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(54) **PROCESS FOR PRODUCING TRICHLOROSILANE WITH STRUCTURE-OPTIMISED SILICON PARTICLES**

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(57) **ABSTRACT**

Chlorosilanes and methods of producing chlorosilanes. The process for producing chlorosilanes includes the step of selecting a chlorosilane having a general formulae (1) H_nSiCl_{4-n} and (2) $H_mCl_{6-m}Si_2$ wherein n is 0 to 3 and m is from 0 to 4. The chlorosilane selected is then placed within a fluidized bed reactor. A hydrogen chloride-containing reaction gas is reacted with a particulate contact mass containing silicon at temperatures of 280° C. to 400° C. Where the operating granulation, understood as meaning the granulation or granulation mixture introduced into the fluidized bed reactor, contains at least 1% by mass of silicon-containing particles S described by a structural parameter S and wherein S has a value of at least 0 and is calculated as follows

$$S = (\varphi_s - 0.70) \cdot \frac{\rho_{SD}}{\rho_F}$$

Wherein φ_S is symmetry-weighted sphericity factor, ρ_{SD} is poured density [g/cm^3], and ρ_F is average particle solids density [g/cm^3].
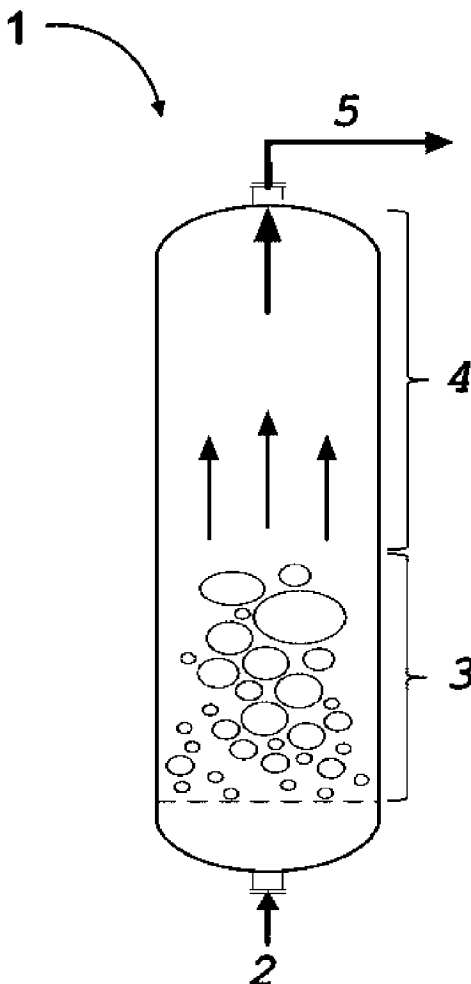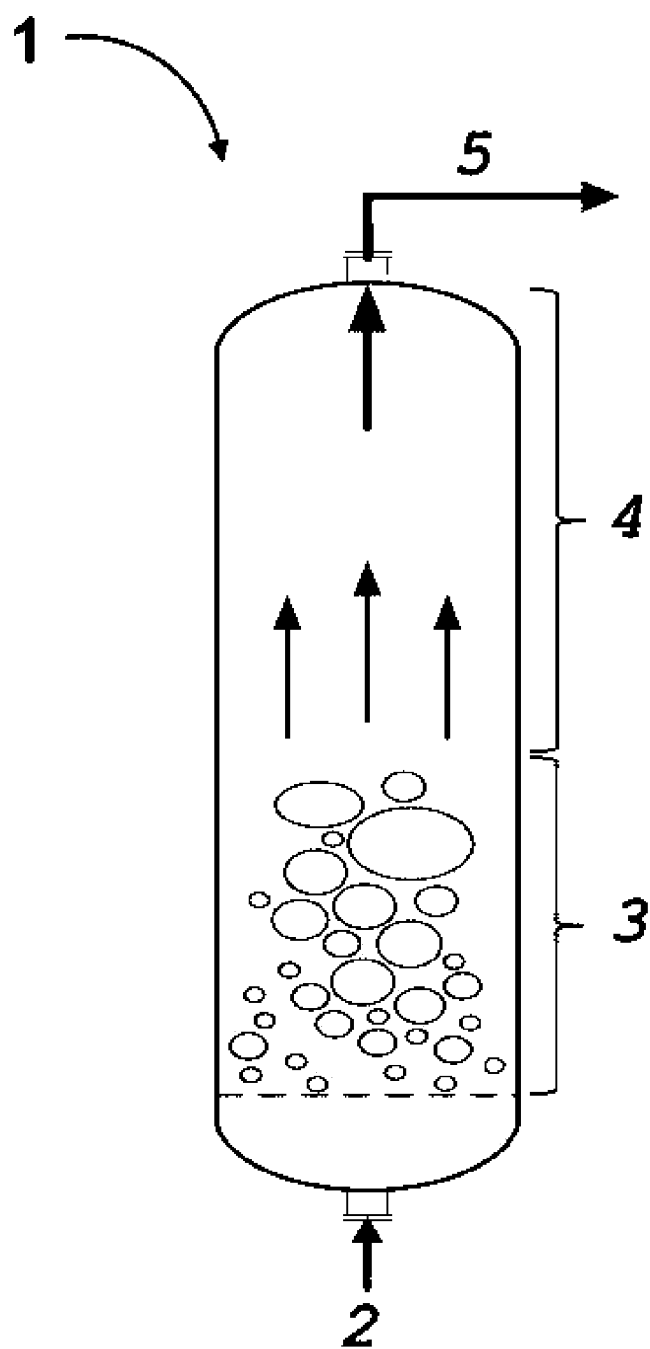
Fig. 1

PROCESS FOR PRODUCING TRICHLOROSILANE WITH STRUCTURE-OPTIMISED SILICON PARTICLES
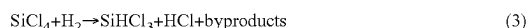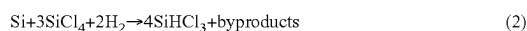
CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation application of the co-pending U.S. patent application Ser. No. 17/614,958 filed on Nov. 29, 2021, which claims priority to PCT Application No. PCT/EP2019/064116 filed on May 29, 2019, the disclosures of which are incorporated by reference herein in their entirety.

[0002] The invention relates to a process for producing chlorosilanes from a hydrogen chloride-containing reaction gas and a particulate silicon contact mass containing structurally optimized silicon particles in a fluidized bed reactor.

[0003] The production of polycrystalline silicon as a starting material for the manufacture of chips or solar cells is typically carried out by decomposition of volatile halogen compounds thereof, in particular trichlorosilane (TCS, $HSiCl_3$).

[0004] Polycrystalline silicon (polysilicon) may be produced in the form of rods by the Siemens process, wherein polycrystalline silicon is deposited on heated filament rods in a reactor. The process gas employed is typically a mixture of TCS and hydrogen. Alternatively, polycrystalline silicon granulate may be produced in a fluidized bed reactor. Silicon particles are fluidized in a fluidized bed by means of a gas flow, wherein said flow is heated to high temperatures via a heating apparatus. Addition of a silicon-containing reaction gas such as TCS brings about a pyrolysis reaction at the hot particle surface, thus causing the particles to increase in diameter.

[0005] The production of chlorosilanes, in particular TCS, may be carried out essentially by three processes which according to WO2016/198264A1 are based on the following reactions:

$$Si+3HCl \rightarrow SiHCl_3+H_2+byproducts \qquad (1)$$

$$Si+3SiCl_4+2H_2 \rightarrow 4SiHCl_3+byproducts \qquad (2)$$

$$SiCl_4+H_2 \rightarrow SiHCl_3+HCl+byproducts \qquad (3)$$

[0006] The hydrochlorination (HC) according to reaction (1) makes it possible to produce chlorosilanes from silicon (typically metallurgical silicon (Si_{mg})) by addition of hydrogen chloride (HCl) in a fluidized bed reactor, wherein the reaction proceeds exothermically. This generally affords TCS and STC (silicon tetrachloride) as the main products.

[0007] A further option for producing chlorosilanes, in particular TCS, is the thermal conversion of STC and hydrogen in the gas phase in the presence or absence of a catalyst in accordance with reaction (3).

[0008] The low temperature conversion (LTC) according to reaction (2) is a weakly endothermic process and is typically performed in the presence of a catalyst (for example copper-containing catalysts or catalyst mixtures). The LTC may be carried out in a fluidized bed reactor in the presence of Si_{mg} under high pressure (0.5 to 5 MPa) at temperatures between 400° C. und 700° C. An uncatalyzed reaction mode is possible using Si_{mg} and/or by addition of HCl to the reaction gas. However, other product distributions may result and/or lower TCS selectivities may be achieved than in the catalyzed variant.

[0009] The high temperature conversion according to reaction (3) is an endothermic process. This process is typically carried out in a reactor under high pressure at temperatures between 600° C. and 1200° C.

[0010] The demands on the silicon in terms of chemical composition and particle size distribution for the synthesis of chlorosilanes are relatively well studied; by contrast the structural makeup of silicon particles and the influence thereof on the reaction with halide-containing reaction gases has hitherto only been described in relation to intermetallic phases—especially for MRDS (Müller-Rochow direct synthesis). It has not hitherto been described how all three influencing factors must interact in order to operate a particularly high output chlorosilane production process.

[0011] Thus, DE4303766 A1 discloses a process for producing methylchlorosilanes from silicon and chloromethane in the presence of a copper catalyst and optionally promoter substances, wherein the production rate of the individual methylchlorosilanes based on the surface area of the employed silicon are controlled through the structure of the silicon, wherein the process is characterized in that the silicon having the desired structure is selected according to a structural index QF, wherein the structural index QF is determined such that

  [0012] a) silicon test specimens are cut open to form a cut surface,

  [0013] b) on the cut surface the areas of precipitations of intermetallic phases having an elongate shape are summed to form an area number A,

  [0014] c) on the cut surface the areas of precipitations of intermetallic phases having a rounded shape are summed to form an area number B,

  [0015] d) the quotient described as the structural index QF is formed from the area number A and the area number B.

[0016] The correlation of QF of different silicon structure types with their behavior in MRDS allows identification of optimal structural features in the silicon and thus control of selectivity and yields for the desired methylchlorosilanes in the desired direction. In this document the term "structure" relates to the size of the crystals of the polycrystalline silicon and the composition and position of the intermetallic phases, which are precipitated with silicon from the main impurities, for example Al, Ca, Fe and Ti, in the course of cooling and solidification. This document thus merely expands on findings relating to previously mentioned demands on the silicon in terms of chemical composition and for synthesis of organochlorosilanes. Furthermore, this type of manipulation entails the purchase of tailored silicon types and/or operation of corresponding in-house silicon production and enormous analytical effort. The structural index OF may be used to refine the structural parameter S of the present invention but is not essential. Furthermore the application of MRDS findings to HC is possible only to a limited extent, if at all.

[0017] DE3938897 A1 discloses a process for producing trichlorosilanes by reaction of silicon powder with HCl gas in a fluidized/moving bed reactor between 280° C. and 300° C., characterized by the use of a silicon powder obtained by gas atomization of molten silicon. In this process the silicon powder preferably has particle sizes between 50 and 800 μm. This results in higher HCl conversions and reduced byproduct formation compared to conventional processes, an increase in HCl conversion from 90-95% to 97-98% and a reduction of STC in the product gas of 3% to 5% being cited. Since no methods of measurement are reported, no data on the composition of the product gas are provided and it is unclear whether the latter refers to percent by weight, mole percent or percent by volume values, it is not possible to determine to what extent the process represents an optimi-

zation compared to the conventional processes mentioned. Apart from range limits for the particle sizes of the silicon powder, said powder is not characterized in any detail.

[0018] In addition to undesirably high formation of STC and high boilers, process costs are in principle increased as a result of unconverted HCl and unconverted silicon.

[0019] It is known in the production of chlorosilanes in fluidized bed reactors to specifically remove fine grain fractions of the silicon particles to be employed. For example Lobusevich, N. P et al, *"Effect of dispersion of silicon and copper in catalysts on direct synthesis", Khimiya Kremniiorganich. Soed.* 1988, 27-35, recite an operating granulation for silicon of 70 to 500 μm, wherein 70 μm is the minimum and 500 μm is the maximum grain size (grain size limits or range limits) and the values are equivalent diameters. Lobusevich et al. report that when choosing the contact mass grain size for the synthesis of methylchlorosilanes, ethyl chlorosilane and TCS the interaction between solids and gas must be considered in order to achieve maximum stability and efficiency of the process. Thus in the synthesis of TCS (at 400° C.) an operating granulation of 2 to 3 mm resulted in a reduction of the reaction rate by about 25% to 30% compared to an operating granulation of 70 to 500 μm. When copper-containing catalysts are added, the reaction with silicon particles of the operating fraction 2 to 3 mm occurs already at 250° C. The reaction rate matches that of the uncatalyzed variant at 400° C. In both cases-both for the catalyzed variant and for the uncatalyzed variant-increasing the silicon particle size results in an increased TCS selectivity and in a reduced formation of poly(chloro) silanes (high boilers).

[0020] Increasing the particle size in principle entails greater energy costs since a higher reaction temperature is required to accelerate the reaction and a higher gas velocity is required to generate the fluidized bed. While Lobusevich et al. report that use of a proportion of smaller silicon particles in the context of a polydisperse particle mixture enhances the activity of the silicon on account of an increased surface area, the use of proportions of small silicon particles is associated with difficulties since increased discharge of silicon particles from the reactor and aggregation of the particles can occur. It is therefore advantageous according to Lobusevich et al., despite the higher energy costs, to reduce the breadth of the grain size distribution of the employed silicon particles and to increase the average particle size.

[0021] The present invention has for its object to provide a particularly economic process for chlorosilane production via HC.

[0022] The present invention provides a process for producing chlorosilanes which are selected from the general formulae 1 and 2

$$H_nSiCl_{4-n} \tag{1},$$

$$H_mCl_{6-m}Si_2 \tag{2},$$

[0023] in which

[0024] n is 0 to 3 and

[0025] m is from 0 to 4,

[0026] in a fluidized bed reactor, wherein a hydrogen chloride-containing reaction gas is reacted with a particulate contact mass containing silicon at temperatures of 280° C. to 400° C.,

[0027] wherein the operating granulation, understood as meaning the granulation or granulation mixture intro-

duced into the fluidized bed reactor, contains at least 1% by mass of silicon-containing particles S described by a structural parameter S, wherein S has a value of at least 0 and is calculated as follows:

$$S = (\varphi_s - 0.70) \cdot \frac{\rho_{SD}}{\rho_F}, \tag{equation (1)}$$

[0028] wherein

[0029] φ_S is symmetry-weighted sphericity factor

[0030] ρ_{SD} is poured density [g/cm³]

[0031] ρ_F is average particle solids density [g/cm³].

[0032] It has now been found that, surprisingly, the production of chlorosilanes in fluidized bed reactors may be performed particularly economically when silicon-containing particles having certain structural properties are employed in the operating granulation. It was found that this effect is already significantly detectable above a proportion of 1% by mass of the structurally optimized silicon particles S in the operating granulation. The use of precisely such silicon particles S brings about a lasting reduction in the dust fraction <70 μm described in Lobusevich, N. P et al, *"Effect of dispersion of silicon and copper in catalysts on direct synthesis", Khimiya Kremniiorganich. Soed.* 1988, 27-35 in the production process due to a reduction in dust formation through abrasion. This gives rise to several advantages over the prior art:

[0033] higher TCS selectivity

[0034] reduced formation of high boilers

[0035] higher utilization of HCl

[0036] higher silicon utilization (lower losses through dust emission)

[0037] more homogeneous contact mass in terms of particle size distribution and resulting improvement in fluid mechanical properties of the fluidized bed

[0038] reduction in blocked and/or clogged plant parts due to aggregation of finely divided particles or of dust fractions (particles having a particle size <70 μm)

[0039] improved conveyability of the particle mixture

[0040] xtended reactor uptime (higher plant availability) due to reduced wear

[0041] The prejudice of Lobusevich et al. according to which in chlorosilane production TCS selectivity increases only for granulation mixtures of increasing average particle size is also overcome. This is because, according to the invention, the particles S having a structural parameter S of ≥0 preferably have lower average particle sizes than particles having a structural parameter S of <0, thus reducing the average particle size of the operating granulation. Surprisingly, the negative effects to be expected upon reducing average particle size according to the present understanding of the art such as elevated emission of relatively small silicon particles from the reactor and the occurrence of aggregation effects were not observed. On the contrary, the process according to the invention exhibited improved fluidization characteristics of the contact mass in addition to the previously recited advantages.

[0042] The term "granulation" is to be understood as meaning a mixture of silicon-containing particles producible for example by so-called atomization or granulation of silicon-containing melts and/or by comminution of chunk silicon by means of crushing and milling plants. The chunk silicon may preferably have an average particle size of >10

mm, particularly preferably >20 mm, in particular >50 mm. Granulation may be classified into fractions essentially by sieving and/or sifting.

[0043] A mixture of different granulations may be described as a granulation mixture and the granulations making up the granulation mixture as granulation fractions. Granulation fractions may be graded relative to one another according to one or more properties of the fractions such as for example into coarse grain fractions and fine grain fractions. A granulation mixture may in principle be graded into more than one granulation fraction in defined relative fractions.

[0044] The operating granulation describes the granulation or granulation mixture introduced into the fluidized bed reactor.

[0045] The symmetry-weighted sphericity factor φ_S is the product of the symmetry factor and the sphericity. Both shape parameters are determinable by dynamic image analysis according to ISO 13322, wherein the obtained values represent the volume-weighted average over the particular sample of the relevant particle mixture of the operating granulation.

[0046] The symmetry-weighted sphericity factor of the particles S is preferably at least 0.70, particularly preferably at least 0.72, very particularly preferably at least 0.75, in particular at least 0.77 and at most 1.

[0047] The sphericity of a particle describes the ratio between the surface area of a particle image and the circumference. Thus a spherical particle would have a sphericity approaching 1, while a jagged, irregular particle image would have a roundness approaching zero.

[0048] When determining the symmetry factor of a particle the centre of gravity of a particle image is initially determined. Routes from edge to edge through the particular centre of gravity are then drawn in each measurement direction and the ratio of the two resulting route sections measured. The value of the symmetry factor is calculated from the smallest ratio of these radii. For high-symmetry figures such as circles or squares the value of the particular symmetry factor is equal to 1.

[0049] Further shape parameters determinable by dynamic image analysis are the width/length ratio (a measure of the extension/elongation of a particle) and the convexity of particles. However, since said parameters are already indirectly contained in the structural parameter S in the form of the symmetry factor they need not be determined in the process according to the invention.

[0050] The poured density is defined as the density of a mixture of a particulate solid (so-called bulk solid) and a continuous fluid (for example air) that fills the voids between the particles. The poured density of the grain fraction of the operating granulation having a structural parameter S≥0 is preferably 0.8 to 2.0 g/cm³, particularly preferably 1.0 to 1.8 g/cm³, very particularly preferably 1.1 to 1.6 g/cm³, in particular 1.2 to 1.5 g/cm³. Poured density is determinable according to DIN ISO 697 via the ratio of the mass of the bulk material to the occupied volume of the bulk material.

[0051] The average, mass-weighted particle solids density of the particles S of the grain fraction having a structural parameter S≥0 is preferably 2.20 to 2.70 g/cm³, particularly preferably 2.25 to 2.60 g/cm³, very particularly preferably 2.30 to 2.40 g/cm³ in particular 2.31 to 2.38 g/cm³. Determination of the density of solid substances is described in DIN 66137-2:2019-03.

[0052] The grain fraction having a structural parameter S≥0 is present in the operating granulation preferably in a mass fraction of at least 1% by mass, particularly preferably of at least 5% by mass, very particularly preferably of at least 10% by mass, in particular of at least 20% by mass.

[0053] Particles S with S≥0 preferably have a particle size parameter d_{50} which is 0.5 times to 0.9 times the particle size parameter d_{50} of the particles with S<0.

[0054] The operating granulation preferably has a particle size parameter d_{50} of 70 to 1000 μm, particularly preferably of 80 to 800 μm, very particularly preferably of 100 to 600 μm, in particular of 120 to 400 μm.

[0055] The difference between the particle size parameters d_{90} and d_{10} is a measure of breadth of a granulation or a granulation fraction. The quotient of the breadth of a granulation or a granulation fraction and the respective particle size parameter d_{50} corresponds to the relative breadth. This may be used for example to compare particle size distributions having very different average particle sizes.

[0056] The relative breadth of the granulation of the operating granulation is by preference 0.1 to 500, preferably 0.25 to 100, particularly preferably 0.5 to 50, in particular 0.75 to 10.

[0057] Determination of particle sizes and particle size distribution may be carried out according to ISO 13320 (laser diffraction) and/or ISO 13322 (image analysis). Calculation of particle size parameters from particle size distributions may be carried out according to DIN ISO 9276-2.

[0058] In a further preferred embodiment the operating granulation has a mass-weighted surface area of 80 to 1800 cm²/g, preferably of 100 to 600 cm²/g, particularly preferably of 120 to 500 cm²/g, in particular of 150 to 350 cm²/g.

[0059] The granulation mixture of the operating granulation preferably has a p-modal volume-weighted distribution density function, wherein p=1 to 10, preferably p=1 to 6, particularly preferably p=1 to 3, in particular p=1 or 2. For example a 2-modal distribution density function has two maxima.

[0060] The use as the contact mass of granulation mixtures having a polymodal (for example p=5 to 10) distribution density function makes it possible to avoid sifting effects (separation of individual grain fractions in the fluidized bed, for example a bipartite fluidized bed). These effects occur especially when the maxima of the distribution density function of the granulation mixture are far apart.

[0061] The contact mass is in particular the granulation mixture in contact with the reaction gas. The contact mass thus preferably comprises no further components. Said mass is preferably a silicon-containing granulation mixture containing at most 5% by mass, particularly preferably at most 2% by mass, in particular at most 1% by mass, of other elements as impurities. Said mass is preferably Si_{mg} which typically has a purity of 98% to 99.9%. A typical contact mass is for example a composition comprising 98% by mass of silicon metal, wherein the remaining 2% by mass is generally very largely composed of the following elements selected from: Fe, Ca, Al, Ti, Cu, Mn, Cr, V, Ni, Mg, B, C, P and O. The contact mass may also contain the following elements selected from: Co, W, Mo, As, Sb, Bi, S, Se, Te, Zr, Ge, Sn, Pb, Zn, Cd, Sr, Ba, Y and Cl. The use of silicon having a lower purity of 75% to 98% by mass is also

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possible. However, the silicon metal proportion is by preference greater than 75% by mass, preferably greater than 85% by mass, particularly preferably greater than 95% by mass.

[0062] Some of the elements present in the silicon as impurities have a catalytic activity. The addition of a catalyst is therefore not required in principle. However, the process may be positively influenced by the presence of an additional catalyst, in particular in terms of its selectivity.

[0063] The catalyst may be one or more elements from the group comprising Fe, Cr, Ni, Co, Mn, W, Mo, V, P, As, Sb, Bi, O, S, Se, Te, Ti, Zr, C, Ge, Sn, Pb, Cu, Zn, Cd, Mg, Ca, Sr, Ba, B, Al, Y, Cl. The catalyst is preferably selected from the group comprising Fe, Al, Ca, Ni, Mn, Cu, Zn, Sn, C, V, Ti, Cr, B, P, O, Cl and mixtures thereof. As mentioned, these catalytically active elements are already present in silicon in a certain proportion as an impurity, for example in oxidic or metallic form, as silicides or in other metallurgical phases or as oxides or chlorides. Their proportion depends on the purity of the silicon employed.

[0064] The catalyst may be added to the operating granulation and/or contact mass for example in metallic, alloyed and/or salt form. Said catalyst may in particular be chlorides and/or oxides of the catalytically active elements. Preferred compounds are CuCl, $CuCl_2$, CuO or mixtures thereof. The operating granulation may further contain promoters, for example Zn and/or zinc chloride.

[0065] The elemental composition of the employed silicon and the contact mass may be determined for example by X-ray fluorescence analysis (XFA), ICP-based analytical methods (ICP-MS, ICP-OES) and/or atomic absorption spectrometry (AAS).

[0066] Based on silicon the catalyst is preferably employed in a proportion of 0.1% to 20% by mass, particularly preferably of 0.5% to 15% by mass, in particular of 0.8% to 10% by mass, especially preferably of 1% to 5% by mass.

[0067] The grain fractions having structural parameters S<0 and S≥0 are preferably supplied to the fluidized bed reactor as a pre-prepared granulation mixture. Any further constituents of the contact mass may likewise be present. The inventive proportion of a fraction having a structural parameter S≥0 of at least 1% by mass in the operating granulation results in the latter having inter alia better flow and thus conveying characteristics.

[0068] The grain fractions having structural parameters S<0 and S≥0 may also be supplied to the fluidized bed reactor separately, in particular via separate feed conduits and containers. Mixing then takes place in principle upon formation of the fluidized bed (in situ). Any further constituents of the contact mass may likewise be supplied separately or as a constituent of either of the two grain fractions.

[0069] The process is preferably carried out at a temperature of 280° C. to 400° C., particularly preferably 340° C. to 360° C. The absolute pressure in the fluidized bed reactor is preferably 0.01 to 0.6 MPa, particularly preferably 0.03 to 0.35 MPa, in particular 0.05 to 0.3 MPa.

[0070] Before entry into the reactor the reaction gas preferably comprises at least 50% by volume, preferably at least 70% by volume, particularly preferably at least 90% by volume, of HCl. In addition to HCl the reaction gas may further contain one or more components selected from the group comprising H_2, H_nSiCl_{4-n} (n=0 to 4), $H_mCl_{6-m}Si_2$

(m=0 to 6), $H_qCl_{6-q}Si_2O$ (q=0 to 4), $(CH_3)_uH_vSiCl_{4-u-v}$ (u=1 to 4 and v=0 or 1) CH_4, C_2H_6, CO, CO_2, O_2, N_2. These components may derive from HCl recovered in an integrated system. HCl and silicon are by preference present in an HCl/Si molar ratio of 5:1 to 2.5:1, preferably 4:1 to 3:1, particularly preferably 3.6:1 to 3:1, in particular of 3.4:1 to 3.1:1. HCl and the contact mass/granulation mixture or the grain fractions thereof are in particular continuously added during the reaction such that the abovementioned ratio is established.

[0071] The reaction gas may further contain one or more components selected from the group of H_nSiCl_{4-n} (n=0 to 4), $H_mCl_{6-m}Si_2$ (m=0 to 6), $H_qCl_{6-q}Si_2O$ (q=0 to 4), $(CH_3)_uH_vSiCl_{4-u-v}$ (u=1 to 4 and v=0 or 1) CH_4, C_2H_6, CO, CO_2, O_2, N_2. These components may derive from hydrogen recovered in an integrated system for example.

[0072] The reaction gas may further contain a carrier gas which does not take part in the reaction, for example nitrogen or a noble gas such as argon.

[0073] The composition of the reaction gas is typically determined by Raman and infrared spectroscopy and gas chromatography before it is supplied to the reactor. This may be done either via samples taken in the manner of spot checks and subsequent "off-line analyses" or else via "online" analytical instruments connected to the system.

[0074] It is preferable when a quotient of fluidized bed height to reactor diameter in the fluidized bed reactor is 10:1 to 1:1, preferably 8:1 to 2:1, particularly preferably 6:1 to 3:1. The fluidized bed height is the thickness or extent of the fluidized bed.

[0075] The chlorosilanes which are selected from the general formulae 1 and 2 and are produced with the process according to the invention are preferably at least one chlorosilane selected from the group of monochlorosilane, dichlorosilane, TCS, Si_2Cl_6 and HSi_2Cl_5. In the case of chlorosilanes of the general formula 1 TCS is particularly preferred.

[0076] Byproducts that may be generated include further halosilanes, for example monochlorosilane (H_3SiCl), dichlorosilane (H_2SiCl_2), silicon tetrachloride (STC, $SiCl_4$) and di- and oligosilanes. Impurities such as hydrocarbons, organochlorosilanes and metal chlorides may also be byproducts. In order to produce high-purity chlorosilanes which are selected from the general formulae 1 and 2 a distillation of the crude product therefore typically follows.

[0077] The process according to the invention has preferably been incorporated into an integrated system for producing polycrystalline silicon. The integrated system especially comprises the following processes:

[0078] Production of TCS according to the described process.

[0079] Purification of the produced TCS to afford semi-conductor-quality TCS.

[0080] Deposition of polycrystalline silicon, preferably according to the Siemens process or as a granulate.

[0081] Further processing of the obtained polycrystalline silicon.

Recycling of the ultrahigh purity silicon dust generated during production/further processing of the polycrystalline silicon.

[0082] FIG. 1 shows by way of example a fluidized bed reactor 1 for performing the process according to the invention. The reaction gas 2 is preferably blown into the contact mass from below and optionally from the side (for example

tangentially or orthogonally to the gas stream from below), thus fluidizing the particles of the contact mass to form a fluidized bed **3**. To start the reaction the fluidized bed **3** is generally heated using a heating apparatus arranged externally to the reactor (not shown). Heating is typically not required during continuous operation. A portion of the particles is transported out of the fluidized bed **3** into the void **4** above the fluidized bed **3** with the gas flow. The void **4** is characterized by a very low solids density which decreases in the direction of the reactor outlet **5**.

EXAMPLES

[0083] All examples employed silicon of the same type in terms of purity, quality and content of secondary elements and impurities. The grain fractions employed in the operating granulations were produced by crushing chunk Si_{mg} (98.9% by mass Si) and subsequent milling or by atomization techniques known to those skilled in the art to produce particulate Si_{mg} (98.9% by mass Si). Said fractions were optionally classified by sieving/sifting. Grain fractions having certain values for structural parameter S were thus produced in targeted fashion. Contact masses having defined mass fractions of silicon-containing particles having a structural parameter S of not less than 0 were subsequently blended by combining and mixing these grain fractions. The remainder of the grain fractions comprised silicon-containing particles having a structural parameter S of less than 0. The grain fractions together summed to 100% by mass. The granulations employed in the experiments had particle size parameters d_{50} between 330 and 350 μm. To ensure the greatest possible comparability between the individual experiments no additional catalysts or promoters were added.

[0084] The following process was employed in all examples. During the experiments the operating temperature of the fluidized bed reactor was about 320° C. This temperature was kept approximately constant over the entire experimental duration using a cooling means. HCl and the operating granulation were both added in such a way that the height of the fluidized bed remained substantially constant over the entire experimental duration and a constant molar ratio of the reactants (HCl:Si) of 3:1 was established. The reactor was operated at 0.1 MPa of positive pressure over the entire experimental duration. Both a liquid sample and a gas sample were respectively taken at run times of 48 h and 49 h. The condensable proportions of the product gas stream (chlorosilane gas stream) were condensed at −40° C. using a cold trap and analyzed by gas chromatography (GC) before TCS selectivity and the proportion of high boilers [% by weight] were determined therefrom. Detection was via a thermal conductivity detector. The uncondensable content of the product gas stream was analyzed on unreacted HCl [% by volume] using an infrared spectrometer. The obtained values after 48 and 49 h were averaged in each case. After each run the reactor was emptied completely and refilled with contact mass.

[0085] The employed contact masses and the results of the experiments are summarized in table 1. ms is the mass fraction of particles S having a structural parameter S>0.

TABLE 1

Experi-ment	S	mS ≥ 0 [% by mass]	TCS selectivity [% by mass]	Productivity [kg/(kg * h)]	HCl [% by volume]
VB1*	0.005	0.02	84	0.36	8
VB2*	0.005	0.2	85	0.34	7
VB3*	0.005	0.5	85	0.37	8
AB1	0.005	1	87	0.52	4
AB2	0.005	5	88	0.51	4
AB3	0.005	10	88	0.54	3
AB4	0.005	20	89	0.56	3
AB5	0.005	50	89	0.57	3
AB6	0.005	75	90	0.59	2
AB7	0.005	95	88	0.59	2
AB8	0.050	20	90	0.56	3
AB9	0.053	20	91	0.61	2
AB10	0.040	20	89	0.58	3

*not inventive

What is claimed is:

1. A process for producing products, wherein the process comprises:

selecting a chlorosilane having a general formulae (1) or (2)

$$H_nSiCl_{4-n} \qquad (1)$$

$$H_mCl_{6-m}Si_2 \qquad (2)$$

wherein n is 0 to 3 and m is from 0 to 4; and

placing the selected chlorosilane in a fluidized bed reactor, wherein a hydrogen chloride-containing reaction gas is reacted with a particulate contact mass containing silicon at temperatures of 280° C. to 400° C., wherein the operating granulation, understood as meaning the granulation or granulation mixture introduced into the fluidized bed reactor, contains at least 1% by mass of silicon-containing particles S described by a structural parameter S and wherein S has a value of at least 0 and is calculated as follows:

$$S = (\varphi_s - 0.70) \cdot \frac{\rho_{SD}}{\rho_F}, \qquad \text{equation (1)}$$

wherein φ_S is symmetry-weighted sphericity factor,
wherein ρ_{SD} is poured density [g/cm³], and
wherein ρ_F is average particle solids density [g/cm³].

2. The process of claim **1**, wherein the symmetry-weighted sphericity factor φ_S of the particles S is 0.70 to 1 and wherein the sphericity of the particles S describes the ratio between the surface area of a particle image and the circumference.

3. The process of claim **1**, wherein the average particle solids density ρ_F of the particles S has a structural parameter S≥0 is 2.20 to 2.70 g/cm³ and wherein the determination is carried out according to DIN 66137-2:2019-03.

4. The process of claim **1**, wherein the operating granulation has a particle size parameter d_{50} of 70 to 1000 μm and wherein the particle size parameter is determined according to DIN ISO 9276-2.

5. The process of claim **1**, wherein before entry into the reactor the reaction gas comprises at least 50% by volume of hydrogen chloride.

6. The process of claim **1**, wherein the HCl and silicon are present in a molar ratio of HCl/Si of 5:1 to 2.5:1.

7. The process of claim **1**, wherein the produced chlorosilane of general formula (1) is trichlorosilane (TCS).

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