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(54) Title: PROCESS FOR THE PREPARATION OF PALLADIUM INTERMETALLIC COMPOUNDS AND USE OF THE COMPOUNDS TO PREPARE ORGANOHALOSILANES

(57) Abstract: Palladium intermetallic compounds, such as palladium silicides, e.g., PdSi and/or Pd₂Si, can be selectively prepared in a two step process including the steps of (1) vacuum impregnating silicon with a metal halide comprising a palladium halide, and (2) ball milling the product of step (1). A method of preparing organohalosilanes may be performed combining an organohalide having the formula RX, where R is a hydrocarbyl group having 1 to 10 carbon atoms and X is a halogen atom, with a contact mass comprising at least 2% of the palladium intermetallic compound.



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PROCESS FOR THE PREPARATION OF PALLADIUM INTERMETALLIC COMPOUNDS
AND USE OF THE COMPOUNDS TO PREPARE ORGANOHALOSILANES

Technical Field

5 **[0001]** A process selectively produces an intermetallic compound, such as a palladium silicide and an intermetallic compound comprising Cu, Pd, and Si. The intermetallic compound can be used as a catalyst for preparing organohalosilanes. A method of using the intermetallic compound comprises combining an organohalide with a contact mass to form an organohalosilane, where the contact mass comprises at least 2% of the
10 intermetallic compound.

Background

[0002] Methods of preparing organohalosilanes are known in the art. Typically, organohalosilanes are produced commercially by the Mueller-Rochow Direct Process, which comprises passing an organohalide over zero-valent silicon in the presence of a
15 copper catalyst and various optional promoters. A mixture of organohalosilanes, the most important of which is dimethyldichlorosilane, are produced by the Direct Process.

[0003] The typical process for making the zero-valent silicon used in the Direct Process consists of the carbothermic reduction of SiO_2 in an electric arc furnace. Extremely high temperatures are required to reduce the SiO_2 , so the process is very energy intensive.
20 Consequently, production of zero-valent silicon adds costs to the Direct Process for producing organohalosilanes. Therefore, there is a need for a more economical method of producing organohalosilanes that avoids or reduces the need of using zero-valent silicon.

[0004] Another method for preparing organohalosilanes comprises combining an organohalide with a contact mass to form the organohalosilane, where the contact mass
25 includes a metal silicide. WO2011/094140 mentions a method of preparing organohalosilanes comprising combining an organohalide having the formula RX (I), wherein R is a hydrocarbyl group having 1 to 10 carbon atoms and X is Br, Cl, F, and I, with a contact mass comprising at least 2% of a palladium silicide of the formula Pd_xSi_y (II), wherein x is an integer from 1 to 5 and y is 1 to 8, or a platinum silicide of formula Pt_zSi (III), wherein z is 1 or 2, in a reactor at a temperature from 250 to 700 °C to form an
30 organohalosilane.

BRIEF SUMMARY OF THE INVENTION

[0005] A process for preparing an intermetallic compound comprises:
(1) vacuum impregnating a metal halide comprising a palladium halide of formula PdX'_2 ,
35 where X' is a halogen atom, on silicon particles thereby producing a mixture, and

(2) mechanochemically processing the mixture under an inert atmosphere, thereby producing a reaction product comprising the intermetallic compound. The intermetallic compound comprised Pd and Si.

- [0006]** A method of preparing an organohalosilane comprises: combining an organohalide having the formula RX^n , where R is a hydrocarbyl group having 1 to 10 carbon atoms and X^n is a halogen atom, with a contact mass comprising at least 2% of the intermetallic compound prepared by the process described above at a temperature ranging from 250 °C to 700 °C to form an organohalosilane.

DETAILED DESCRIPTION OF THE INVENTION

- [0007]** The Brief Summary of the Invention and the Abstract of the Disclosure are hereby incorporated by reference. All ratios, percentages, and other amounts are by weight, unless otherwise indicated. The articles “a”, “an”, and “the” each refer to one or more, unless otherwise indicated by the context of the specification. Abbreviations used herein are defined in Table 1, below.

Table 1 – Abbreviations

Abbreviation	Word
%	percent
°C	degrees Celsius
EDS	energy dispersive spectroscopy
g	gram
h	hour
ICP	inductively coupled plasma
kPa	kiloPascals
mL	milliliters
RT	room temperature of 23 °C
sccm	standard cubic centimeters per minute
SEM	scanning electron microscopy
μm	micrometers
XRD	x-ray diffraction

- [0008]** 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 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. Similarly, the disclosure of

Markush groups includes the entire group and also any individual members and subgroups subsumed therein. For example, disclosure of the Markush group, Br, Cl, F, and I includes the member Br individually; the subgroup Cl and I; and any other individual member and subgroup subsumed therein.

5 **[0009]** "Contact time" means the residence time of gas to pass through a reactor.

[0010] "Mechanochemical processing" means applying mechanical energy to initiate chemical reactions and/or structural changes. Mechanochemical 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, 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.

Process for Making Intermetallic Compounds

[0011] A process comprises:

- 15 (1) vacuum impregnating a halide comprising a palladium halide of formula PdX'_2 on silicon, where X' is as defined above, thereby producing a mixture comprising $\text{Pd}_z\text{Si}_w\text{X}'_{zq}$, where z represents the molar amount of Pd, w represents the molar amount of Si and zq represents a relative molar amount of the halogen atoms in the mixture; and
- (2) mechanochemically processing of the mixture prepared in step (1) under an inert atmosphere, thereby producing a redox reaction product comprising
 - 20 (i) an intermetallic compound of formula $\text{Pd}_z\text{Si}_{(w-y/4)}\text{X}'_{(zq-y)}$, where $y/4$ represents a molar amount of Si removed from the mixture during step (2) and y represents a molar amount of halogen atom removed from the mixture during step (2), and $y < zq$;

25 .

[0012] Step (1) of the process involves vacuum impregnation of a metal halide on silicon (Si) particles. The metal halide comprises a palladium halide of formula PdX'_2 , where each X' is independently a halogen atom. X' may be selected from Br, Cl, F, or I. Alternatively, X' may be Cl or F. Alternatively, X' may be Cl. Vacuum impregnation results in a physical mixture according to the following formula: $z\text{PdX}'_q + w\text{Si} \rightarrow \text{Pd}_z\text{Si}_w\text{X}'_{zq}$, where subscript z represents the molar amount of palladium atoms present in the mixture and subscript w represents the molar amount of silicon atoms present in the mixture. Alternatively, in these formulas, subscripts z and w may have values such that $0 < z < 1$, $0 < w < 1$, and a quantity $(z + w) = 1$.

35 **[0013]** To perform step (1), the metal halide may be dissolved in a solvent, such as water or other polar protic solvent capable of dissolving the metal halide to form a solution. The

selection of solvent will vary depending on factors such as the solubility of the metal halide chosen in the solvent, however, the solvent may comprise a primary alcohol such as methanol or ethanol in addition to, or instead of, the water. The amount of solvent used is sufficient to dissolve the metal halide. The exact amount depends on various factors including the metal halide selected and the solubility of the metal halide in solvent, however, the amount may range from 0.1 % to 99.9 %, alternatively 1 % to 95 %, based on the combined weight of metal halide and solvent. One single metal halide may be used in the solution. Alternatively, two or more metal halides, as described above, may be used in the solution.

10 **[0014]** One or more additional ingredients, such as an acid, an additional metal halide, or both, may optionally be added in the solution. The acid may be, for example, HCl. The amount of HCl may range from 0.1% to 1.0% based on the total weight of the solution.

[0015] The additional metal halide may be a copper halide such as a copper halide of formula CuX' , a copper halide of formula CuX'_2 , or a combination thereof, where X' is as described above. The copper halide may be added in an amount ranging from 0.01% to 0.99% based on total weight of metal halide used.

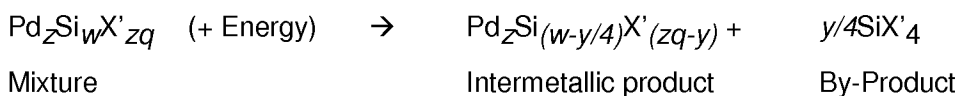
[0016] The silicon may have any convenient solid form, such as particulate. Ground silicon powder may be combined with the solution described above to form a slurry. Ground silicon powder with a particle size of less than 100 μm may be used. Ground silicon powder may have a purity > 99.9 %. Ground silicon powder is commercially available from sources such as Sigma-Aldrich, Inc. of St. Louis, Missouri, U.S.A. The amount of ground silicon powder may range from 0.01% to 0.99%, alternatively > 95%, and alternatively > 90% based on the total weight of the metal halide.

[0017] Vacuum impregnation of the metal halide on the silicon may be performed by any convenient means, such as pulling vacuum on a container containing the slurry. Pressure for vacuum impregnation is below atmospheric pressure (vacuum sufficient enough for the metal halide solution to diffuse into, or interact with sites on, the surfaces of the Si particles). Pressure may be less than 102 kPa, alternatively 3.5 kPa to less than 102 kPa, alternatively 0.01 kPa to 4 kPa. Time for vacuum impregnation depends on various factors including the pressure chosen and the desired intermetallic product.

[0018] The slurry may be dried to form a powder. Drying may be performed by any convenient means, such as heating at atmospheric pressure or under vacuum. Drying may be performed at RT or with heating. Drying may be performed after step (1), concurrently with vacuum impregnation during step (1), or both. Time for drying depends on various factors including the solvent and amount of solvent selected, the pressure selected for vacuum impregnation, and how much solvent is removed during vacuum impregnation.

However, drying may be performed by heating the slurry at 50 °C to 170 °C, alternatively 100 °C to 140 °C, for 1 h to 3 h, alternatively 1 h to 12 h, and alternatively 1 h to 24 h.

[0019] Step (2) of the method described above comprises mechanochemical processing of the mixture prepared in step (1). Step (2) involves a redox reaction of the components in the mixture according to the following formulas.



During mechanochemical processing a chemical reaction occurs, which is a redox reaction. Part of the silicon is oxidized to form volatile SiX_4 [when $\text{X} = \text{Cl}$ or F] and part of the Si

remains with the metal and remaining halide. When $X = \text{Br}$ or I , SiX_4 by-product is not sufficiently volatile. It can be removed from the intermetallic product by chemical separation techniques, such as the use of a solvent. So, the combined amounts of Pd and Si in the intermetallic product change from a quantity $(z + w)$ in the mixture formed in step (1) to $(z + (w - y/4))$, which is less than the quantity $(z + w)$ by $y/4$, in the intermetallic product produced by step (2). The amount for y can be a proportion of the starting amount of halide. The starting amount of halide is zq . In this reaction $y < zq$. Alternatively, the quantity $(z + w)$ may be equal to 1, and the combined amounts of Pd and Si in the intermetallic product may change from a quantity $(z + w) = 1$ in the mixture formed in step (1) to a quantity $(z + (w - y/4))$, which is less than 1 by $y/4$.

[0020] Mechanochemical processing may be performed as described above.

Mechanochemical processing parameters such as temperature, time, type of mill and type of balls used are selected to react the metal halide and the Si in the mixture. In common laboratory equipment, temperature for mechanochemical processing may range from RT to 40 °C. Conventional equipment and techniques may be used, as described above. For example, ball milling may be performed in a stainless steel container by adding the product of step (1) and metal balls, such as stainless steel or tungsten balls, and milling for a time ranging from 0.15 h to 24 h, alternatively 0.15 h to 1 h, alternatively 2 h to 8 h, and alternatively 1 h to 24 h. Weight ratio of steel balls to powdered mixture obtained from step (1) may range from 5 to 50, alternatively 5 to 20, alternatively 10 to 15, and alternatively 30 to 50. The amount and size of the balls used for ball milling depends on various factors including the amount of mixture and the size of the container in which ball milling is performed, however, the balls may have a diameter ranging from 6 mm to 12 mm, alternatively 6.5 mm to 9.5 mm, and alternatively 9.5 mm to 12 mm.

[0021] The method described above may optionally comprise one or more additional steps. For example, the method may further comprise the step of activating the silicon before step (1). Activating the silicon may be performed, for example, by dissolving an

ionic metal salt compound, such as CsF in a solvent, combining the resulting solution with the silicon as described above, and vacuum impregnating under conditions as described above for step (1). Alternatively, the ionic metal salt may be selected from the group consisting of KF, KCl, LiF, and KOH. The resulting activated silicon may optionally be
 5 dried as described above, and then used as a starting material in step (1). The method may optionally further comprise step (3), removing all or a portion of the by-product. The SiX'_4 by-product is volatile and may be removed from the intermetallic compound through heating or by exposure to a stream of air or inert gas such as nitrogen.

[0022] The product prepared by the method described above is a redox reaction product.

10 The product comprises an intermetallic compound and a by-product comprising a silicon tetrahalide of formula SiX'_4 , where X' is as described above. The intermetallic compound may have formula $\text{Pd}_z\text{Si}_{(w-y/4)}\text{X}'_{(zq-y)}$, where a quantity $(z + (w-y/4))$ represents the molar amount of silicon atoms remaining in the mixture and y represents a molar amount of halogen atom removed from the mixture during step (2), and $y < zq$. After step (2), the
 15 molar amounts of Si and X' in the intermetallic compound are less than the molar amounts of Si and X' present in the mixture in step (1); *i.e.*, a quantity $(zq - y) < zq$ because some of the silicon and halide form the by-product SiX'_4 . Alternatively, the quantity $(z + (w-y/4))$ may have a value < 1 .

[0023] The intermetallic compound may comprise a palladium silicide. Alternatively, the
 20 intermetallic compound may comprise a species selected from the group consisting of PdSi ; Pd_2Si ; $\text{Pd}_z\text{Si}_{(w-y/4)}\text{X}'_{(zq-y)}$, where $0.01zq < y < 0.99zq$. Alternatively, the intermetallic compound may have more than one metal. For example, the intermetallic compound may comprise $\text{Cu}_n\text{Pd}_m\text{Si}_{(w-y/4)}\text{X}'_{(zq-y)}$; where n represents the molar amount of Cu, m represents a molar amount of Pd and $0.01zq < y < 0.99zq$. Alternatively,
 25 subscripts n , m , w , and z may have values such that a quantity $(m + n) = z$; $(z + w) < 1$; $0 < z < 1$; and $0 < w < 1$.

[0024] The intermetallic compound described above is useful as a catalyst for preparing an organohalosilane. A method of preparing an organohalosilane comprises: combining an organohalide having the formula RX'' , where R is a hydrocarbyl group having 1 to 10
 30 carbon atoms and X'' is a halogen atom, with a contact mass comprising at least 2 % of the intermetallic compound described above at a temperature ranging from 250 °C to 700 °C to form the organohalosilane.

[0025] The hydrocarbyl groups represented by R in formula RX'' may have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms, and alternatively from 1 to 4 carbon
 35 atoms. Acyclic hydrocarbyl groups containing at least three carbon atoms can have a

- branched or unbranched structure. Examples of hydrocarbyl groups include, but are not limited to, alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl;
- 5 cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; aryl, such as phenyl and naphthyl; alkaryl, such as tolyl, and xylyl; aralkyl such as benzyl and phenylethyl; alkenyl, such as vinyl, allyl, and propenyl; aralkenyl, such as styryl and cinnamyl; and alkynyl, such as ethynyl and propynyl. The halogen atom for X" in the formula may be the same as, or different from, the halogen atom described above for X' in the intermetallic compound.
- 10 Alternatively, the halogen atom for X" in the formula RX'' may be the same as the halogen atom described above for X' in the intermetallic compound
- [0026]** Examples of organohalides include, but are not limited to, methyl chloride, methyl bromide, methyl iodide, ethyl chloride, ethyl bromide, ethyl iodide, chlorobenzene, bromobenzene, iodobenzene, vinyl chloride, vinyl bromide, vinyl iodide, allyl chloride, allyl
- 15 bromide, and allyl iodide. Methods of preparing organohalides are known in the art; many of these compounds are commercially available.
- [0027]** The contact mass comprises at least 2%, alternatively at least 25%, alternatively at least 50%, alternatively at least 75 %, alternatively at least 90%, alternatively at least 95%, alternatively about 100%, based on the total weight of the contact mass, of an
- 20 intermetallic compound prepared as described above. The intermetallic compound may comprise a palladium silicide. Examples of palladium silicides include, but are not limited to, PdSi, Pd₂Si, Pd₃Si, Pd₅Si, and Pd₂Si₈. The palladium silicide may be a single palladium silicide or a mixture of two or more palladium silicides. Alternatively, the intermetallic compound may comprise Cu, Pd, and Si.
- 25 **[0028]** The contact mass may further comprise up to 98 %, alternatively up to 75%, alternatively up to 50 %, alternatively up to 25%, alternatively up to 10%, alternatively up to 5%, based on the total weight of the contact mass, zero-valent silicon. In another embodiment, the contact mass comprises essentially no zero-valent silicon. As used herein, "essentially no zero-valent silicon" is intended to mean that there is no zero-valent
- 30 silicon other than at the level of an impurity. For example, essentially no zero-valent silicon means that there is from 0 to 1%, alternatively 0 to 0.5 %, alternatively 0%, based on the total weight of the contact mass, zero-valent silicon.
- [0029]** The zero-valent silicon is typically chemical or metallurgical grade silicon; however, different grades of silicon, such as solar or electronic grade silicon may be used.
- 35 Chemical and metallurgical grades of silicon are known in the art and can be defined by the silicon content. For example, chemical and metallurgical grades of silicon typically

comprise at least 98.5% silicon. Chemical and metallurgical grades of silicon may also contain additional elements as described below for the contact mass. Methods of making zero-valent silicon are known in the art. These grades of silicon are available commercially.

5 **[0030]** The contact mass may comprise other elements such as Fe, Ca, Ti, Mn, Zn, Sn, Al, Pb, Bi, Sb, Ni, Cr, Co, and Cd and their compounds. Each of these elements may be present at an amount ranging from 0.0005% to 0.6% based upon the total weight of the contact mass.

10 **[0031]** The contact mass may be a variety of forms, shapes and sizes, up to several centimeters in diameter, but the contact mass is typically finely-divided. Finely divided, as used herein, is intended to mean that the contact mass is in the form of a powder.

15 **[0032]** The contact mass may be produced by standard methods for producing particulate silicon from bulk silicon, such as silicon ingots. For example, attrition, impact, crushing, grinding, abrasion, milling, or chemical methods may be used. Grinding is typical. The contact mass may be further classified as to particle size distribution by means of, for example, screening or by the use of mechanical aerodynamic classifiers such as a rotating classifier.

20 **[0033]** If the contact mass comprises more than a single intermetallic compound, for example if the contact mass comprises at least two intermetallic compound or an intermetallic compound and zero-valent silicon, these components may be mixed. The mixing may be accomplished by standard techniques known in the art for mixing solid particles. For example, the mixing may be accomplished by stirring or shaking. Further, mixing may be accomplished in the processing to produce the contact mass particle size mass distribution as described and exemplified above. For example, mixing may be
25 accomplished in a grinding process. Still further, the mixing may be accomplished during the production of the intermetallic compound, such as the palladium silicide.

30 **[0034]** The method of the invention can be carried out in a suitable reactor for conducting the Direct Process. For example, a sealed tube, an open tube, a fixed bed, a stirred bed, or a fluidized bed reactor may be used.

35 **[0035]** The organohalide and contact mass may be combined by charging the reactor with the contact mass followed by flowing the gaseous organohalide through the contact mass. Alternatively, the reactor may be first charged with the organohalide followed by introduction of the contact mass.

40 **[0036]** The rate of addition of the organohalide to the contact mass is not critical; however, when using a fluidized bed, the organohalide is introduced into the reactor bed at a rate sufficient to fluidize the bed but below a rate that will completely entrain the bed.

The rate will depend upon the particle size mass distribution of the particles in the bed and the dimensions of the fluidized bed reactor. One skilled in the art would know how to determine a sufficient rate of organohalide addition to fluidize the bed while not completely entraining the contact mass from the bed. When not using a fluidized bed, the rate at which the organohalide is added to the bed is typically selected to optimize contact mass reactivity.

[0037] The method may optionally further comprise combining the organohalide and contact mass in the presence of an inert gas. For example, an inert gas may be added with the organohalide to the contact mass. Examples of the inert gas that may be introduced with the organohalide include a gas selected from nitrogen, helium, argon and mixtures thereof. The method may optionally further comprise a step of activating the contact mass before and/or during combining the organohalide and contact mass, as described above. Activating the contact mass may be performed by exposing the contact mass to hydrogen gas, or a combination of the inert gas and hydrogen gas, at a temperature ranging from 200 °C to 600 °C for a time ranging from 30 min to 6 h, alternatively 30 min to 4 h.

[0038] The method may be conducted with agitation of the reactants. Agitation may be accomplished by methods known in the art for catalyzed reactions between gases and solids. For example, reaction agitation may be accomplished within a fluidized bed reactor, in a stirred bed reactor, a vibrating bed reactor and the like. However, the method may be conducted without agitation of the reactants by, for example, flowing the organohalide as a gas over a packed bed comprising the intermetallic compound.

[0039] The method may be carried out at atmospheric pressure conditions, or slightly above atmospheric pressure conditions, or elevated pressure conditions may be used.

[0040] The temperature at which the contact mass and organohalide are combined may range from 250 °C to 750 °C, alternatively 280 °C to 700 °C, alternatively 300 °C to 700 °C, and alternatively 400 °C to 700 °C. The temperature at which the contact mass and organohalide are combined may influence the selectivity of the method for producing monoorganohalosilane or diorganohalosilane in the organohalosilane product. The composition of the intermetallic compound may also influence the selectivity of the method for producing monoorganohalosilane or diorganohalosilane. Without wishing to be bound by theory, it is thought that an intermetallic compound containing a relatively high amount of the palladium silicide of formula PdSi may selectively produce an organohalosilane comprising a diorganodihalosilane and an intermetallic compound containing a relatively high amount of the palladium silicide of formula Pd₂Si may selectively produce an

organohalosilane comprising monoorganotrihalosilane. The selectivity may be determined by gas chromatography, or through other suitable analytical techniques.

[0041] The contact mass and organohalide are typically combined for sufficient time to form an organohalosilane from the reaction of the intermetallic compound with the organohalide. For example, in a batch-type reactor, the contact mass and organohalide may be combined for a contact time ranging from 5 minutes to 24 h, alternatively 1 h to 7 h, alternatively 4 h to 7 h, at a temperature ranging from 300 °C to 700 °C. In a continuous or semi-continuous process, where additional contact mass may be added to the reactor, and organohalide gas is continuously passed through the contact mass, the contact time may range from a fraction of a second up to 30 seconds, alternatively from 0.01 second to 15 seconds, alternatively from 0.05 second to 5 seconds.

[0042] When the organohalide is a liquid or solid, the method may optionally further comprise pre-heating and gasifying the organohalide before it is introduced into the reactor.

[0043] The method may optionally further comprise pre-heating the contact mass in an inert atmosphere and at a temperature up to 700 °C, alternatively up to 400 °C, alternatively 280 °C to 525 °C, prior to contacting with the organohalide.

[0044] The method may optionally further comprise introducing additional contact mass or zero-valent silicon into the reactor to replace the silicon that has reacted with the organohalide to form organohalosilanes.

[0045] The method may optionally further comprise recovering the organohalosilane produced. The organohalosilane may be recovered by, for example, removing gaseous organohalosilane from the reactor followed by condensation. The organohalosilane may be recovered and a mixture of organohalosilanes separated by distillation.

[0046] The organohalosilanes prepared according to the present method typically have the formula $R'_qSiX''_{4-q}$, where each R' is independently H or as described and exemplified above for R in the organohalide of formula RX'' , and X'' is as described and exemplified above for the organohalide, and the subscript " q " is an integer with a value of 0 to 3, alternatively 1 to 3.

[0047] Examples of organohalosilanes prepared according to the present method include, but are not limited to, dimethyldichlorosilane (*i.e.*, $(CH_3)_2SiCl_2$), dimethyldibromosilane, diethyldichlorosilane, diethyldibromosilane, trimethylchlorosilane (*i.e.*, $(CH_3)_3SiCl$), methyltrichlorosilane (*i.e.*, $(CH_3)SiCl_3$), phenyltrichlorosilane, diphenyldichlorosilane, triphenylchlorosilane, and methylhydrodichlorosilane (*i.e.*, $(CH_3)HSiCl_2$). The method may also produce small amounts of halosilane and organosilane products such as trichlorosilane, tetrachlorosilane, and tetramethylsilane.

[0048] The method described above can produce organohalosilanes from a silicon source other than zero-valent silicon and produces commercially desirable organohalosilanes in good yield and proportion to less desirable silanes.

[0049] The organohalosilanes produced by the present method are the precursors of most of the products in the silicone industry. For example, dimethyldichlorosilane may be hydrolyzed to produce linear and cyclic polydimethylsiloxanes. Other organohalosilanes, such as methyltrichlorosilane, produced by the method may also be used to make other silicon-containing materials such as silicone resins or sold into a variety of industries and applications.

EXAMPLES

[0050] 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.

Example A – Intermetallic Compound Preparation and Analysis

[0051] An amount of metal chloride was dissolved in 0.3 mL distilled water. Ground silicon powder with particle size less than 100 μm was added, and the resulting composition was vacuum impregnated for 1 h at room temperature of 23 $^{\circ}\text{C}$ and pressure of 4 kPa to form a slurry.

[0052] The slurry was dried at 120 $^{\circ}\text{C}$ for 2 h, and a fine black powder was obtained. The powder was ball milled using a SPEX 8000 mixer/mill in a stainless steel container with 12 mm diameter stainless steel balls under a nitrogen atmosphere. After ball milling, the resulting solid was retrieved and analyzed by XRD and SEM/EDS.

Examples 1-5

[0053] Samples were prepared and analyzed according to the method of Example A. The metal chloride selected, the amounts of metal chloride and ground silicon, the molar ratio of silicon to metal chloride, the amount of powder ball milled, the time the powder was ball milled, and the weight ratio of steel balls to powder are shown below in Table 2, and the results are in Table 3.

Table 2 – Experimental Conditions for Examples 1-5

Ex.	Metal Chloride	Metal Chloride Amt. (g)	Ground Si Amt. (g)	Molar ratio of Silicon to Metal Chloride	Amt. of Powder added to Ball Mill (g)	Time for Ball Milling (h)	Weight Ratio of Steel Balls and Powder
1	PdCl_2	0.61	0.61	6.3	0.45	2	15
2	PdCl_2	0.61	0.61	6.3	0.45	8	15

Ex.	Metal Chloride	Metal Chloride Amt. (g)	Ground Si Amt. (g)	Molar ratio of Silicon to Metal Chloride	Amt. of Powder added to Ball Mill (g)	Time for Ball Milling (h)	Weight Ratio of Steel Balls and Powder
3	PdCl ₂	0.47	0.075	1.0	0.55	8	13
4	PdCl ₂	0.47	0.15	2.0	0.62	8	11
5	PdCl ₂	0.47	0.11	1.5	0.58	8	12

Table 3 – Results of Experiments in Table 2

Example	Results
1	Analytical data suggested loss of chloride, and based on EDS elemental mapping, the sample showed a composition containing Pd _{2.7} Si _{17.2} Cl _{2.4} with a stoichiometry corresponding to Pd ₁ Si _{6.37} Cl _{0.88} . This corresponded to an estimate of 53.2mol% Si loss and 61.4mol% chloride loss. XRD data suggested the sample contained crystalline phase Pd ₂ Si (52mol%) and PdSi (21mol%) as well as the presence of Si and Pd (balance).
2	Analytical data suggested loss of chloride, and based on EDS elemental mapping, the sample showed a composition containing Pd _{6.9} Si _{39.8} Cl _{1.9} with a stoichiometry corresponding to Pd ₁ Si _{5.7} Cl _{0.27} . This corresponded to an estimate of 57.6mol% Si loss and 88mol% chloride loss. XRD data suggested the sample contained crystalline phase Pd ₂ Si (23mol%) and PdSi (47mol%) as well as the presence of Si (balance).
3	Analytical data suggested loss of chloride, and based on EDS elemental mapping, the sample showed a composition containing Pd _{32.1} Si _{21.5} Cl _{4.0} with a stoichiometry corresponding to Pd ₁ Si _{0.67} Cl _{0.12} . XRD data suggested the sample contained crystalline phase Pd ₂ Si (>90mol%) and Pd(balance) with no silicon left behind.
4	Analytical data suggested loss of chloride, and based on EDS elemental mapping, the sample showed a composition containing Pd ₂₇ Si _{31.2} Cl _{2.1} with a stoichiometry corresponding to Pd ₁ Si _{1.15} Cl _{0.08} . XRD data suggested the sample contained crystalline phase Pd ₂ Si (65mol%), and PdSi (31mol%) as well as presence of silicon (balance) with no palladium left behind.

Example	Results
5	Analytical data suggested loss of chloride, and based on EDS elemental mapping, the sample showed a composition containing $\text{Pd}_{2.1}\text{Si}_{26.2}\text{Cl}_{3.1}$ with a stoichiometry corresponding to $\text{Pd}_1\text{Si}_{1.25}\text{Cl}_{0.148}$. XRD data suggested the sample contained crystalline phase PdSi (93mol%), and Pd_2Si (7mol%) with no silicon and palladium left behind.

Example 6

- [0054]** A sample was prepared according to the method of Example A. After the ball milling process was complete, the lid on the steel vial containing the sample was opened and a piece of pH paper shown into it turned red. ICP analysis on the solid retrieved
- 5 showed loss of chloride (92mol%) and loss of Si (42mol%) as volatile species (SiCl_4). Based on the elemental analyses, the solid composition had a stoichiometry corresponding to $\text{Pd}_1\text{Si}_{0.67}\text{Cl}_{0.136}$. XRD results indicated that Pd_2Si was present.

Table 4 – Example 6 conditions

Ex.	Metal Chloride	Metal Chloride Amt. (g)	Ground Si Amt. (g)	Molar ratio of Silicon to Metal Chloride	Amt. of Powder added to Ball Mill (g)	Time for Ball Milling (h)	Weight Ratio of Steel Balls and Powder
6	PdCl_2	0.8	0.13	1.0	0.6	8	12

10 Example B – Two Step Sample Preparation and Analysis

- [0055]** An amount of CsF (0.3 g) was dissolved in 0.3 mL distilled water; and 0.57 g of ground silicon powder with particle size less than 100 μm was added. The resulting composition was vacuum impregnated for 1 h at room temperature of 23 °C and pressure of 4 kPa to form a slurry mixture. The slurry mixture was dried at 120 °C for 2 h, and an
- 15 activated silicon was obtained.

- [0056]** PdCl_2 and CuCl_2 were dissolved in 0.3 mL of distilled water, and the resulting solution was added to 0.9 g of the activated silicon. The resulting mixture was vacuum impregnated for 1 h at room temperature of 23 °C and pressure of 4 kPa and subsequently dried at 120 °C for 2 h.

- 20 **[0057]** The resulting powder was ball milled using a SPEX 8000 mixer/mill in a stainless steel container with 12 mm diameter stainless steel balls under a nitrogen atmosphere. After ball milling, the resulting solid mixture was retrieved and analyzed by XRD and SEM/EDS.

Examples 7 and 8

[0058] Samples were prepared according to the method of Example B. The amounts of PdCl₂ and CuCl₂, the amount of powder ball milled, the time the powder was ball milled, and the weight ratio of steel balls to powder, and the results are shown below in Table 5.

5 Table 5 – Conditions and Results for Examples 7 and 8

Ex.	PdCl ₂ Amt. (g)	CuCl ₂ Amt (g)	Amt. of Powder added to Ball Mill (g)	Time for Ball Milling (h)	Wt. Ratio of Balls & Powder	Composition
7	0.5	0.1	0.5	2	14	Cu _{0.18} Pd _{1.82} Si (42mol%), CsCl (8mol%) and Si (51mol%).
8	0.5	0.1	0.5	8	14	Cu _{0.18} Pd _{1.82} Si (31mol%), PdSi (8mol%), CsCl (18mol%) and Si (42mol%).

Example 9 - Chlorosilane Production

[0059] An intermetallic compound was prepared using a method as described above in example 5, and 0.5 g was loaded into a quartz tube flow through reactor. The reactor was initially purged with argon for 1 h. The sample was treated with H₂ (20 sccm) at 500 °C for 2 h and subsequently the reactor temperature was reduced to 300 °C. H₂ flow was stopped followed by purging with argon. Next, MeCl (1 sccm) was flowed through the sample bed, and the evolution of volatiles were analyzed by combination of GC and GC-MS. At 300 °C, high selectivity towards Me₂SiCl₂ (76 mol%) was observed, with the rest as MeSiCl₃ (24 mol%). As the reaction continued, the selectivity of the reaction for producing Me₂SiCl₂ dropped and a 1:1 ratio of Me₂SiCl₂/MeSiCl₃ was observed at 350 °C after 1 h. Continuing the reaction at 400 °C for 1 h lead to significant drop in Me₂SiCl₂ selectivity and product composition contained Me₂SiCl₂ (10 mol%), MeSiCl₃ (77 mol%) and SiCl₄(13 mol%).

20 Example 10 – Chlorosilane Production

[0060] An intermetallic compound was prepared by the method as described above in example 8, and 0.5 g was loaded into a quartz tube flow through reactor. The reactor was initially purged with argon for 1 h. The sample was treated with H₂ (20 sccm) at 500 °C for 2 h and subsequently the reactor temperature was reduced to 300 °C. Hydrogen flow was

stopped, followed by purging with argon. Next, MeCl (1 sccm) was flowed through the sample bed and the evolution of volatiles were analyzed by combination of GC and GC-MS. At 300 °C, Me₂SiCl₂ (83 mol%) was observed along with MeSiCl₃ (11 mol%) and Me₃SiCl (6 mol%). As the reaction continued at 300 °C, the selectivity of the reaction for producing Me₂SiCl₂ dropped, and after 1 h, it reduced to 13mol% Me₂SiCl₂ and the rest as MeSiCl₃ (82 mol%) and SiCl₄ (5 mol%). At 350 °C and higher, Me₂SiCl₂ production stopped. At 400 °C, the product composition contained MeSiCl₃ (83 mol%) and SiCl₄ (17 mol%).

Comparative Examples 1 and 2 – Omit Ball Milling Step

10 **[0061]** Samples of the fine black powders obtained by drying the slurry mixtures prepared in examples 1 and 7 were analyzed by XRD and SEM/EDS before ball milling. In each comparative example, analytical data suggested the presence of Si and metal chlorides, indicating binary/ternary silicide did not form. For the slurry from example 1, which produced PdCl₂/Si sample (C1), EDS elemental mapping on the sample showed a
15 composition containing Pd_{4.9}Si_{66.7}Cl_{11.2}, with a stoichiometry corresponding to Pd₁Si_{13.6}Cl_{2.28}. For the slurry from example 7, which produced PdCl₂-CuCl₂/Si sample (C2), EDS elemental mapping on the sample showed a composition containing Pd₃Cu_{0.5}Si_{50.3}Cl₇, with a stoichiometry corresponding to Pd₁Cu_{0.29}Si_{7.29}Cl_{1.13}.

[0062] The intermetallic compounds described herein are useful as catalysts for
20 preparing organohalosilanes. PdSi is useful as a selective catalyst for forming diorganodihalosilanes. The intermetallic compound comprising PdSi formed by the method described herein may be used in the methods for preparing diorganodihalosilanes mentioned in WO2011/094140 and WO2011/149588, which are both hereby incorporated by reference. The intermetallic compound comprising Pd₂Si is useful as a selective
25 catalyst for forming monoorganotrihalosilanes.

[0063] The process described herein may be used to selectively control the stoichiometry of the intermetallic compound produced. Without wishing to be bound by theory, it is thought that formation of PdSi over Pd₂Si may be optimized by controlling the molar ratio of palladium halide and silicon used in step (1) of the process described herein, for
30 example Si: PdX'₂ molar ratio may be greater than 2:1, alternatively 2:1 to 1.5:1. Without wishing to be bound by theory, it is thought that mechanochemical processing in step (2) of the method described above offers the advantage of not requiring extreme temperatures as compared to an electrochemical method or high temperature arc melting process, which may require extreme temperatures.

CLAIMS:

1. A process comprises:
 - (1) vacuum impregnating a metal halide on silicon, where the metal halide comprises a palladium halide of formula PdX'_2 , where each X' is independently a halogen atom, thereby producing a mixture comprising $\text{Pd}_z\text{Si}_w\text{X}'_{zq}$, where z represents a molar amount of Pd, w represents a molar amount of Si and zq represents a molar amount of the halogen atoms in the mixture; and
 - (2) mechanochemically processing the mixture under an inert atmosphere, thereby producing a redox reaction product comprising
 - (i) an intermetallic compound of formula $\text{Pd}_z\text{Si}_{(w-y/4)}\text{X}'_{(zq-y)}$, where y represents a molar amount of halogen atom removed from the mixture during step (2), and $y < zq$; and
 - (ii) a by-product comprising SiX'_4 .
2. The process of claim 1, where in step (1), $0 < z < 1$, $0 < w < 1$, and a quantity $(z + w) = 1$; and in step (2), a quantity $(z + (w-y/4)) < 1$.
3. The process of claim 1 or claim 2, where a molar ratio of Si to PdX'_2 is at least 1:1, or where the molar ratio of Si to PdX'_2 is at least 1.5:1, or where the molar ratio of Si to PdX'_2 is from 1.5:1 to 10:1.
4. The process of any one of the preceding claims, further comprising:
 - step (3) removing all or a portion of the by-product, or
 - step (0) activating the silicon before step (1), or
 - both step (3) and step (0).
5. The process of any one of the preceding claims, where in addition to the metal halide of formula PdX'_2 , the metal halide further comprises a copper halide selected from the group consisting of CuX' , CuX'_2 , and a combination thereof.
6. An intermetallic compound prepared by the process of any one of the preceding claims.
7. A method comprising:
 - combining an organohalide having the formula RX'' , where R is a hydrocarbonyl group having 1 to 10 carbon atoms and X'' is a halogen atom, with a contact mass comprising at

least 2% of the intermetallic compound of claim 5 at a temperature from 250 °C to 750 °C to form an organohalosilane.

8. The method of claim 7, where the hydrocarbyl group has 1 to 6 carbon atoms and X" is Cl; or where the organohalide is methyl chloride, methyl bromide, or methyl iodide.

9. The method of claim 7 or claim 8, where the contact mass comprises at least 90% of an intermetallic compound comprising one or more compounds of formulae: PdSi; Pd₂Si; Pd_zSi_(w-y/4)X_(zq-y), where 0.01zq < y < 0.99zq; Cu_nPd_mSi_(w-y/4)X_(zq-y), where 0.01zq < y < 0.99zq; and a combination thereof.

10. The method of claim 9, further comprising replenishing the contact mass with a zero-valent silicon or with additional contact mass as the organohalosilane is produced.

11. The method of any one of claims 7 to 10, further comprising a step of: activating a contact mass comprising at least 2 % of the intermetallic compound, where activating the contact mass may be performed by a technique comprising exposing the contact mass to hydrogen at a temperature of 200 °C to 600 °C for a time ranging from 30 min to 6 h.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/029552

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J37/04 B01J37/02 B01J23/44 C07F7/16 C22C29/18 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 C07F C22C		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 862 023 A (JOHNSON HARLAN B) 21 January 1975 (1975-01-21) example 4 -----	6
X	US 2009/004370 A1 (ZURCHER FABIO [US] ET AL ZUERCHER FABIO [US] ET AL) 1 January 2009 (2009-01-01) paragraph [0095] -----	6
X	US 4 956 326 A (YONEDA NORIYUKI [JP] ET AL) 11 September 1990 (1990-09-11) examples 3,13 -----	6
☐ 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		
Date of the actual completion of the international search 13 June 2013		Date of mailing of the international search report 16/09/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Zieba, Roman

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/029552

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-6

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-6

A process of making an intermetallic compound comprising palladium and silicon and said intermetallic compound.

2. claims: 7-11

A method of producing an organohalosilane.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/029552

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3862023	A	21-01-1975	NONE
US 2009004370	A1	01-01-2009	US 2009004370 A1 01-01-2009
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