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(54) Title: METHOD FOR MAKING HALOSILANES FROM SILICA

(57) Abstract: A method includes: (i) combining ingredients to form a reactant, (ii) contacting H₂ with the reactant to form an activated reactant; and (iii) contacting an organohalide with the activated reactant to form a spent reactant and a reaction product including a halosilane. The ingredients used in step (i) are: (a) SiO₂, (b) a reducing agent, and (c) a silicide precursor. The halosilane produced by the method has formula R_nH_mSiX_(4-n), where subscript n is 0 to 3, subscript m is 0 to 2, a quantity (n + m) ≤ 3, each R is independently a hydrocarbyl group, and each X is independently a halogen atom.



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METHOD FOR MAKING HALOSILANES FROM SILICA

[0001] Methods of preparing halosilanes are known in the art. Typically, halosilanes are produced commercially by the Mueller-Rochow Direct Process, which comprises passing an organohalide compound over zero-valent silicon (Si^0) in the presence of a copper catalyst and various optional promoters. Mixtures of halosilanes are produced by the Direct Process.

[0002] The Si^0 used in the Direct Process is typically made by carbothermic reduction of SiO_2 in an electric arc furnace. Extremely high temperatures are required to reduce the SiO_2 , so the process is energy intensive. Consequently, production of Si^0 adds costs to the Direct Process for producing halosilanes. Therefore, there is a need for a more economical method of producing halosilanes that avoids or reduces the need of producing Si^0 via this energy intensive carbothermic reduction process.

[0003] Various halosilanes find use in different industries. Tetrahalosilanes can be used as precursors to make organohalosilanes. Organohalosilanes are hydrolyzed to produce a wide range of polyorganosiloxanes, such as polydiorganosiloxanes and/or polyorganosiloxane resins.

BRIEF SUMMARY OF THE INVENTION

[0004] A method for forming a reaction product comprising a halosilane is disclosed. The method comprises:

- (i) combining ingredients to form a reactant, where the ingredients comprise
 - (a) SiO_2 ,
 - (b) a reducing agent, and
 - (c) a silicide precursor;

(ii) contacting H_2 with the reactant to form an activated reactant; and

(iii) contacting an organohalide with the activated reactant to form a spent reactant and the halosilane, where the halosilane has formula $\text{R}_n\text{H}_m\text{SiX}_{(4-n-m)}$, where subscript n is 0 to 3, subscript m is 0 to 2, a quantity $(n + m) \leq 3$, each R is independently a hydrocarbyl group, and each X is independently a halogen atom.

DETAILED DESCRIPTION OF THE INVENTION

[0005] The Brief Summary of the Invention and the Abstract are hereby incorporated by reference. All ratios, percentages, and other amounts are by weight, unless otherwise indicated.

[0006] The method for forming the reaction product comprising the halosilane comprises:

(i) combining ingredients to form a reactant, where the ingredients comprise

(a) SiO_2 ,

(b) a reducing agent, and

(c) a silicide precursor;

(ii) contacting H_2 with the reactant to form an activated reactant; and

(iii) contacting an organohalide with the activated reactant to form a spent reactant and the halosilane, where the halosilane has formula $\text{R}_n\text{H}_m\text{SiX}_{(4-n-m)}$, where subscript n is 0 to 3, subscript m is 0 to 2, a quantity $(n + m) \leq 3$, each R is independently a hydrocarbyl group, and each X is independently a halogen atom.

[0007] Ingredient (a) is silica, which is commercially available. Ingredient (b) may be any species that can reduce silica. Ingredient (b) may be a reducing agent selected from magnesium (Mg), aluminum (Al), zirconium (Zr), hafnium (Hf), calcium (Ca), titanium (Ti), carbon (C), boron (B), or a combination thereof. Alternatively, ingredient (b) may be a reducing agent selected from sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), magnesium (Mg), aluminum (Al), zirconium (Zr), hafnium (Hf), calcium (Ca), titanium (Ti), carbon (C), boron (B), or a combination thereof. Combinations include physical mixtures and/or alloys of two or more of the reducing agents.

[0008] For example, ingredient (b) may be a group 1 metal of the periodic table of the elements, *e.g.*, Na, K, Rb, and Cs. Alternatively, the group 1 metal may be Na or K. Alternatively, the group 1 metal may be Na. Alternatively, the group 1 metal may be K.

[0009] Alternatively, alloys may be used as ingredient (b). The alloy may be an alloy of two or more group 1 metals, for example, such alloys include sodium-potassium alloys, alloys containing two or more of K, Cs, and Rb with each other, and alternatively, alloys containing Na and further comprising one or more of K, Cs, and/or Rb may be used. Alternatively, the alloy may be a sodium-potassium alloy.

[0010] Alternatively, ingredient (b) may be a group 2 metal of the periodic table of the elements or an alloy of said metals. The group 2 metal may be selected from Mg, Ca, and alloys thereof.

[0011] Alternatively, ingredient (b) may be a group 4 metal of the periodic table of the elements or an alloy of said metals. The group 4 metal may be selected from Zr, Hf, Ti, and alloys thereof.

[0012] Alternatively, ingredient (b) may be selected from Mg, Al, Zr, Hf, Ca, Ti, C, B, or a combination thereof. Alternatively, ingredient (b) may be magnesium. Ingredients (a) and (b) may be present in amounts sufficient to provide a molar ratio of ingredient (b) to ingredient (a) ((b):(a) ratio) of 0.25:1 to 4:1, alternatively 2:1 to 4:1. Ingredient (b) is commercially available.

[0013] Ingredient (c) may be a metal halide of formula MX_a , where M is a metal selected from the group consisting of chromium (Cr), manganese (Mn), iron (Fe), ruthenium (Ru), rhenium, (Re), rhodium (Rh), iridium (Ir), copper (Cu), cobalt (Co), molybdenum (Mo), nickel (Ni), palladium (Pd), platinum (Pt), and tungsten (W); subscript a is 1 to the maximum valence of the metal selected for M; and each X is independently a halogen atom. Alternatively, M may be selected from Cu, Co, Mo, Ni, Pd, Pt, and W. Alternatively, M may be selected from Cu, Pt, Ni, and Pd. Alternatively, M may be selected from Cu, Ni, and Pt. Alternatively, ingredient (c) may be PdX_2 . Ingredients (a) and (c) are present in amounts sufficient to provide a molar ratio of the amounts of metal atom M from ingredient (c) and the amount of Si from ingredient (a) (M:Si ratio) of 1:2 to 1:10.

[0014] The method described above may optionally further comprise steps (iv) and (v). Step (iv) is contacting H_2 with the spent reactant to re-activate the spent reactant, thereby re-forming the activated reactant; and step (v) is contacting additional organohalide with the activated reactant formed in step (iv). The method may optionally further comprise step (vi): repeating steps (iv) and (v) one or more times. Alternatively, steps (iv) and (v) may be repeated 10^5 or more times, alternatively 10^5 to 10^7 times, and alternatively 2 to 15 times. The method may optionally further comprise step (vii) repeating steps (i)-(v) one or more times. The method may optionally further comprise step (viii) recovering the halosilane from the reaction product.

[0015] Step (i) of the method described above may be performed by (I) mechanochemically processing ingredients (a) and (b) to form a combination, and (II) combining the combination and ingredient (c). The combination of ingredients (a) and (b) may be combined with ingredient (c) by (IIA) impregnating the combination with ingredient (c), and/or (IIB) mechanochemically processing the combination and ingredient (c). Without wishing to be bound by theory, it is thought that ingredient (b) acts as a reducing agent of silica (oxygen getter), and combining ingredients (a) and (b)

before adding ingredient (c) may generate elemental silicon and possibly silicon that has weak associations with the surrounding oxygen atoms. The combining of ingredient (c) that follows may generate a silicide species upon exposure to high temperature H_2 , which become the precursor for the chlorosilanes upon reaction with the organohalide.

5 **[0016]** Step (i) may be performed at ambient temperature or with heating, *e.g.*, temperature in step (i) may be 23 °C to 600 °C, alternatively 23 °C to 200 °C, and alternatively 23 °C to 150 °C, and alternatively 23 °C to 40 °C. The time for step (i) depends on various factors including the temperature and amount of ingredient (b) selected. However, mechanochemically processing in step (i) may be performed for up
10 to 48 hours, alternatively up to 24 hours, and alternatively 1 to 4 hours.

[0017] The method described above further comprises step (ii) and step (iii). Step (ii) and step (iii) of the method may be performed separately and consecutively.

“Separately” means that step (ii) and step (iii) do not overlap or coincide.

“Consecutively” means that step (iii) is performed after step (ii) in the method; however,

15 additional steps may be performed before step (i), between steps (ii) and (iii), and/or after step (iii), as described herein. “Separately” refers to either spatially or temporally or both. “Consecutively” refers to temporally (and furthermore occurring in a defined order).

[0018] The organohalide used in step (iii) of the method described above may have
20 the formula RX , where R is a monovalent organic group and X is a halogen. R may be a hydrocarbyl selected from the group consisting of alkyl, aralkyl, alkenyl, alkynyl, aryl, and carbocyclic, as defined herein. Alternatively, R may be an alkyl group or a cycloalkyl group. The alkyl groups for R may have 1 to 10 carbon atoms, alternatively 1 to 6 carbon atoms, and alternatively 1 to 4 carbon atoms. The cycloalkyl groups for R may
25 have 4 to 10 carbon atoms, alternatively 6 to 8 carbon atoms. Alkyl groups containing at least three carbon atoms may have a branched or unbranched structure. Alternatively, R may be Me, Et, or Ph. Alternatively, R may be Me. Alternatively, X may be Br, Cl or I; alternatively Br or Cl; and alternatively Cl. Examples of the organohalide include, but are not limited to, methyl chloride, methyl bromide, methyl iodide, ethyl chloride, ethyl
30 bromide, ethyl iodide, cyclobutyl chloride, cyclobutyl bromide, cyclohexyl chloride, and cyclohexyl bromide.

[0019] Alternatively, the organohalide may be an aliphatic hydrocarbyl halide. The aliphatic hydrocarbyl halide may be a compound of formula $H_xC_yX_z$, where subscript x

represents average number of hydrogen atoms present, subscript y represents average number of carbon atoms present, and subscript z represents average number of halogen atoms present. Subscript x is 0 or more, subscript y is 1 or more, and subscript z is 1 or more. When the organohalide is a noncyclic aliphatic hydrocarbyl halide, then a quantity
5 $(x + z) = a$ quantity $(2y + 2)$. When the organohalide is a monocyclic cycloalkyl halide, then the quantity $(x + z) = 2y$. Each X is independently a halogen atom, as described above. Alternatively, subscript y may be 1 to 10, alternatively 1 to 6, alternatively 1 to 4, and alternatively 1. Alternatively, subscript z may be 1 to 4. Alternatively, subscript z may be at least 2, alternatively 2 to 4. Examples of suitable organohalides include, but
10 are not limited to, methyl chloride (H_3CCl), methylene chloride (H_2CCl_2), chloroform (HCCl_3), carbon tetrachloride (CCl_4), and dichloroethane.

[0020] Steps (ii) and (iii) of the method described herein can be performed in any reactor suitable for the combining of gases and solids. In one embodiment, steps (ii) and (iii) may be performed in the same reactor. Alternatively, steps (ii) and (iii) may be
15 performed in different reactors. However, the reactor configuration for each of steps (ii) and (iii) can be a batch vessel, packed bed, stirred bed, vibrating bed, moving bed, re-circulating beds, or a fluidized bed. Alternatively, the reactor may be a packed bed, a stirred bed, or a fluidized bed. To facilitate reaction, the reactor should have means to control the temperature of the reaction zone, *i.e.*, the portion of the reactor in which the
20 H_2 contacts the reactant in step (ii) and the portion of the reactor in which the organohalide contacts the activated reactant in step (iii).

[0021] The temperature at which the H_2 and the reactant are contacted in step (ii) of the method described above is at 500°C to 1000°C , alternatively 500°C to 850°C .

Without wishing to be bound by theory, it is thought that if temperature is less than
25 500°C , then the reactant may not be activated sufficiently to react in step (iii); and if the temperature is greater than 1000°C , then the reactant may decompose.

[0022] The pressure at which the H_2 and the reactant are contacted can be sub-atmospheric, atmospheric, or super-atmospheric. For example, the pressure may range from 0 kilopascals gauge (kPag) to 2000 kPag; alternatively 100 kPag to 1000 kPag; and
30 alternatively 100 kPag to 800 kPag.

[0023] The residence time for the H_2 to contact the reactant in step (ii) is sufficient to form the activated reactant. For example, a sufficient residence time may be at least

0.01 seconds (s); alternatively at least 0.1 s; alternatively from 0.1 s to 10 minutes (min); alternatively from 0.1 s to 1 min; and alternatively from 1 s to 10 s. The desired residence time may be achieved by adjusting the flow rate of the H₂, or by adjusting the total reactor volume, or by any combination thereof.

5 **[0024]** The temperature at which the organohalide and the activated reactant are contacted in step (iii) of the method described above is 200 °C to 500 °C, alternatively 250 °C to 400 °C, and alternatively 300 °C to 400 °C. Without wishing to be bound by theory, it is thought that if temperature is less than 200 °C, then the halosilane may not be formed in step (iii); and if the temperature is greater than 500 °C, then the
10 organohalide may decompose.

[0025] The pressure at which the organohalide and the activated reactant are contacted can be sub-atmospheric, atmospheric, or super-atmospheric. For example, the pressure may range from 0 kilopascals gauge (kPag) to 2000 kPag; alternatively 100 kPag to 1000 kPag; and alternatively 100 kPag to 800 kPag.

15 **[0026]** The residence time for the organohalide to contact the activated reactant in step (iii) is sufficient to form the halosilane. For example, a sufficient residence time may be at least 0.01 s, alternatively, up to 2 h, and alternatively 0.1 s to 2 h. The desired residence time may be achieved by adjusting the flow rate of the organohalide, or by adjusting the total reactor volume, or by any combination thereof.

20 **[0027]** If the organohalide is a liquid at or below standard temperature and pressure, the method may further comprise pre-heating and vaporizing the organohalide by known methods before contacting the organohalide with the activated reactant in step (iii).

[0028] If the organohalide is a solid at or below standard temperature and pressure, the method may further comprise pre-heating above the melting point and liquefying or
25 vaporizing the organohalide before contacting it with the activated reactant in step (iii).

[0029] The method described above may optionally further comprise steps (iv) and (v). Step (iv) is contacting H₂ with the spent reactant to re-activate the spent reactant, thereby re-forming the activated reactant; and step (v) is contacting additional organohalide with the activated reactant formed in step (iv). The method may optionally
30 further comprise step (vi): repeating steps (iv) and (v) one or more times. Alternatively, steps (iv) and (v) may be repeated 10⁵ or more times, alternatively 10⁵ to 10⁷ times, and alternatively 2 to 15 times. For the sake of brevity, the description of the conditions (e.g., temperature, pressure, and residence time) of step (iii) herein may also apply to

step (iv); and the description of the conditions of step (iii) may also apply to step (v). Without wishing to be bound by theory, it is thought that steps (iv) and (v) may be repeated until the silicon is spent; *e.g.*, insufficient silicon is present to continue producing the halosilane. When this happens, step (i) may be repeated to add additional reactant, and steps (ii)-(v) may be repeated.

[0030] The method may optionally further comprise step (viii). Step (viii) comprises recovering the halosilane from the reaction product. The halosilane may be recovered from the reaction product by, for example, removing gaseous product from the reactor followed by isolation by distillation. The reaction product produced by the method described herein comprises a halosilane of formula $R_nH_mSiX_{(4-n-m)}$, where subscripts n and m , and R and X , are as described above. Alternatively, R is hydrocarbyl and X is a halogen; alternatively, each R is alkyl and each X is Cl . Exemplary halosilanes include organotrihalosilanes and/or diorganodihalosilanes. Organotrihalosilanes are exemplified by methyltrichlorosilane, methyltribromosilane, and ethyltrichlorosilane. Examples of diorganodihalosilanes prepared according to the present process include, but are not limited to, dimethyldichlorosilane (*i.e.*, $(CH_3)_2SiCl_2$), dimethyldibromosilane, diethyldichlorosilane, and diethyldibromosilane. Examples of other organohalosilanes that may be produced in addition to the diorganodihalosilane include, but are not limited to, methyltrichlorosilane (*i.e.*, CH_3SiCl_3), and methyltribromosilane (*i.e.*, CH_3SiBr_3).

[0031] The halosilanes produced by the method described herein may be hydrolyzed in known processes for producing polyorganosiloxanes. The polyorganosiloxanes thus produced find use in many industries and applications. The method can produce halosilanes, such as chlorosilanes, directly from SiO_2 . Without wishing to be bound by theory, it is thought that the method described herein provides the benefits that Si^0 is not isolated, and the starting material, SiO_2 , is inexpensive and readily available.

Furthermore, as shown in the examples below, the method may be used to produce diorganodihalosilanes, such as Me_2SiCl_2 with minimal amounts of $SiCl_4$ being produced

EXAMPLES

[0032] These examples are intended to illustrate some embodiments of the invention and should not be interpreted as limiting the scope of the invention set forth in the claims. The comparative examples are non-invention examples. SiO_2 was purchased

from Fischer Scientific and Sigma Aldrich. Mg and PdCl₂ were purchased from Sigma Aldrich.

[0033] **Comparative Example A** - A sample of SiO₂ was ball milled for 30 min to decrease the particle size and increase the surface area. The resulting milled SiO₂ was then reacted with H₃CCl (MeCl). A peak identified in GC-TCD as MeHSiCl₂ was observed in the reactor effluent at an instantaneous maximum 0.15% yield.

[0034] **Comparative Example B** - Magnesium was ball milled with SiO₂ in a 4:1 molar ratio for 1 hour and with SiO₂ in a 2:1 ratio for 4 hours. The resulting Mg-SiO₂ combinations were then reacted with H₃CCl (MeCl). The 4:1 Mg:SiO₂ reaction with H₃CCl (MeCl) resulted in very small peaks in the GC-TCD spectra that were identified as MeSiCl₃ and Me₂SiCl₂. The XRD detected MgO, silicon, Mg₂SiO₄ and SiO₂. The presence of silicon in the material most likely accounts for the chlorosilanes observed in the GC-TCD of the reactor effluent. For the 2:1 Mg:SiO₂ experiment, no Si products were observed in the GC spectra upon reaction with H₃CCl (MeCl). The XRD revealed the presence of MgO, Si and Mg₂SiO₄. Without wishing to be bound by theory, it is thought that the Si was either not accessible and/or had very low activity. The SEM/EDS for the 2:1 Mg:SiO₂ found the sample to contain primarily oxygen and magnesium, with some silicon and carbon and very little chlorine.

[0035] **General Procedure for the Examples** - PdCl₂ was combined with the ball milled 2:1 Mg:SiO₂ prepared in Comparative Example B. Several mole ratios of Pd:Si (based on the amount of Si present in Mg-SiO₂ sample) were tested. The ratios tested were 1:2.2, 1:2.5, 1:3, 1:4.4, and 1:6. The Pd:Mg-SiO₂ solids were ball milled for a prolonged period of time prior to placing them in the methylation reactor used in comparatives examples 1 and 2. For each sample, the Pd:Mg-SiO₂ was treated with H₂ at temperatures ≥550 °C first and then reacted with H₃CCl (MeCl) at 300 °C until the production of methyl chlorosilanes decreased significantly. Then the high temperature H₂ treatment was repeated again. Each H₂ treatment followed by H₃CCl (MeCl) reaction was defined as a cycle. Variable numbers of cycles (usually ≤ 20) were used depending on the initial data and the rate of production of methyl chlorosilanes.

[0036] Example 1 – 1:2.2 Pd:Si molar ratio - In a flow reactor, 0.5 g of 1:2.2 PdCl₂:Mg-SiO₂ was loaded into a glass tube. The activation was performed with 100 sccm H₂ at 850 °C for 2-3 hours. The reaction tube was then cooled to 300 °C while H₂ flow continued at 10 sccm. Once 300 °C was reached, the H₂ was turned off, and the H₃CCl (MeCl) feed was started at 1.86 sccm. Samples were taken from the reaction stream and injected into a GC-TCD for analysis using an online switching valve. Total H₃CCl (MeCl) reaction time was 2 hours.

[0037] Online GC-TCD analysis provided the production of the chlorosilanes data listed in Table 1. In some instances, the catalyst was cycled several times. Overall conversion of Si was 2.8%.

Table 1. List of chlorosilanes produced in reaction with their respective weight % in the reactor effluent and % selectivity.

Chlorosilane	Weight % in Effluent	Selectivity (%)
Me ₃ SiCl	2.51	1.1
SiCl ₄	12.53	27.91
Me ₂ SiCl ₂	5.01	2.84
MeSiCl ₃	79.95	68.16

[0038] Example 2 – 1:2.5 Pd:Si molar ratio - In a flow reactor, 0.5 g of 1:2.5 PdCl₂:Mg-SiO₂ was loaded into a glass tube. The activation was performed with 100 sccm H₂ at 850 °C for 2-3 hours. The reaction tube was then cooled to 300 °C while H₂ flow continued at 10 sccm. Once 300 °C was reached, the H₂ was turned off, and the H₃CCl (MeCl) feed was started at 1.86 sccm. Samples were taken from the reaction stream and injected into a GC-TCD for analysis using an online switching valve. Total H₃CCl (MeCl) reaction time was 2 hours.

[0039] Online GC-TCD analysis provided the production of the chlorosilanes data listed in Table 2. In some instances, the catalyst was cycled several times. Overall conversion of Si was 24%.

Table 2. List of chlorosilanes produced in reaction with their respective weight % in the reactor effluent and % selectivity.

Chlorosilane	Weight % in Effluent	Selectivity (%)
Me ₃ SiCl	18.25	6.25
SiCl ₄	0.95	10.7
Me ₂ SiCl ₂	52.82	34.28
MeSiCl ₃	27.97	48.77

[0040] Example 3 – 1:3 Pd:Si molar ratio - In a flow reactor, 0.5 g of 1:3 PdCl₂:Mg-SiO₂ was loaded into a glass tube. The Activation was performed with 100 sccm H₂ at 850 °C for 2-3 hours. The reaction tube was then cooled to 300 °C while H₂ flow continued at 10 sccm. Once 300 °C was reached, the H₂ was turned off, and the H₃CCl (MeCl) feed was started at 1.86 sccm. Samples were taken from the reaction stream and injected into a GC-TCD for analysis using an online switching valve. Total H₃CCl (MeCl) reaction time was 2 hours.

[0041] Online GC-TCD analysis provided the production of the chlorosilanes data listed in Table 3. In some instances, the catalyst was cycled several times. Overall conversion of Si was 21%.

Table 3. List of chlorosilanes produced in reaction with their respective weight % in the reactor effluent and % selectivity.

Chlorosilane	Weight % in Effluent	Selectivity (%)
Me ₃ SiCl	33.19	31.41
SiCl ₄	5.8	9.55
Me ₂ SiCl ₂	35.34	27.98
MeSiCl ₃	25.67	31.05

[0042] Example 4 – 1:4.4 Pd:Si molar ratio - In a flow reactor, 0.5 g of 1:4.4 PdCl₂:Mg-SiO₂ was loaded into a glass tube. The activation was performed with 100 sccm H₂ at 850 °C for 2-3 hours. The reaction tube was then cooled to 300 °C while H₂ flow continued at 10 sccm. Once 300 °C was reached, the H₂ was turned off, and the

H₃CCl (MeCl) feed was started at 1.86 sccm. Samples were taken from the reaction stream and injected into a GC-TCD for analysis using an online switching valve. Total H₃CCl (MeCl) reaction time was 2 hours.

[0043] Online GC-TCD analysis provided the production of the chlorosilanes data listed in Table 4. In some instances, the catalyst was cycled several times. Overall conversion of Si was 26%.

Table 4. List of chlorosilanes produced in reaction with their respective weight % in the reactor effluent and % selectivity.

Chlorosilane	Weight % in Effluent	Selectivity (%)
Me ₃ SiCl	2.03	2.3
SiCl ₄	2.47	2.74
Me ₂ SiCl ₂	55.06	48.89
MeSiCl ₃	40.44	46.07

[0044] Example 5 – 1:6 Pd:Si molar ratio - Example 4 was repeated, except using 0.5 g of 1:6 PdCl₂:Mg-SiO₂ (instead of 0.5 g of 1:4.4 PdCl₂:Mg-SiO₂).

[0045] Online GC-TCD analysis provided the production of the chlorosilanes data listed in Table 5. In some instances, the catalyst was cycled several times. Overall conversion of Si was 21%.

Table 5. List of chlorosilanes produced in reaction with their respective weight % in the reactor effluent and % selectivity.

Chlorosilane	Weight % in Effluent	Selectivity (%)
Me ₃ SiCl	24.12	9.65
SiCl ₄	2.08	4.87
Me ₂ SiCl ₂	48.11	37.78
MeSiCl ₃	25.7	47.69

[0046] For purposes of this application, the following terms are as defined below.

The articles 'a', 'an', and 'the' each refer to one or more, unless otherwise indicated by the context of the specification.

[0047] “Alkyl” means an acyclic, branched or unbranched, saturated monovalent hydrocarbon group. Examples of alkyl groups include Me, Et, Pr, 1-methylethyl, Bu, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, 1-methylbutyl, 1-ethylpropyl, pentyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, 2-ethylhexyl, octyl, nonyl, and decyl. Alkyl groups have at least one carbon atom. Alternatively, alkyl groups may have 1 to 12 carbon atoms, alternatively 1 to 10 carbon atoms, alternatively 1 to 6 carbon atoms, alternatively 1 to 4 carbon atoms, alternatively 1 to 2 carbon atoms, and alternatively 1 carbon atom.

[0048] “Aralkyl” and “alkaryl” each refer to an alkyl group having a pendant and/or terminal aryl group or an aryl group having a pendant alkyl group. Exemplary aralkyl groups include benzyl, tolyl, xylyl, phenylethyl, phenyl propyl, and phenyl butyl. Aralkyl groups have at least 4 carbon atoms. Monocyclic aralkyl groups may have 4 to 12 carbon atoms, alternatively 4 to 9 carbon atoms, and alternatively 4 to 7 carbon atoms. Polycyclic aralkyl groups may have 7 to 17 carbon atoms, alternatively 7 to 14 carbon atoms, and alternatively 9 to 10 carbon atoms.

[0049] “Alkenyl” means an acyclic, branched, or unbranched unsaturated monovalent hydrocarbon group, where the monovalent hydrocarbon group has a double bond. Alkenyl groups include Vi, allyl, propenyl, and hexenyl. Alkenyl groups have at least 2 carbon atoms. Alternatively, alkenyl groups may have 2 to 12 carbon atoms, alternatively 2 to 10 carbon atoms, alternatively 2 to 6 carbon atoms, alternatively 2 to 4 carbon atoms, and alternatively 2 carbon atoms.

[0050] “Alkynyl” means an acyclic, branched, or unbranched unsaturated monovalent hydrocarbon group, where the monovalent hydrocarbon group has a triple bond. Alkynyl groups include ethynyl and propynyl. Alkynyl groups have at least 2 carbon atoms. Alternatively, alkynyl groups may have 2 to 12 carbon atoms, alternatively 2 to 10 carbon atoms, alternatively 2 to 6 carbon atoms, alternatively 2 to 4 carbon atoms, and alternatively 2 carbon atoms.

[0051] “Aryl” means a cyclic, fully unsaturated, hydrocarbon group. Aryl is exemplified by, but not limited to, Ph and naphthyl. Aryl groups have at least 5 carbon atoms. Monocyclic aryl groups may have 6 to 9 carbon atoms, alternatively 6 to 7 carbon atoms, and alternatively 6 carbon atoms. Polycyclic aryl groups may have 10 to 17 carbon atoms, alternatively 10 to 14 carbon atoms, and alternatively 12 to 14 carbon atoms.

[0052] “Carbocycle” and “carbocyclic” refer to a hydrocarbon ring. Carbocycles may be monocyclic or alternatively may be fused, bridged, or spiro polycyclic rings.

Carbocycles have at least 3 carbon atoms. Monocyclic carbocycles may have 3 to 9 carbon atoms, alternatively 4 to 7 carbon atoms, and alternatively 5 to 6 carbon atoms.

5 Polycyclic carbocycles may have 7 to 17 carbon atoms, alternatively 7 to 14 carbon atoms, and alternatively 9 to 10 carbon atoms. Carbocycles may be saturated or partially unsaturated.

[0053] “Cycloalkyl” refers to a saturated hydrocarbon group including a saturated carbocycle. Cycloalkyl groups are exemplified by cyclobutyl, cyclopentyl, cyclohexyl,
10 and methylcyclohexyl. Cycloalkyl groups have at least 3 carbon atoms. Monocyclic cycloalkyl groups may have 3 to 9 carbon atoms, alternatively 4 to 7 carbon atoms, and alternatively 5 to 6 carbon atoms. Polycyclic cycloalkyl groups may have 7 to 17 carbon atoms, alternatively 7 to 14 carbon atoms, and alternatively 9 to 10 carbon atoms.

[0054] “Metallic” means that the metal has an oxidation number of zero.

15 **[0055]** “Residence time” means the time which a material takes to pass through a reactor system in a continuous process, or the time a material spends in the reactor in a batch process. For example, residence time may refer to the time during which one reactor volume of the reactant makes contact with H₂ in step (ii) of the method; or the time during which one reactor volume of the activated reactant makes contact with the
20 organohalide in step (iii) as the reactant or activated reactant passes through the reactor system in a continuous process or during which the reactant or activated reactant is placed within the reactor in a batch process. Alternatively, residence time may refer to the time for one reactor volume of reactant gases to pass through a reactor charged with the reactant or activated reactant, *e.g.*, the time for one reactor volume of the
25 organohalide to pass through a reactor charged with the activated reactant.

[0056] “Mechanochemically processing” means applying mechanical energy to initiate chemical reactions and/or structural changes. Mechanochemically processing may be performed, for example, by techniques such as milling, *e.g.*, ball milling. Milling may be performed using any convenient milling equipment such as a mixer mill, planetary mill,
30 attritor, or ball mill. Mechanochemical processing may be performed, for example, using the methods and equipment described in, “Mechanical alloying and milling” by C. Suryanarayana, *Progress in Materials Science* 46 (2000) 1-184.

[0057] “Spent reactant” refers to the reactant after it has been contacted with the organohalide in step (iii) (or after step (v), when step (v) is present in the method). The spent reactant after step (iii) (or step (v)) is the mass that remained in the reactor when the yield of the organosilane volatile components was reduced to trace amounts. This
5 can be after step (iii) or step (v), when step (v) is present in the method.

[0058] The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. For example, disclosure of a range of 2.0 to 4.0 includes not only the range of 2.0 to 4.0, but also 2.1, 2.3, 3.4, 3.5, and 4.0 individually, as well as any other number subsumed in the range. Furthermore, disclosure of a range of, for
10 example, 2.0 to 4.0 includes the subsets of, for example, 2.1 to 3.5, 2.3 to 3.4, 2.6 to 3.7, and 3.8 to 4.0, as well as any other subset subsumed in the range.

[0059] With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, it is to be appreciated that different, special, and/or unexpected results may be obtained from each member of the respective

15 Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination with any other member or members of the group, and each member provides adequate support for specific embodiments within the scope of the appended claims. For example, disclosure of the Markush group: alkyl, aryl, and carbocyclic includes the member alkyl individually;
20 the subgroup alkyl and aryl; and any other individual member and subgroup subsumed therein.

[0060] It is also to be understood that any ranges and subranges relied upon in describing various embodiments of the present disclosure independently and collectively fall within the scope of the appended claims, and are understood to describe and
25 contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. The enumerated ranges and subranges sufficiently describe and enable various embodiments of the present disclosure, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range “of 200 to 1400” may be further
30 delineated into a lower third, *i.e.*, from 200 to 600, a middle third, *i.e.*, from 600 to 1000, and an upper third, *i.e.*, from 1000 to 1400, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of

the appended claims. In addition, with respect to the language which defines or modifies a range, such as “at least,” “greater than,” “less than,” “no more than,” and the like, it is to be understood that such language includes subranges and/or an upper or lower limit.

As another example, a range of “at least 0.1%” inherently includes a subrange from

5 0.1% to 35%, a subrange from 10% to 25%, a subrange from 23% to 30%, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims.

Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims.

10 For example, a range of “1 to 9” includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[0061] The subject matter of all combinations of independent and dependent claims,

15 both singly and multiply dependent, is expressly contemplated but is not described in detail for the sake of brevity. The disclosure has been described in an illustrative

manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Many modifications and variations of the present disclosure are possible in light of the above teachings, and

20 the disclosure may be practiced otherwise than as specifically described.

CLAIMS:

1. A method for forming a reaction product comprising a halosilane comprises:

(i) combining ingredients to form a reactant, where the ingredients comprise

(a) SiO_2 ,

(b) magnesium, and

(c) a silicide precursor, where ingredient (c) is a metal halide of formula MX_a ,

where M is a metal selected from the group consisting of copper, cobalt, molybdenum, nickel, palladium, platinum, and tungsten; subscript a is 1 to maximum valance of the metal selected for M; and each X is independently a halogen atom; thereby forming the reactant;

(ii) contacting H_2 with the reactant to form an activated reactant; and

(iii) contacting an organohalide with the activated reactant to form a spent reactant and the halosilane, where the halosilane has formula $\text{R}_n\text{H}_m\text{SiX}_{(4-n-m)}$, where subscript n is 0 to 3, subscript m is 0 to 2, a quantity $(n + m) \leq 3$, each R is independently a hydrocarbyl group, and X is as defined above,

optionally (iv) contacting H_2 with the spent reactant to re-activate the spent reactant, thereby forming a re-activated reactant,

optionally (v) contacting additional organohalide with the re-activated reactant,

optionally (vi) repeating steps (iv) and (v) one or more times, and

optionally (vii) repeating step (i) and repeating steps (ii)-(v) one or more times.

2. The method of claim 1, where

Step (i) is performed at 23°C to 200°C, and/or

Step (ii) is performed at 500°C to 1000°C, and/or

Step (iii) is performed at 200°C to 500°C, and/or

Step (iv) is present, and step (iv) is performed at 500°C to 1000°C, and/or

Step (v) is present, and step (v) is performed at 200°C to 500°C.

3. The method of claim 1 or claim 2, where

Step (i) is performed for 1 to 4 hours, and/or

Step (ii) is performed for 2 to 3 hours, and/or

Step (iii) is performed for up to 2 hours, and/or

Step (iv) is present, and step (iv) is performed for 2 to 3 hours, and/or

Step (v) is present, and step (v) is performed for up to 2 hours.

4. The method of any one of the preceding claims, where steps (iv), (v), and (vi) are present, and steps (iv) and (v) are performed 2 to 15 times.

5. The method of any one of the preceding claims, further comprising (viii) recovering the halosilane.

6. The method of any one of the preceding claims, where R is methyl and X is Cl.

7. The method of any one of the preceding claims, where the halosilane comprises dimethyldichlorosilane.

8. The method of any one of the preceding claims, further comprising hydrolyzing the halosilane.

9. A polyorganosiloxane prepared by the method of claim 8.

10. The method of any one of claims 1 to 8, where step (i) is performed by (I) mechanochemically processing ingredients (a) and (b) to form a combination, and (II) combining the combination and ingredient (c).

11. The method of claim 10, where step (II) is performed by

(IIA) impregnating the combination with ingredient (c), and/or

(IIB) optionally mechanochemically processing the combination and ingredient

(c).

12. The method of claim 10, where step (II) is performed by mechanochemically processing the combination and ingredient (c).

13. A method for preparing a reactant comprises:

(1) mechanochemically processing ingredients (a) and (b) to form a combination,
where

Ingredient (a) is SiO_2 ,

Ingredient (b) is magnesium, and

5 (2) combining the combination and ingredient (c), where ingredient (c) is a metal
halide of formula MX_a , where M is a metal selected from the group consisting of copper,
cobalt, molybdenum, nickel, palladium, platinum, and tungsten; subscript a is 1 to
maximum valence of the metal selected for M; and each X is independently a halogen
atom; thereby forming the reactant.

10

14. The method of claim 13, where ingredient (c) is PdX_2 .

15. The method of claim 13 or claim 14, where step (2) is performed by

(2A) impregnating the combination with ingredient (c), and/or

15 (2B) optionally mechanochemically processing the combination and ingredient
(c).

16. The method of claim 15, where step (2) is performed by mechanochemically
processing the combination and ingredient (c).

20

17. A reactant prepared by the method of any one of claims 13 to 16.

18. The method of any one of claims 1-8 or 10-16, where the ingredients (a) and (b) are
present in a molar ratio of (b):(a) of 0.25:1 to 4:1.

25

19. The method of any one of claims 1-8 or 10-16, where the ingredients are present in
amounts sufficient to provide a molar ratio of M:Si of 1:2 to 1:10 based on the amounts
of metal atom M from ingredient (c) and the amount of Si from ingredient (a).

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/011754

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J21/10 B01J23/58 C01B33/06 C01B33/107 C07F7/12
C07F7/16

ADD.

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)

B01J C01B C07F

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 213 730 A (HIDA GEORGE T [US]) 25 May 1993 (1993-05-25)	13,15-19
Y	claims 1,3 column 6, line 45 - line 59 -----	1-8, 10-12,14
X	WO 2012/102957 A1 (DOW CORNING [US]; ANDERSON KURT E [US]; DASH ASWINI K [US]; HALL CHARL) 2 August 2012 (2012-08-02)	9
Y	paragraphs [0003], [0015] claims 1-17 examples 1-6 -----	1-8, 10-12,14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/011754

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5213730	A	25-05-1993	NONE	

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