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(54) Method for redistribution and purification of methylsilanes

(57) A redistribution process for enriching a low-boiling methylsilane mixture in a methylchlorosilane selected from dimethylhydrochlorosilane and trimethylchlorosilane. The process comprises contacting a low-boiling methylsilane mixture, resulting from the contact of methyl chloride with silicon, with alumina under non-equilibrium conditions at a temperature greater than 150°C. we have surprisingly found that the concentrations of dimethylhydrochlorosilane and trimethylchlorosilane reach maximum levels under non-equilibrium conditions occurring at a temperature greater than 150°C. The process is also useful for facilitating the removal of olefin and chlorocarbon organic contaminants from the low-boiling methylsilane mixture.

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Description

The present invention is a redistribution process for enriching a low-boiling methylsilane mixture in a methylchlorosilane selected from dimethylhydrochlorosilane or trimethylchlorosilane. The process comprises contacting a low-boiling methylsilane mixture, resulting from the contact of methyl chloride with silicon, with alumina under non-equilibrium conditions at a temperature greater than 150°C. We have surprisingly found that the concentrations of dimethylhydrochlorosilane and trimethylchlorosilane reach maximum levels under non-equilibrium conditions occurring at temperatures above 150°C. The present process is also useful for removing olefin and chlorocarbon organic contaminants from the low-boiling methylsilane mixture.

Methylchlorosilanes are the basic monomers from which a wide variety of organosilicon containing fluids, rubbers and resins are formed. Commercially these methylchlorosilane monomers are produced by a process typically referred to as the "direct process." In the direct process, methyl chloride is reacted with silicon in the presence of a catalyst comprising copper. This process was first described by Rochow in U.S. Patent 2,380,995. Commercially, production of polydimethylsiloxanes represent the highest use of methylchlorosilanes from the direct process. Therefore, considerable effort is directed toward optimizing the direct process to produce dimethyldichlorosilane, for example, Ward et al., U.S. Patent 4,500,724.

Despite all attempts to optimize this process, the basic effluent from the reactor is still a mixture of methylsilanes and higher boiling materials which includes disilanes, polysiloxanes, silylmethylenes and particulates. Typically, the effluent exiting the reactor is distilled to separate the methylsilanes from the higher-boiling materials. The methylsilane distillate comprises a mixture having dimethyldichlorosilane as a major component and minor components comprising, for example, tetramethylsilane, dimethylhydrochlorosilane, methylhydrodichlorosilane, trimethylchlorosilane and methyltrichlorosilane. These minor components can represent as much as 15 weight percent of the monosilanes produced in the direct process.

Commercial demand for methylsilanes can make it desirable to increase the proportion of certain of these minor component methylsilanes, such as dimethylhydrochlorosilane and trimethylchlorosilane. Although it is possible to alter methylsilane ratios exiting the reactor by process changes, manufacturers are reluctant to risk process upsets on which considerable resource has been expended to optimize dimethyldichlorosilane production. Therefore, new methods are desirable to alter the product mix from the direct process outside of the reactor.

The present method introduces a process whereby the concentration of dimethylhydrochlorosilane and/or trimethylchlorosilane in the effluent from the direct process is increased. This method comprises contacting a low-boiling methylsilane mixture, resulting from the reaction of methyl chloride with silicon, with alumina under non-equilibrium conditions at a temperature greater than 150°C. Unexpectedly, we have also found that under non-equilibrium conditions much higher concentrations of dimethylhydrochlorosilane and trimethylchlorosilane can be obtained in the low-boiling methylsilane mixture than would be predicted by standard equilibrium calculations.

Our process is also useful for removing olefin and chlorocarbon organic contaminants from the low-boiling mixture. Under our process conditions, olefin and chlorocarbon organic contaminants are reacted with silicon-bonded hydrogen to convert the contaminants to saturated alkanes. Therefore, the present invention also provides a process where redistribution of methylsilane and the removal of organic contaminants are effected in a single step.

Wynn, U.S. Patent 3,704,260, teaches that trimethylchlorosilane and methylhydrodichlorosilane can be rearranged in the presence of aluminum trichloride to form dimethylhydrochlorosilane. This rearrangement is preferably carried out at a temperature of 110°C. to 140°C. for 0.25 to 8 hours.

Viego et al., U.S. Patent 3,769,310, claim the redistribution of methylhydrodichlorosilane with trimethylchlorosilane to produce dimethylhydrochlorosilane using a catalyst selected from a group consisting of $AlCl_3$, $KAlCl_4$ and BF_3. The process is run until equilibrium conditions are established at a temperature of 50°C. to 250°C. for a time of 2 to 7 hours.

Marko et al., U.S. Patent 4,774,347, describes a process for reducing the chlorocarbon content of alkylsilanes. This process comprises contacting crude alkylsilanes, containing as a minor portion chlorocarbons, and a hydrogen-containing silane with a catalyst that facilitates the reaction to convert the chlorocarbons to an alkane. Alumina is disclosed as a useful catalyst in the process. During the process, some rearrangement of more highly alkylated silanes with other alkylhalosilanes may also occur. The process is run at a temperature within a range of 25°C. to less than 150°C.

The present process for enriching a low-boiling methylsilane mixture in a methylchlorosilane comprises (A) contacting a low-boiling methylsilane mixture, resulting from the contact of methyl chloride with silicon, with alumina under non-equilibrium conditions at a temperature greater than 150°C. and (B) recovering a methylsilane mixture enriched in a methylchlorosilane selected from dimethylhydrochlorosilane or trimethylchlorosilane.

This process is run in standard reactors for contacting liquids and gases with a heterogeneous catalyst. The process can be run as a continuous, semi-continuous or batch process. Preferred is when our process is run as a continuous process using a packed-bed of alumina as catalyst.

The low-boiling methylsilane mixture can comprise, for example, tetramethylsilane, trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, dimethylhydrochlorosilane and methylhydrodichlorosilane. The preferred low-boiling methylsilane mixture is a distilled effluent from the direct process. Such a process is described, for example, in Ward et al., U.S. Patent 4,500,724, from which a suitable low-boiling methylsilane mixture can be isolated for use in the present process. Typical components in such an effluent are further described in Wynn, U.S. Patent 3,704,260 or Chadwick et al., U.S. Patent 5,292,909. This effluent can include monosilanes such as described above for the methylsilane mixture; higher-boiling components such as disilanes, siloxanes and silylmethylenes; solids such as silicon containing solids and insoluble compounds of copper or other metals. The typical effluent from the direct process may also contain olefins and chlorinated hydrocarbons.

By "low-boiling" it is meant that the methylsilane mixture comprises those compounds having a boiling point less than 100°C. Preferred is when this methylsilane mixture comprises those compounds having a boiling point of less than 70°C. More preferred is a low-boiling methylsilane mixture which is a low-boiling fraction resulting from the distillation of the product from a direct process reactor.

In the present process, the low-boiling methylsilane mixture is contacted with alumina. We believe that alumina functions therein as a redistribution catalyst. It is preferred that the alumina have a low sodium content and also have both high porosity and a large surface area. More preferred is when the alumina has a porosity of at least 0.4 cm^3/g and a surface area of at least 150 m^2/g. Even more preferred is an alumina porosity of at least 0.7 cm^3/g and a surface area of at least 200 m^2/g. The upper limits for porosity and surface area are not restricted and are primarily determined by availability and the likelihood to contain and handle the material.

The concentration of alumina in relation to the low-boiling methylsilane mixture used in our process is not critical and can be any concentration which effects enrichment of the low-boiling methylsilane mixture in the methylchlorosilane. In a preferred process, our process is run as a continuous process in a packed-bed reactor. In this case, the amount of alumina comprising the packed-bed will depend on such factors as acceptable pressure drop across the bed and the desired through put and residence time of the methylsilane mixture in the alumina bed.

The present process is run under non-equilibrium conditions and the low-boiling methylsilane mixture is enriched in a methylchlorosilane selected from dimethylhydrochlorosilane or trimethylchlorosilane. By "enriched", it is meant that the amount of dimethylhydrochlorosilane and trimethylchlorosilane is increased over that amount present in the mixture before contact with the alumina and is further increased over that obtained in an equilibrium mixture. We have surprisingly found that the maximum concentrations of dimethylhydrochlorosilane and/or trimethylchlorosilane in the low-boiling methylsilane mixture is achieved under non-equilibrium conditions. The non-equilibrium conditions at which this maximum is reached can easily be determined by those of ordinary skill in the art given the guidance provided herein. Such conditions depend upon the methylchlorosilane in which the low-boiling methylsilane mixture is to be enriched and the specific composition of the methylsilane mixture.

When it is desired to enrich the low-boiling methylsilane mixture in dimethylhydrochlorosilane, it is preferred that the low-boiling mixture comprise at least methylhydrodichlorosilane and/or trimethylchlorosilane and that the non-equilibrium conditions comprise a temperature within a range of 150°C. to 300°C. and a contact time of the mixture with the alumina of 0.1 to 90 minutes. Preferred conditions are a temperature of 180°C. to 220°C. and a contact time of 5 to 60 minutes.

When it is desired to enrich the low-boiling methylsilane mixture in trimethylchlorosilane, it is preferred that the low-boiling mixture comprise at least tetramethylsilane and/or dimethyldichlorosilane and that the non-equilibrium conditions comprise a temperature within a range of 180°C. to 340°C. and a contact time of 30 to 120 minutes. Preferred conditions are a temperature of 200°C. to 250°C. and a contact time of 45 minutes to 90 minutes.

The pressure at which the present process is run is not critical and is generally within a range of 0.1 to 1.5 MPa (15 to 215 psi). It is preferred that our process be run with the low-boiling methylsilane mixture in the liquid phase. Therefore, the present process should be run at a pressure which, at the temperature the process is run, maintains a major portion of the low-boiling methylsilane mixture in the liquid phase. A preferred pressure is within a range of 0.6 to 1.5 MPa (95 to 215 psi).

A methylsilane mixture enriched in a methylchlorosilane selected from dimethylhydrochlorosilane or trimethylchlorosilane is recovered from the present process. By "recovered", it is meant that the enriched methylsilane mixture is separated from the alumina. When our process is run as a continuous process in a fixed-bed reactor, recovery consists of merely collecting the effluent from the reactor. Recovery of the enriched methylsilane mixture can further comprise such steps as filtration to remove residual alumina or other particulates and distillation to separate the enriched methylsilane mixture into individual methylsilane compounds or mixtures of methylsilanes compounds.

The present process is also useful for removing olefin and chlorocarbon organic contaminants from a low-boiling methylsilane mixture resulting from the contact of methyl chloride with silicon. Olefins are known to cause color problems in the preparation of methylsilanes or polyorganosiloxane intermediates and products. Chlorocarbons create a problem due to their thermal instability, potentially decomposing into an olefin and hydrogen chloride. These olefins and chlorocarbons have boiling points similar enough to those of the methylsilanes to make separation by distillation difficult. In our process, the olefins and chlorocarbons are reacted with silane species having hydrogen bonded to silicon in the presence of alumina to form alkanes. U.S. Patent 4,774,347, describes a similar process where olefins and chlorocarbons were reacted with silane species having hydrogen bonded to silicon in the presence of Lewis acid forming materials at a temperature less than 150°C. to form alkanes. Our process extends the teachings of that patent to include a process having a temperature greater than 150°C.

The chlorocarbon materials which are converted to alkanes can be, for example, 2-chloropropane, 1-chlorobutane, 2-chlorobutane, 2-chloro-2-methylpropane, 1-chloropentane, 2-chloro-2-methylbutane, 1-chlorohexane, 2-chlorohexane, 3-chloro-2-methylpentane, 2-chloro-2,3-dimethylbutane, 3-chlorooctane and 2-chlorodecane.

Olefins which are converted to alkanes by the present process include the dehydrohalogenation by-products of the above listed chlorocarbons.

The silane having hydrogen bonded to silicon is, for example, dichlorosilane, dimethylsilane, methylchlorosilane, methyldichlorosilane, dimethylchlorosilane and trimethylsilane. The hydrogen-containing silane is normally a minor portion of the low-boiling methylsilane mixture. However, to assure that a sufficient quantity of the hydrogen bonded to silicon is present to maximize the conversion of olefins and chlorocarbons to saturated hydrocarbons, a silane having hydrogen bonded to silicon may be added to the low-boiling methylsilane mixture.

The following examples are provided to further illustrate the present invention.

Example 1

The redistribution of a low-boiling methylsilane mixture in a packed-bed of alumina was evaluated.

The reactor comprised a 1.9 cm inside diameter by 30 cm length stainless steel tube. The reactor was packed with 1.6 mm x 6.4 mm alumina pellets (United Catalysts, Louisville, KY). The reactor was immersed in a temperature controlled oil bath. A low-boiling methylsilane mixture comprising the methylsilanes reported in Table la was fed to the reactor at a rate providing a residence time within the reactor of 5 minutes. The pressure of the reactor was maintained at 792.9 kPa (115 psi). The "Control" values represent the concentration of the methylsilanes in the mixture prior to feed to the reactor. At the temperatures reported in Table la, a sample of the effluent from the reactor was analyzed by gas chromatography using a thermal conductivity detector (GC-TC). The results of this analysis are also reported in Table la. Also reported for comparison purposes is the calculated equilibrium concentrations for each of the methylchlorosilanes after redistribution ("Equil."). These calculations were made using standard thermodynamic calculations.

The effluent from the reactor was also analyzed by GC-TC for chlorocarbon content. Prior to passing through the reactor, the methylsilane mixture contained 792 ppm chlorocarbons. The percent reduction of chlorocarbons in the mixture at each reactor temperature is reported in Table 1b.

Table 1a

Non-Equilibrium Redistribution of Methylsilane Mixture						
Weight Percent						
Temp.(°C)	Me_4Si	Me_2HSiCl	$MeHSiCl_2$	Me_3SiCl	$MeSiCl_3$	Me_2SiCl_2
90	0.08	1.25	4.14	2.75	6.05	84.73
120	0.01	1.19	4.14	2.88	6.08	84.78
150	0.00	1.13	3.80	2.91	6.19	85.10
180	0.00	1.51	3.43	3.02	6.79	84.32
210	0.00	1.72	3.12	3.15	7.38	83.61
(Control)	0.12	1.33	3.92	2.67	6.06	85.05
(Equil.)	0.00	1.15	3.89	3.68	6.92	83.51

Table 1b

Chlorocarbon Removal	
Temp. (°C.)	% Reduction Chlorocarbons
90	61
120	66
150	82
180	89

Table 1b (continued)

Chlorocarbon Removal	
Temp. (°C.)	% Reduction Chlorocarbons
210	92

Example 2

The redistribution of a second low-boiling methylsilane mixture in a packed-bed of alumina was evaluated at a residence time of five minutes. The reactor was as described in Example 1. A methylsilane mixture of the composition described in Table 2a as "Control" was fed to the reactor at a rate providing for a residence time in the reactor of 5 minutes. The pressure of the reactor was maintained at 792.9 kPa (115 psi). At the temperatures reported in Table 2a, a sample of the effluent from the reactor was collected and analyzed by GC-TC. The results of this analysis are reported in Table 2a. Also reported for comparison purposes is the calculated equilibrium concentrations for each of the methylsilanes after redistribution.

The effluent from the reactor was also analyzed by GC-TC for olefin and chlorocarbon content. Prior to passing through the reactor, the methylsilane mixture contained 81 ppm olefins and 170 ppm chlorocarbons. The percent total reduction in olefins and chlorocarbons at each reactor temperature is reported in Table 2b.

Table 2a

Non-Equilibrium Redistribution of Methylsilane Mixture						
Weight Percent						
Temp.(°C)	Me_4Si	Me_2HSiCl	$MeHSiCl_2$	Me_3SiCl	$MeSiCl_3$	Me_2SiCl_2
90	0.04	0.28	2.17	1.90	5.59	89.78
120	0.00	0.39	1.99	2.04	5.80	89.40
150	0.00	0.56	1.78	2.06	6.08	89.08
210	0.00	0.81	1.43	2.11	6.64	88.65
240	0.00	0.91	1.33	2.26	6.95	88.15
(Control)	0.07	0.31	2.25	1.87	5.59	89.62
(Equil.)	0.00	0.55	2.00	3.56	7.60	86.08

Table 2b

Reduction in Olefins and Chlorocarbons	
Temp. (°C.)	% Reduction
90	97
120	97
150	99
210	99
240	99

Example 3

The methylsilane mixture of Example 2 was redistributed in a packed-bed of alumina at a residence time of 45 minutes. The procedure was the same as described in Example 2 with the exception of the residence time. The results are reported in Table 3a. The effluent from the reactor was also analyzed by GC-TC for olefins and chlorocarbons content. The percent total reduction in olefins and chlorocarbons at each reactor temperature is reported in Table 3b.

Table 3a

Non-Equilibrium Redistribution of Methylsilane Mixture						
Weight Percent						
Temp.(°C)	Me_4Si	Me_2HSiCl	$MeHSiCl_2$	Me_3SiCl	$MeSiCl_3$	Me_2SiCl_2
90	0.00	0.25	2.14	1.97	5.58	89.74
120	0.00	0.61	1.66	2.13	6.29	88.96
150	0.00	0.80	1.39	2.17	6.63	88.69
210	0.00	0.82	1.24	2.86	7.74	86.83
240	0.00	0.80	1.30	4.03	9.20	84.06
(Control)	0.07	0.31	2.25	1.87	5.59	89.62
(Equil.)	0.00	0.55	2.00	3.56	7.60	86.08

Table 3b

Reduction in Olefins and Chlorocarbons	
Temp. (°C.)	% Reduction
90	99
120	99
150	100
210	98
240	98

Claims

1. A process for enriching a low-boiling methylsilane mixture in a methylchlorosilane comprising (A) contacting a low-boiling methylsilane mixture, resulting from the contact of methyl chloride with silicon, with alumina under non-equilibrium conditions at a temperature greater than 150°C. and (B) recovering a methylsilane mixture enriched in a methylchlorosilane selected from dimethylhydrochlorosilane and trimethylchlorosilane.

2. A process according to claim 1, wherein the low-boiling methylsilane mixture comprises methylhydrodichlorosilane and trimethylchlorosilane and the non-equilibrium conditions comprise a temperature within a range of 150 to 300°C. and a contact time within a range of 0.1 to 90 minutes and wherein the methylsilane mixture is enriched in dimethylhydrochlorosilane.

3. A process according to claim 1, wherein the low-boiling methylsilane mixture comprises tetramethylsilane and dimethyldichlorosilane and the non-equilibrium conditions comprise a temperature within a range of 180 to 340°C. and a contact time within a range of 30 to 120 minutes and wherein the methylsilane mixture is enriched in trimethylchlorosilane.

4. A process according to any or claims 1 to 3, wherein the process is conducted as a continuous process for contacting low-boiling methylsilane mixture with a fixed-bed of alumina.

5. A process according to any of claims 1 to 4, wherein the low-boiling methylsilane mixture has a boiling point less than 100°C. and is a distillate of product from a process comprising the reaction of methyl chloride with silicon.

6. A process according to any of claims 1 to 5, wherein the alumina has a porosity of at least 0.4 cm^3/g and a surface area of at least 150 m^2/g.

7. A process according to any of claims 1 to 6, wherein the low-boiling methylsilane mixture is contacted with the alumina at a pressure within a range of 0.1 to 1.5 MPa (15 to 215 psi).

8. A process according to any of claims 1 to 3, wherein low-boiling methylsilane mixture comprises a silane having

hydrogen bonded to silicon and a contaminant selected from olefins and chlorocarbons and the recovered methylsilane mixture enriched in methylchlorosilane has a reduced concentration of the contaminant in comparison to that present in the low-boiling methylsilane mixture.