amount of silicon consumed, is increased.

The present invention further relates to a method for the production of silicon containing less than 50 ppmw manganese by carbothermic reduction of quartz for use in the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C and at a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, which method is characterized in that the manganese content in the silicon produced is controlled by selecting raw materials having a low content of manganese and by using electrodes, electrode paste and electrode casings having a low content of manganese.

In order to further reduce the manganese content in the silicon produced by the present invention the silicon may after solidification be leached, preferably with HF, HCl and/or FeCl₃ solution.

The present invention also relates to a method for grinding and milling silicon containing less than 50 ppmw manganese for use in the production of trichlorosilane by reaction of the silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, which method is characterized in that the milling and grinding are carried out using grinding bodies having a low manganese content.

Finally, the present invention relates to the use of silicon containing less than 50 ppmw manganese for the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas.

**Short description of the drawings**

Figures 1 and 2 show diagrams for theoretical conversion of STC (based on equilibrium calculation).

Figures 3 to 6 show diagrams for STC conversion in a fluidized bed reactor, described as first pass STC conversion in the process of the present invention.
Detailed description of the invention

The following examples 1 to 4 were all carried out in a continuous laboratory fluidized bed reactor made from carbon steel and embedded in a heated copper block. The temperature and pressure in the reactor was kept at 550°C and 4 bar respectively. For each test, 5 gram of silicon having a particle size of between 125 and 180 µm was added to the reactor. 5 grams of silicon is maintained in the reactor by continuously replacing reacted silicon with new silicon. 0.08 grams of CuCl (equal to 1% copper) was added to the reactor with the first 5 grams charged to the reactor. A mixture of 335 normal ml/min of hydrogen, 168 normal ml/min (69 grams/hour) silicon tetrachloride and 56 normal ml/min argon were supplied to the reactor. The composition of the product gas from the reactor, mainly STC and TCS was measured with a gas chromatograph (GC). Argon is used as an internal standard for the GC measurements. The reactivity of the samples was measured as first pass conversion of silicon tetrachloride.

Example 1

Synthetic silicon samples of highly pure silicon alloyed with 0.21% Fe, 0.12% Al and 25, 50 and 200 ppmw Mn respectively were produced in an induction furnace, milled and screened to a particle size between 125 and 180 µm (samples A, B, C). A silicon with a very low Mn content of 1 ppmw was produced in the same way and is identified as sample D.

The chemical compositions of samples A, B, C and D are given in Table 1.

Table 1. Chemical analysis of the synthetic silicon samples A through D

<table>
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<tr>
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<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al weight %</td>
<td>0.094</td>
<td>0.076</td>
<td>0.104</td>
<td>0.119</td>
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<tr>
<td>Ca weight %</td>
<td>0.0009</td>
<td>0.0008</td>
<td>0.0014</td>
<td>0.0009</td>
</tr>
<tr>
<td>Fe weight %</td>
<td>0.175</td>
<td>0.173</td>
<td>0.192</td>
<td>0.213</td>
</tr>
<tr>
<td>Zr ppmw</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Cu ppmw</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Ni ppmw</td>
<td>7</td>
<td>3</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Cr ppmw</td>
<td>8</td>
<td>0</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>V ppmw</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ti ppmw</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>B ppmw</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P ppmw</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mn ppmw</td>
<td>8</td>
<td>35</td>
<td>182</td>
<td>1</td>
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</table>
Samples A, B, C and D were used to produce trichlorosilane at 550°C in a continuous laboratory fluidized bed reactor as described above. The STC conversion obtained with samples A, B, C and D is shown in Figure 3.

As can be seen from Figure 3, the STC conversion increases with decreasing manganese content in the silicon with a very high STC conversion for samples A, B and D according to the invention.

**Example 2**

Silicon, produced by Elkem AS, Bremanger Smelteverk, containing 5 ppmw manganese was milled and screened to a particle size between 125 and 180 µm (sample E). 50 mg (1% by weight) of manganese powder was added to the reactor when about 25% of the initial silicon had been consumed.

The chemical analysis of sample E is shown in Table 2.

STC conversion of sample E without any manganese addition and STC conversion of sample E with manganese addition is shown in Figure 4.

As can be seen from Figure 4, addition of 1% by weight Mn reduces the STC conversion with more than 75%. This clearly shows that if the manganese content in the reactor is increased, the STC conversion drops dramatically.

**Example 3**

A synthetic silicon sample of highly pure silicon alloyed with 0.21% Fe, 0.12% Al was produced in an induction furnace, milled and screened to a particle size between 125 and 180 µm (sample D).

The chemical compositions of sample D is given in Table 1.

Sample D was used to produce trichlorosilane at 550°C in a continuous laboratory fluidized bed reactor as described above.

10 mg (200 ppmw) of manganese powder was added to the reactor when about 28% of the initial silicon had been consumed.

The STC conversion obtained with sample D with an addition of 200 ppmw manganese is shown in Figure 5.
As can be seen from Figure 5, addition of 200 ppmw Mn reduces the STC conversion with about 35%. It is thus important to keep the amount of Mn in the reactor at low level in order to maintain a high STC conversion. The STC conversion is very high for samples E and F according to the invention.

Example 4
Several silicon samples with varying manganese content were milled and screened to a particle size between 125 and 180 µm (samples E, F, G, H, I).

The chemical analyses of the samples E through I are shown in Table 2.

Samples E, F, G, H and I were used to produce trichlorosilane at 550°C in a continuous laboratory fluidized bed reactor as described above. Two runs were made with sample E. The STC conversion obtained with samples E through I is shown in Figure 6.

As can be seen from Figure 6, the STC conversion drops with increasing manganese content. The STC conversion is very high for samples E and F according to the invention.

<table>
<thead>
<tr>
<th></th>
<th>Sample E</th>
<th>Sample F</th>
<th>Sample G</th>
<th>Sample H</th>
<th>Sample I</th>
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<tbody>
<tr>
<td>Al weight %</td>
<td>0.140</td>
<td>0.247</td>
<td>0.096</td>
<td>0.090</td>
<td>0.120</td>
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<td>Ca weight %</td>
<td>0.015</td>
<td>0.020</td>
<td>0.062</td>
<td>0.030</td>
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<tr>
<td>Fe weight %</td>
<td>0.095</td>
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<td>0.410</td>
<td>0.170</td>
<td>0.400</td>
</tr>
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<td>15</td>
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<td>13</td>
<td>10</td>
<td>21</td>
</tr>
<tr>
<td>Cu ppmw</td>
<td>1</td>
<td>2</td>
<td>650</td>
<td>7</td>
<td>980</td>
</tr>
<tr>
<td>Ni ppmw</td>
<td>1</td>
<td>3</td>
<td>26</td>
<td>60</td>
<td>16</td>
</tr>
<tr>
<td>Cr ppmw</td>
<td>3</td>
<td>2</td>
<td>9</td>
<td>5</td>
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<tr>
<td>V ppmw</td>
<td>3</td>
<td>2</td>
<td>73</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>Ti ppmw</td>
<td>93</td>
<td>160</td>
<td>150</td>
<td>200</td>
<td>260</td>
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<tr>
<td>B ppmw</td>
<td>25</td>
<td>26</td>
<td>7</td>
<td>45</td>
<td>18</td>
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<tr>
<td>P ppmw</td>
<td>32</td>
<td>31</td>
<td>26</td>
<td>20</td>
<td>24</td>
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<td>Mn ppmw</td>
<td>5</td>
<td>10</td>
<td>77</td>
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Claims:

1. Method for the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, and a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, characterized in that the silicon supplied to the reactor contains less than 50 ppmw manganese.

2. Method according to claim 1, characterized in that the silicon supplied to the reactor contains less than 35 ppmw manganese.

3. Method for production of silicon containing less than 50 ppmw manganese by carbothermic reduction of quartz for use in production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, and at a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, characterized in that the manganese content in the silicon is controlled by selecting raw materials having a low content of manganese.

4. Method according to claim 3, characterized in that the silicon with less than 50 ppmw is produced by using electrodes, electrode paste and electrode casings having a low content of manganese.

5. Method according to claim 3, characterized in that the silicon after solidification is leached with HF, HCl and/or FeCb to reduce the manganese content.

6. Method for milling and/or grinding of silicon containing less than 50 ppmw manganese for use in production of trichlorosilane by reaction of the silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, and a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, characterized in that the silicon is milled using grinding bodies having a low content of manganese.

7. Method for production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and
800°C and a pressure of 0.1 to 30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, characterized in that the content of a manganese in the reactor is kept at a maximum of 200 ppmw based on weight of the silicon in the reactor.

8. Method according to claim 7, characterized in that the manganese content in the reactor is kept at maximum of 150 ppmw based on the weight of silicon in the reactor.

9. Use of silicon containing less than 50 ppmw manganese for the production of trichlorosilane by reaction of silicon with silicon tetrachloride and hydrogen gas at a temperature between 400 and 800°C, and a pressure of 0.1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor.
Figure 4

- Sample E
- Sample E, Mn added

1% Mn from top
1% Mn from bottom
A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: COIB

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<td>X1</td>
<td>T. Lobreyer et al., Silicon for trichlorosilane production basic research and development, Silicon for the chemical industry III, Sandefjord, Norway, June 18-20, 1996, pages 147-155 page 1, abstract</td>
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Further documents are listed in the continuation of Box C.

Date of the actual completion of the international search: 19 December 2006

Date of mailing of the international search report: 28-12-2006

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Moa Grönkvist/MP
Telephone No. + 46 8 782 25 00

Form PCT/IS A/210 (second sheet) (April 2005)
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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<tr>
<td>A</td>
<td>M. Rong et al., &quot;Aluminium as a promotor for the direct process to methyl chlorosilanes&quot;, Silicon for the chemical industry III, Sandefjord, Norway, June 18-20, 1996, pages 157-167 table 1, abstract</td>
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<td>A</td>
<td>A. Schei et al., &quot;Impurity distribution in silicon&quot;, Silicon for the chemical industry III, Sandefjord, Norway, June 18-20, 1992, pages 11-23 table 1, abstract</td>
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<td>WO 2006031120 A1 (ELKEM AS), 23 March 2006 (23.03.2006), whole document</td>
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International patent classification (IPC)

COlB 33/107 (2006.01)

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Cited literature, if any, will be enclosed in paper form.
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