NOVEL CONCEPT FOR GENERATING POWER VIA AN INORGANIC NITROGEN CYCLE, BASED ON SAND AS THE STARTING MATERIAL AND PRODUCING HIGHER SILANES

Inorganic silicon-nitrogen cycle

Combustion of NH₃ to N₂ and H₂O, generation of energy
Conversion of Si₃N₄ into ammonia NH₃, for instance to NH₃⁺ (SiO₄)²⁻

Sand SiO₂

Silicon

SiₓHₓNₓ+₂ synthesis by modified Muller-Rochow process

Combustion of SiₓHₓNₓ+₂ + Si powder with air (20% O₂/80% N₂) to H₂O + Si₃N₄ generation of energy

The invention relates to a novel energy concept that relates to an artificial silicon-nitrogen cycle and that constitutes the complement to the natural carbon-oxygen cycle. Pure silicon is produced from sand using solar energy. By repeated Muller-Rochow synthesis with silylchlorides the silicon is converted to higher silanes. The silylchlorides used are either silicons derived from chemical wastes or are economically produced from monosilanes or disilanes. They are mixed with silicon powder and combusted with air to give H₂O and silicon nitride SiₓHₓNₓ thereby generating power. The silicon nitride is converted to ammonia NH₃ under alkaline conditions, thereby producing silicates. Part of the NH₃ is converted to follow-on products, the major portion however is combusted with air to give H₂O and N₂, thereby generating power. The N₂ cycle is thereby closed.
Combustion of Si -- Si powder (20% O₂/80% N₂) to H₂O + Si₃N₄ generation of energy

Sand SiO₂ ↓ Silicon

Inorganic silicon-nitrogen cycle

Combustion of NH₃ to N₂ and H₂O generation of energy

Conversion of Si₃N₄, for instance to NH₃ + [SiO₂]ₙ

Si₃H₂₄synthesis by modified Miller-Hackow process

Figure 1
NOVEL CONCEPT FOR GENERATING POWER VIA AN INORGANIC NITROGEN CYCLE, BASED ON SAND AS THE STARTING MATERIAL AND PRODUCING HIGHER SILANES

[0001] In the periodic system of elements silicon is situated directly below carbon and is very similar to it. However, the hydrogen compounds of the silicon have some differences with respect to the hydrocarbons. Already Friedrich Wöhler discovered the silicon homologue of the methan CH₄, i.e. monosilane SiH₄ during the change of the century. At the beginning of the 20th century Prof. Alfred Stock, Karlsruhe was able to produce the longer-chain homologues of the hydrocarbons ethane, propane and butane, namely the disilane Si₂H₆, trisilane Si₃H₈ and tetrasilane n-Si₄H₁₀ which, however, are all self-igniting in air.

[0002] 1951 the silane research started in Cologne with Prof. Franz Fehér. At the beginning of the seventies his assistant Peter Plichta succeeded in producing the so-called higher silanes of the pentasilane Si₅H₁₂ to the decasilane Si₅R₂₂ for the first time which were unknown until this date (German patent 21 39 155 (1976)). One came to know that—in contrast to the opinion up to this date higher silanes do not become instable with increasing chain length but, in contrast, become more stable so that, for instance, already the heptasilane (n-Si₇H₁₄) is no more

[0003] Copper Oxide in the Direct Process, a Dangerous Mixture?). self-igniting at ambient temperature. Higher silanes are handle-safe, non-toxic liquids similar to diesel oil and thus pumpable.

[0004] Silanes can be used as energy producing fuels (German patent 42 15 835 (1994), U.S. Pat. No. 5,775,036 (1998)).

[0005] In the following the combustion of hydrocarbons is compared with the combustion of silicon hydrides.

[0006] As one knows, when combustining hydrocarbons not only the hydrogen portion but also the carbon portion reacts only with the 20% oxygen portion of the air:

\[
\begin{align*}
H₂ + 1/2O₂ &\to H₂O \\
C₄H₁₀ + 13/2O₂ &\to 4CO₂ + 5H₂O
\end{align*}
\]

[0007] Disadvantages: The nitrogen portion of the air which is 80% remains unused. Furthermore, the breathing poison carbon dioxide is generated.

[0008] In contrast to carbon, silicon has the characteristic to form a very stable nitride compound, i.e. the industrially known silicon(tetra)nitride Si₃N₄;

\[
3Si + 2N₂ → Si₃N₄ + 750 \text{kJ}
\]

[0009] The technical production of Si₃N₄ was carried out up to now by the reaction of molecular nitrogen with Si powder at 1100-1400°C. However, tests carried out at Wacker Chemie AG have shown that even cold (about 200°C) nitrogen reacts with silicon (catalytically) or ignites (Congress “Silicon for the Chemical Industry V”, May 29-Jun. 2, 2000, Tromso (Norway), speech of Dr. G. Tamme: “Silicon Cyclone Dust and Copper Oxide in the Direct Process, a Dangerous Mixture?”).

[0010] In an air breathing driving mechanism the following reactions are possible:

\[
\begin{align*}
3Si + 2N₂ &\to Si₃N₄ + 750 \text{kJ} \\
H₂ + 1/2O₂ &\to H₂O \\
SiO₂ &\to SiO₂
\end{align*}
\]

[0011] Advantages: The nitrogen of the air can be co-utilized during the combustion of silanes.

[0012] It is the aim of a combustion with silicon hydrides to combust the hydrogen portion stoichiometrically with oxygen of the air in a combustion chamber (as with hydrocarbons), however, to simultaneously let the nitrogen portion of the air react with silicon. In order to reach the complete combustion of the added nitrogen of the air one might add dispersed silicon powder to the silane fuel (German patent 196 12 507 (1997), U.S. Pat. No. 5,996,332 (1999)). The silane/silicon mixture remains pumpable.

[0013] For instance, if one selects the n-heptasilane Si₇H₁₄ (boiling point 226.8°C, density 0.859 g/cm³) the following stoichiometrical combustion of a normal air mixture consisting of 20% O₂ and 80% N₂ results:

\[
\begin{align*}
16H + 10O₂ &\to 8H₂O \\
7Si + 10N₂ &\to 17 \text{dispersed Si} + 8Si₃N₄
\end{align*}
\]

[0014] The chemical equations show that indeed the sucked amount of air can be used as oxidizing agent with a yield of 100%. During this reaction the inert gas nitrogen has the function of an oxidant. Furthermore, during this reaction no breathing poison but in addition to water only silicon nitride is generated which can be even collected or filtered.

[0015] In order to be able to carry out such a combustion in practice a jet engine was already developed which manipulates the very hot combustion gases in the combustion chambers arranged behind one another in such a manner that a shaft can be driven (German patent 196 12 507 (1997), U.S. Pat. No. 5,996,332 (1999)). This jet engine serves as substitute for conventional explosion motors. Furthermore, an air breathing rocket motor (without oxidation tank) is known which is to be used in supersonic aircrafts and space shuttles (German patents 44 37 524 (1996) and 44 39 073 (1996)).

[0016] With the German patent applications 100 46 037 of Sep. 18, 2000 and of Sep. 29, 2000 it is known to produce higher silanes by the repeated use of the modified Muller-Rochow synthesis (i.e. with silylchlorides instead of methylchlorides) in a cheap manner.

[0017] Accordingly, the presuppositions are present to make silanes for the central component of the energy supply of the future.

[0018] It is the object of the present invention to indicate a novel chemical, inorganic cycle according to which silicon dioxide, the main component of the earth crust, at first is converted into pure silicon by means of the sunlight. Thereafter, higher silanes produced therefrom are combusted with nitrogen of the air with the production of energy wherein silicon nitride Si₃N₄ is generated. This Si₃N₄ is converted into ammonia NH₃ in an alkaline manner. During this reaction silicates are generated either which, however, have not to be introduced into the cycle since SiO₂ is available.
without any costs. When combusting NH₃, again N₂ is generated with the production of energy so that the nitrogen cycle is closed.

[0019] On principle, the individual steps are known, can be found in chemistry books or are already protected.

[0020] However, the present invention describes the idea to connect the individual known steps to a cyclic system which is similar to that of the natural carbon cycle. The conventional carbon cycle consists of the dualism or the symbiosis of the organisms on the one side and of the living beings on the other side: CO₂ is assimilated in the plants by photosynthesis with the assistance of sunlight and O₂ is generated. The products of hydrocarbons generated in the plants during this procedure serve as food for animals and human beings. The oxygen generated by the plants is breathed by the animals and human beings wherein energy is produced. During this procedure CO₂ is generated which is needed by the plants for surviving.

[0021] During the millions of years of the evolution a balance adjusted which keeps the carbon dioxide portion in the atmosphere constant. However, this balance has become more and more unsteady with the beginning of the industrial era up to now. The more and more increasing industrial CO₂ output threatening the whole ecological system worldwide is accompanied by the fact that the crude oil reserves become more and more shorter.

[0022] Furthermore, it is an object of the present invention to show a way out of this more and more critical situation.

[0023] The advantages of the use of silanes as fuels is the unlimited availability of the element silicon in contrast to the very limited crude oil sources, 25% of the earth crust consist of silicon. For instance, sand has the chemical formula SiO₂.

[0024] (I) The high demand for pure silicon can be met by reducing the sand (SiO₂) with coal and solar current in an electrical arc furnace in situ to obtain pure silicon. In the same manner as the sunlight provides in the plants for the use of electrons for the C-C-coupling, in the here described inorganic cycle electrical current is generated by means of solar cells consisting of silicon, the generated electrical current being required for the production of pure silicon in the arc furnace.

[0025] The pure CO₂ generated in this process can be used for the generation of the basic organic chemical substance methanol so that the CO₂ does not enter the atmosphere. Methanol is an upgraded form of coal. The hydrogen required for the upgrading of CO₂ for methanol CH₃OH according to the formula CO₂+3H₂→CH₃OH+H₂O is generated by electrolysis wherein the electrical current necessary herefor is generated by the solar cells.

[0026] (II) In the next step higher silanes are produced from the silicon by the modified Müller-Rochow synthesis with silylchlorides. For this, as silylchlorides ideally industrial waste of the silicon chemistry, as methyl chlorosilanes, which otherwise have to be discarded in an expensive manner, is to be used. Alternatively, one obtains the silylchlorides by the chlorination of monosilanes and disilanes generated in large amounts during the acidic decomposition of magnesium silicide.

[0027] (III) In the third step the higher silanes are combusted to water HO₃ and silicon nitride Si₃N₄ with the addition of dispersed silicon powder with atmospheric air (20% O₂, 80% N₂). This silicon nitride Si₃N₄ which is also required in the industry is a grey-white completely non-toxic dust which melts only at temperatures of about 1900° C. with decomposition.

[0028] (IV) Si₃N₄ can be solved in lyes and can be converted into ammonia NH₃. The silicates which are generated in this process are harmless and have not to be recycled since sand SiO₂ is available in large amounts. Parts of the ammonia can be used for the production of artificial fertilizer.

[0029] (V) However, the major part should be combusted in the next step with atmospheric air to nitrogen N₂ and water HO₃ again with a high output of heat. By this, nitrogen is again introduced into the atmosphere which is then again available for the combustion of the higher silanes.

[0030] The above-described reactions result in their cooperation in a novel chemical cycle which is shown in FIG. 1.

[0031] The described silicon-nitrogen cycle represents a completely novel energy concept. This cycle is the artificial complement to the natural carbon-oxygen cycle. The silicon era was announced by the introduction of silicon rectifiers, transistors, diodes, memory chips etc. in physics and with the introduction of silicon oils and silicon plastics in chemistry, with the cycle introduced here it finally succeeds. It has to be emphasized that the energy set free from the described cycle, in the last analysis, stems from the sunlight, as this is the case with the photosynthesis.

[0032] Indeed, the five individual steps of the cycle are not novel per se. However, the complete cycle is novel in the art.

1. A method of generating energy in the course of an inorganic hydrogen-silicon cycle, characterized in that cyclically the following steps are carried out:
   a. Generating pure silicon by the reduction of sand SiO₂ with coal in an electrical arc furnace with the production of pure CO₂;
   b. generating higher silanes Si₆H₂ₓ+2 by repeated use of the modified Muller-Rochow synthesis with silylchlorides;
   c. generating energy by stoichiometrically combusting the silanes with dispersed silicon powder in air N₂/O₂ with the generation of H₂O and Si₃N₄, for instance in motors of different vehicles;
   d. collecting or filtrating the Si₃N₄ dust and converting the same in an alkaline manner to obtain ammonia NH₃ with the generation of silicates (silicon oxides);
   e. working up the NH₃ in small parts to obtain artificial fertilizer, however, mainly combusting NH₃ with air with the generation of H₂O and N₂.

2. The method according to claim 1, characterized in that the electrical current required for the electrical arc furnace is generated in solar cells.

3. The method according to claim 1, characterized in that the pure CO₂ generated during the reduction of the silicon dioxide is upgraded to methanol CH₃OH.
4. The method according to claim 3, characterized in that the hydrogen \( \text{H}_2 \) required for the upgrading of the \( \text{CO}_2 \) to methanol is generated by electrolysis with solar current.

5. The method according to claim 1, characterized in that the silyl chlorides are produced by the chlorination with HCl from monosilanes and disilanes which are obtained in large amounts during the acidic decomposition of magnesium silicide.

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