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(54) **Methods and systems for reducing metal oxides**

(57) The present invention relates to methods for reducing metal oxides under reduced pressure and by using concentrated solar energy; to solar thermochemical reactors and systems adapted to such methods; to the use of such methods and reactors in the production of metals and metal containing compounds, and in perform-

ing thermochemical redox cycles for producing hydrogen and/or carbon monoxide and/or hydrocarbons (fuels) from water and/or carbon dioxide, in producing ammonia and in performing thermochemical redox cycles for separating oxygen from gases.

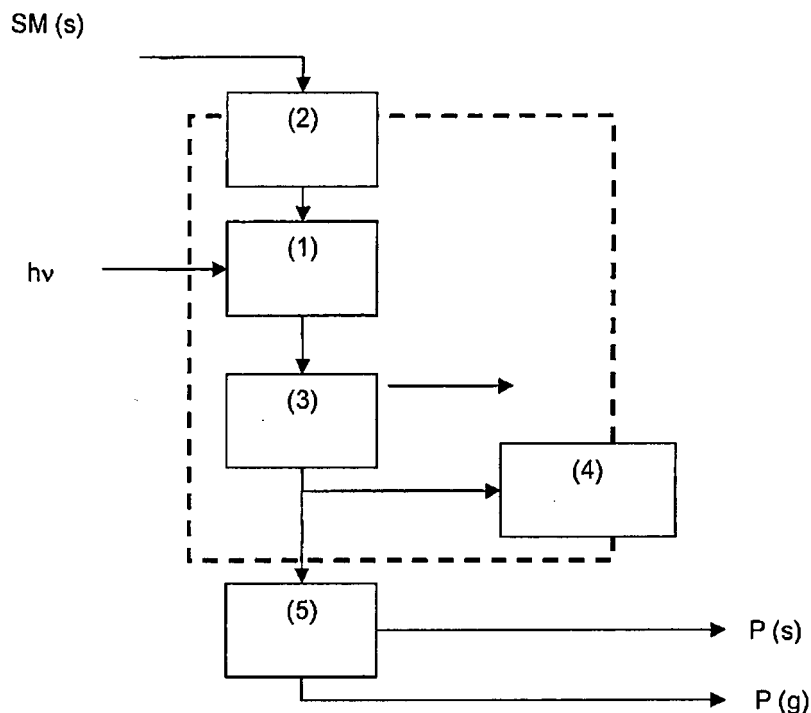


Fig. 1

## Description

[0001] The present invention relates to methods for reducing metal oxides under reduced pressure and by using solar energy; to reactors and systems adapted to such methods; to the use of such methods and reactors in the production of metals and metal containing compounds; in producing fuels, such as hydrogen and/or carbon monoxide and/or hydrocarbons, from water and/or carbon dioxide; in producing ammonia via thermochemical redox cycles; and in performing thermochemical redox cycles for separating oxygen from gases.

[0002] The solar-driven reduction of metal oxides is well known and has a lot of applications, either in the presence or absence, of a reducing agent. Using concentrated solar energy as a source of high-temperature heat has a number of benefits, but requires specific equipment, adapted to the specific process.

[0003] In one field of application, carbothermal reduction of metal oxides is used for the manufacturing of metals, such as aluminum; see e.g. Kruesi et al (Metallurgical and materials transactions B, Feb 2011, 428, 254), which are incorporated by reference.

[0004] In a further field of application, solar thermal reduction of metal oxides is used as part of a thermochemical redox cycle, such as manufacturing of hydrogen from water or manufacturing of syngas from water and a carbon source such as CO<sub>2</sub>, see e.g. Weimer et al, US2006/0188433 and Furler et al (Energy Environ Sci, 2012, 5, 6098), which are incorporated by reference.

[0005] In a further field of application, solar thermal reduction of metal oxides is used as part of a thermochemical redox cycle, such as the Ammonia Production via a 2-Step Al<sub>2</sub>O<sub>3</sub>/AlN Thermochemical Cycle, see e.g. Galvez et al (Industrial & Engineering Chemistry Research, Vol. 46, pp. 2042-2046, 2007).

[0006] In a further field of application, solar thermal reactions are used for separating oxygen; see e.g. Haenchen et al (Industrial & Engineering Chemistry Research, Vol. 51, p. 7013 ff, 2012), disclosing a Thermally-Driven Copper Oxide Redox Cycle for the Separation of Oxygen from Gases.

[0007] Until now, the above applications operate on a laboratory and pilot scale, but have not succeeded to large technical applications. This is attributed to the high temperatures required for obtaining acceptable conversion rates and selectivity. The high temperatures in turn require specific equipment and / or result in high maintenance costs for the reactors and systems involved.

[0008] Thus, it is an object of the present invention to mitigate at least some of these drawbacks of the state of the art. In particular, there is a need for improved processes & methods and for improved reactors and systems allowing solar thermal and solar carbothermal reduction of metal oxides.

[0009] These objectives are achieved by the manufacturing method as defined in claim 1 and by the reactor as defined in claim 12. Further aspects of the invention are disclosed in the specification and independent claims, preferred embodiments are disclosed in the specification and the dependent claims.

[0010] The present invention will be described in more detail below. It is understood that the various embodiments, preferences and ranges as provided / disclosed in this specification may be combined at will. Further, depending of the specific embodiment, selected definitions, embodiments or ranges may not apply.

[0011] The present invention will be better understood by reference to the **figures**.

Fig. 1 shows a solar thermochemical system comprising a feeding subsystem (2), a solar thermochemical reactor (1) as defined herein, a quenching subsystem (3), a vacuum generating subsystem (4) a work up subsystem (5). The part of the solar thermochemical system operating under reduced pressure is indicated by the dotted line. The solar concentrating subsystem is not shown, only the incident concentrated solar energy is indicated as "hv". Starting materials are indicated SM; products are indicated as P(s) and P(g); the indices referring to solid or gaseous material.

Fig. 2 shows an inventive solar thermochemical reactor (1), adapted to operate under reduced pressure. This solar thermochemical reactor comprises reaction tubes (11) equipped with vacuum-proof inlet (12) and a vacuum proof outlet (13); a housing (14) which is equipped with inlet (15) an outlet (16) and with a transparent window (17). The housing (14) may be sealed and filled or purged with a non-oxidizing gas.

Fig. 3 shows a scheme of the experimental setup including vacuum box (2), tubular section (1) and condenser unit (3).

[0012] In the present invention, the following **definitions** shall apply, unless otherwise specified.

[0013] The terms **reactant(s)** and **starting material(s)** are used synonymous and relate to the materials provided to the chemical reaction (such as Me<sub>x</sub>O<sub>y</sub>, Red, Add) .

[0014] The term **product(s)** covers the ending materials of the chemical reaction (such as Me).

[0015] The term **reactor** is known in the field and relates to any device allowing for a chemical reaction. In the context of the present invention, a term preferably refers to a solar thermochemical reactor, as defined herein.

[0016] The term **solar thermochemical reactor** is known in the field. Particularly, the term relates to a reactor where

the energy is supplied, in part or in full, preferably fully, by a source of concentrated solar energy. The energy supplied is predominantly, or solely, in the form of heat.

Such solar thermochemical reactors may operate continuously or discontinuously, preferably continuously. In the context of this invention, a continuous operation refers to an operation mode, where reactants are provided to the reactor and products are removed from the reactor while the reaction is running. Due to the availability of solar energy, the operation of such reactor is intermittent. Accordingly, such reactor is equipped with means for supplying reactants and removing products under reaction conditions, optionally with means for controlling the temperature and with means for receiving concentrated solar energy.

To allow for thermochemical reactions, the reactor material is appropriately chosen, as known to the skilled person.

**[0017]** The term **thermochemical reaction** is known in the field and includes thermal reduction of metal oxides and carbothermal reduction of metal oxides, both as defined herein.

**[0018]** The term **thermal reduction of metal oxides** is known in the field. Particularly, the term relates to the mere thermal decomposition of a metal oxide ( $\text{Me}_x\text{O}_y$ ) to oxygen and a lower valence metal oxide ( $\text{Me}_{x/2}\text{O}_{y/2}$ ) or to a metal (Me).

**[0019]** The term **carbothermal reduction of metal oxides** is known in the field. Particularly, the term relates to the thermal reduction of a metal oxide ( $\text{Me}_x\text{O}_y$ ) in the presence of a carbonaceous reducing agent to carbon monoxide and/or carbon dioxide and a lower valence metal oxide ( $\text{Me}_{x/2}\text{O}_{y/2}$ ), or to a metal (Me), or to a metal carbide, or mixtures thereof. Carbonaceous reducing agents include solid materials (e.g. coke, charcoal) and gaseous materials (e.g. methane, natural gas, hydrocarbons).

**[0020]** In more general terms, in a **first aspect**, the invention relates to methods / processes for reducing metal oxides using solar thermal energy under reduced pressure. As discussed above, reduction of metal oxides using solar thermal energy under ambient pressure is known. It was surprisingly found that these methods may be substantially improved by performing the reaction under reduced pressure. Particularly, it is possible to reduce the reaction temperature, when compared with ambient pressure, while maintaining or even improving conversion rates and product quality. Lowering the reaction temperature is of key importance for industrial applications, as it allows using reactors and systems made of standard materials.

**[0021]** In an advantageous embodiment, the invention relates to a method for reducing metal oxide particles, said method comprising the steps of: (a) providing metal oxide particles ( $\text{Me}_x\text{O}_y$ ), optionally reducing agents (Red) and optionally further components (Add); (b) subjecting the starting materials, or a blend of starting materials, to a reduction reaction; (c) quenching the obtained reaction mixture; (d) optionally further processing the cooled reaction mixture. According to the invention, step (b) is performed by heating the reaction mixture with a source of concentrated sunlight (solar energy). According to the invention, step (b) is performed under a reduced pressure, typically less than 500 mbar.

**[0022]** This aspect of the invention shall be explained in further detail below:

**[0023]** [Reduction Reaction, Products of the process] The present invention provides for a method of reducing metal oxide particles  $\text{Me}_x\text{O}_y$ . The inventive method covers thermal reduction (i.e. without reducing agent) and carbothermal reduction (i.e. with a carbonaceous reducing agent) of metal oxides.

The term reduction of metal oxides is used in its broadest sense, i.e. removal of oxygen from a metal oxide. The invention is applicable for obtaining a broad range of desired products, including metals (i.e. metals and alloys of oxidation state 0), and metal containing compounds (oxides, carbides and nitriles of metals are collectively termed: "metal containing compounds").

In a first embodiment metals of oxidation state 0 (pure metals Me, also including alloys) or metal oxides of a reduced oxidation state  $\text{Me}_{x/2}\text{O}_{y/2}$  ( $y/x > y_2/x_2$ ) or mixed metal oxides (including perovskites) are the products of the inventive method.

Further, depending on the starting materials and reaction conditions further products are obtainable, including metal carbides and oxy-carbides (if present) as well as metal nitriles.

In case of carbonaceous reducing materials, metal carbides and/or metal oxycarbides may be products of the process. Such metal carbides / oxycarbides may be and undesired side product or the main aim of the process.

**[0024]** In case the chemical reaction is performed in the presence of nitrogen, metal nitrides may be products of the process.

Further, metal alloys may be the products of the process. Such alloys may be obtained by providing two or more metal oxides as the starting materials of the process.

In case of the thermochemical redox cycles, oxygen, hydrogen or carbon monoxide may be the key reaction product, while the reduced oxidation state metal formed is transferred to one or more additional reaction step(s) in order to regenerate the starting material.

**[0025]** [Metal oxides] A wide variety of metal oxides and mixed metal oxides ( $\text{Me}^{\text{I}}\text{Me}^{\text{II}}\text{O}_y$ ) are suitable for the method as described herein. The term Metal oxide also includes doped metal oxides and perovskites. Preferred metal oxide particles ( $\text{Me}_x\text{O}_y$ ) are selected from the group consisting of the oxides of zinc, aluminum, iron, magnesium, silicon, manganese, titanium, copper, cerium and calcium; preferably selected from the group consisting of the oxides of zinc, and aluminum.

**[0026]** [Reducing Agents] A wide variety of reducing agents (Red) are suitable for the method as described herein. Preferred are solid reducing agents, typically selected from the group consisting of carbonaceous materials, particularly graphite, carbon black, bio-char, coke, petcoke. Waste carbonaceous materials, such as sludge, tires, fluff can also be applied as reducing agents. Further, biomass, such as agricultural waste and sewage sludge, can also be applied as

reducing agents.

Further preferred as gaseous reducing agents, such as methane, or methane containing mixtures, including natural gas.

**[0027]** [Additives] The inventive method may be facilitated or improved by providing further components, such as natural gas, methane and/or hydrogen.

Further, nitrogen or a nitrogen containing gas, may be added. This allows for the production of metal nitrides.

Further, an inert gas, such as Argon, may be added. Such inert gas may be used as entrainment or sweep gas. The amount of such inert gas may be determined by routine experiments and depends on the reaction conditions and reactor.

**[0028]** [Step a] The starting material is advantageously provided in particulate form, typical particle sizes are in the range of 1-200 microns.

The quality (grade) of the starting material is not crucial and may be chosen according to the desired process by the person skilled in the art. Metal oxides may be purified or may be used as commercially available. Reducing agents, such as graphite or waste biomass, may be used as commercially available or may be pre-treated. For example, non-food grade, waste biomass may be grinded to the specified particle size. Such grinding may be done by using conventional equipment such as hammer-mills.

The starting material is supplied to the reactor (1) by conventional means, such as a conveyor screw.

In case of carbothermal reduction of metal oxides, the ratio of  $C / Me_xO_y$  may vary over a broad range and depends on the stoichiometry of the reaction. Typically, the ratio  $C / Me_xO_y$  is in the range of  $1/2$  to  $3/2$ , preferably  $1/1$ .

**[0029]** [Step b] Known methods operate at atmospheric pressure; hence reaction temperatures required are much higher. In addition, the recombination of the gaseous products (if occurring) is very fast decreasing the yield of the desired product. By lowering reaction pressure, both reaction temperature and concentrations of the gaseous products are lower which decreases the rates of recombination reactions and makes quenching more effective. Typical reaction pressures are below 500 mbar, preferably below 200 mbar. Suitable ranges are, for example 1-500 mbar, preferably 10-250 mbar, particularly 25 - 200 mbar.

The reduction reaction of step (b) is performed by providing the required heat at high temperatures for the endothermic transformation with a source of concentrated solar energy. It is believed that heat needs to be provided not only for heating, but more importantly for the enthalpy change of the reaction.

Typical reaction times  $\tau$  are within the range of 0.1 - 10 sec, such as 1 sec.

**[0030]** [Step c] It was found that a fast quench from the reaction temperature to the condensation temperature of the desired product is beneficial for the inventive method.

Accordingly, the quench temperature depends on the aimed product and is typically below 1000°C, preferably below 500°C.

Further, quenching is "fast" meaning the time for quenching reduces, or inhibits, recombination reactions. Suitable times depend on the specific reaction, but are typically within less than 10 seconds, preferably below 1 second. Suitable quench rates are faster than 600°C/s, preferably faster than 1000°C/s.

A fast quench is particularly beneficial for the carbothermal reduction of alumina (section Al production, eq. 1.1). In this embodiment, quenching to a temperature below 1000°C within 5s, preferably below 900°C within 3s was found beneficial. Further, a fast quench is particularly beneficial for thermal reduction of metal oxides; i.e. for methods where no Reducing agent is present (e.g. section ZnO/Zn+O<sub>2</sub> cycle, eq. 3.1). In this embodiment, quenching to a temperature below 1000°C within 5s was found beneficial. Known methods use an inert gas to quench the product mixture. There are two problems associated with this approach: (1) the substantial amount of inert gas is needed which increases required pumping power for achieving preferred vacuum levels in the reactor and the energy required to recycle the inert gas, and (2) the gas quench is not as efficient hence the product vapors deposit on any cold surfaces within the system, thereby making product recovery tedious and impractical. Accordingly, in one preferred embodiment, the product is quenched by contacting a cold solid surface, preferably a cold solid moving surface. This may be accomplished by using standard equipment, such as ash coolers.

Other quenching methods may be suitable in addition to the above, or as an alternative. In a further embodiment, quenching may be achieved by diluting with inert gas. In a further embodiment, quenching may be achieved by expanding through a de Laval nozzle.

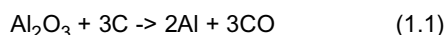
**[0031]** [Step d] The further processing of the products obtained follows known routes and depends on the overall process. Generally speaking, the solid products obtained are either purified and/or further processed (in case of the production of metals); or recycled (in case of the production of fuels).

**[0032]** In an advantageous embodiment, the invention provides for a method as described herein, wherein steps a), b) and c) are performed continuously.

**[0033]** Further, the invention provides for the use of methods, reactors and systems as described herein (i) in the

production of metals and metal containing compounds (such as aluminum and/or aluminum carbide), (ii) in the production of fuels (such as hydrogen and/or carbon monoxide and/or hydrocarbons), from water and/or carbon dioxide via thermochemical redox cycles, and (iii) in performing thermochemical redox cycles for separating oxygen from gases (iv) in the production of ammonia from water and nitrogen via thermochemical redox cycles. These uses shall be explained in further detail below.

**[0034]** [Al production] In an advantageous embodiment, the invention provides for a method as described herein, wherein the metal oxide particles are aluminum oxide particles, the reducing agent is a carbon source (C), such as graphite or methane, and the reaction product is aluminum or an aluminum containing compound.



Consequently, the invention also provides for the use of a method as described herein for manufacturing aluminum or aluminum alloys, or aluminum carbides. The idealized equation (1.1) only provides for the overall reaction, summarizing a myriad of reaction steps.

**[0035]** [ZnO+C/Zn+CO cycle] In a further advantageous embodiment, the invention provides for a method as described herein, wherein the metal oxide particles are Zinc oxide particles, the reducing agent is graphite and the reaction product is zinc. Consequently, the invention also provides for the use of a method as described herein for manufacturing zinc. This reaction may be part of a catalytic cycle where in a first step zinc and water are reacted to give zinc oxide and hydrogen and in a second step zinc oxide and carbon is reduced (as described herein) to give zinc and carbon monoxide.

ZnO + C → Zn + CO (2.1) reduction according to this invention

Zn + H<sub>2</sub>O → ZnO + H<sub>2</sub> (2.2) formation of hydrogen, regeneration of metal

Zn + CO<sub>2</sub> → ZnO + CO (2.3) formation of carbon monoxide, regen. of metal

Zn + zCO<sub>2</sub> + (1-z)H<sub>2</sub>O → ZnO + zCO + (1-z) H<sub>2</sub>, z<1 (2.4) formation of syngas, regen. of metal

H<sub>2</sub>O + C → H<sub>2</sub> + CO (2.5) syngas, reaction of residual carbon, if present.

**[0036]** Consequently, the invention also provides for the use of a method as described herein for manufacturing syngas from water and carbon dioxide (equation 2.4).

**[0037]** [ZnO/Zn+O<sub>2</sub> cycle] In a further advantageous embodiment, the invention provides for a method as described herein, wherein the metal oxide particles are Zinc oxide particles, no reducing agent is provided and the reaction product is zinc. Consequently, the invention also provides for the use of a method as described herein for manufacturing zinc. This reaction may be part of a catalytic cycle where in a first step zinc and water are reacted to give zinc oxide and hydrogen and in a second step zinc oxide is reduced (as described herein) to give zinc and oxygen.

ZnO → Zn + 1/2O<sub>2</sub> (3.1) reduction according to this invention

Zn + H<sub>2</sub>O → ZnO + H<sub>2</sub> (3.2) formation of hydrogen, regeneration of metal

Zn + CO<sub>2</sub> → ZnO + CO (3.3) formation of carbon monoxide, regen. of metal

Consequently, the invention also provides for the use of a method as described herein for thermal splitting of water to hydrogen and oxygen (equations 3.1. and 3.3) and/or or carbon dioxide to carbon monoxide and oxygen (equations 3.1. and 3.2.).

Alternatively, reaction 3.1 in combination with 2.4 provide for the use of a method described herein for producing in separate steps oxygen and syngas from water and carbon dioxide according to equation 3.4.

zCO<sub>2</sub> + (1-z) H<sub>2</sub>O → zCO + (1-z) H<sub>2</sub> + 1/2O<sub>2</sub>, z<1 (3.4) formation of syngas, simultaneous water and carbon dioxide splitting.

**[0038]** [Al<sub>2</sub>O<sub>3</sub> / AlN thermochemical cycle] In a further advantageous embodiment, the invention provides for a method as described herein, wherein in a thermochemical cycle ammonia is produced in a two step process from nitrogen and water. Details of such method are provided in Galvez et al (cited above, incorporated by reference in its entirety), disclosing ammonia production via two step Al<sub>2</sub>O<sub>3</sub> / AlN thermochemical cycle.

Al<sub>2</sub>O<sub>3</sub> + C + N<sub>2</sub> → 2AlN + 3CO (4.1) reduction according to this invention

Al<sub>2</sub>O<sub>3</sub> + 3CH<sub>4</sub> + N<sub>2</sub> → 2AlN + 6H<sub>2</sub> + 3CO (4.2) reduction according to this invention

2AlN + 3H<sub>2</sub>O → Al<sub>2</sub>O<sub>3</sub> + 2NH<sub>3</sub> (4.3) formation of ammonia, regeneration of metal oxide

The first endothermic step is the production of AlN by carbothermal reduction of Al<sub>2</sub>O<sub>3</sub> in a N<sub>2</sub> atmosphere at above 1500°C / without the need of adding a catalyst. This step is performed according to the method as described herein and schematically outlined in eq. 4.1 or 4.2. The second exothermic step is the steam hydrolysis of AlN to produce NH<sub>3</sub> and reform Al<sub>2</sub>O<sub>3</sub>; the latter is recycled to the first step (e.g. 4.3). In this embodiment, it may be beneficial to perform quenching step (c) by diluting with nitrogen.

**[0039]** [Cu<sub>2</sub>O / CuO + O<sub>2</sub> cycle] In a further advantageous embodiment, the invention provides for a method as described herein, wherein in a thermochemical redox cycle oxygen is separated from a gas mixture containing oxygen. Details of such method are provided in Haenchen et al (cited above, incorporated by reference in its entirety) disclosing a two step thermally-Driven Copper Oxide Redox Cycle for the Separation of Oxygen from Gases.

2CuO → Cu<sub>2</sub>O + 1/2O<sub>2</sub> (5.1) reduction according to this invention

$\text{Cu}_2\text{O} + 1/2\text{O}_2 \rightarrow 2\text{CuO}$  (5.2) removal of oxygen; regeneration of metal oxide This process is particularly useful for removal of oxygen from diute gas streams.

The first endothermic step is the reduction of CuO in air at above 1300°C / without the need of adding a reducing agent. This step is performed according to the method as described herein and schematically outlined in eq. 5.1.

[0040] In a **second aspect**, the invention relates to new solar thermochemical reactors and systems. These solar thermochemical reactors and systems are suitable for performing the processes as described herein. This aspect of the invention shall be explained in further detail below, whereby reference is made to fig. 1 regarding the solar thermochemical reactor system and fig. 2 regarding the solar thermochemical reactor.

[0041] [Reactor (1)] The solar thermochemical reactor (1) is an improved and novel alternative to known solar thermochemical reactors. It distinguishes from previously described solar thermochemical reactors at least in means for operating continuously under reduced pressure. Advantageously, the solar thermochemical reactor is a high temperature, low pressure, aerosol flow, solar thermochemical reactor.

[0042] Accordingly, the invention provides for a solar thermochemical reactor (1) comprising one or more reaction tubes (11) equipped with vacuum-proof inlet (12) (for receiving starting materials) and an outlet (13) (for releasing the products) and optionally a housing (14). Such housing may be equipped with inlet (15) and outlet (16) for purge gas and/or with a transparent window (17). Such reactor is adapted to operate under reduced pressure. Typically, the outlet (13) is in communication with a quenching system (3) which operates under vacuum as well. Consequently, the outlet (13) needs not to be vacuum proof.

[0043] In a further embodiment (fig. 2), the invention provides a solar thermochemical reactor as described herein comprising (i) one or more reaction tubes (11) equipped with vacuum-proof inlet (12) and outlet (13) and (ii) a housing (14) which is equipped with inlet (15) and outlet (16) for purge gas and a quartz window (17) and whereby the quartz window (17) is not in direct contact with the reactants / products of the reaction tubes (11). Such reactor is adapted to operate under reduced pressure and avoids a contact of the quartz window with the reactants and with the products.

[0044] In a further embodiment, the invention provides for a solar thermochemical reactor as described herein, comprising a tube or a multitude of tubes (11) and a cylindrical envelope (14), with vacuum or inert gas in the space between the tubes (11) and the cylinder (14). In this embodiment, the cylinder is preferably made of quartz.

[0045] In a further embodiment, such reactor comprises a solar cavity receiver (i.e. means for receiving solare energy). The solar cavity-receiver is designed to efficiently capture concentrated solar radiation entering through an aperture and transfer the resulting high-temperature heat to a solar thermochemical reactor situated within. The aperture may be open to the atmosphere, thereby exposing the interior of the cavity to ambient air. Alternatively, a transparent window (17), made for example of quartz, may be positioned in front of the aperture, thereby isolating the interior of the cavity from the ambient air. The latter allows for an oxygen-free atmosphere within the cavity when it is purged by an inert gas at ambient pressure ensuring no pressure difference across the window.

Tubular solar thermochemical reactors are particularly suitable for the processes described herein. Accordingly, the solar thermochemical reactor is represented by either a single tube or a multitude of tubes (11). These tubes are made of a material having appropriate thermo-mechanical properties, such as graphite. The exterior and/or interior of the tube(s) may be coated by a suitable material which chemically protects it from the reactants, products and / or the surrounding atmosphere. Known approaches for performing solar-thermal reactions under vacuum teach implementing direct irradiation of the material reacting under vacuum (Kruesi et al, as incorporated by reference). This was accomplished by passing the radiation through a quartz window which isolates the reaction zone from the surroundings. There are two problems associated with this approach: (1) the quartz window is subjected to a substantial pressure difference jeopardizing its mechanical integrity and limiting its size, and (2) the quartz window is directly exposed to the reaction environment. The latter could easily cause clouding of the window by the dust carried by the gas evolving from the reaction. All of this has adverse effect on the operability of said concepts. Accordingly, the invention provides a solar thermochemical reactor for solar-thermal reaction where a quartz window (17) is decoupled from the reaction environment and exposed to the same pressure from both sides. This may be accomplished by providing reaction tubes (11) within a housing (14), where the quartz window (17) is located in the housing and the cavity between housing and reaction tubes is purged with an inert gas under ambient pressure. The provision to purge the cavity by an inert gas enables graphite as the material of construction for the tubes. This is a low-cost, machinable material with outstanding thermo-mechanical properties.

Further, maintaining low partial pressures of oxygen (released by the thermal reduction under vacuum) may extend the oxidation of the tubes (11) over a period of time that is long enough to be commercially acceptable. Alternatively, the graphite of the reaction tubes may be protected by a suitable oxidation-resistant coating. According to a further embodiment, oxidation resistant materials - other than graphite - may be used for the reaction tubes (11). Such materials include alumina, zirconia, silicon carbide and sapphire. Although these materials generally have inferior thermochemical properties; they may be beneficial in view of oxidation resistance and/or manufacturing.

According to a further embodiment, conventional materials of construction and standard equipment are used for the solar thermochemical reactor (1).

The tubes (11) are sealed and incorporated into a vacuum system as outlined below. Sealing may be achieved by selecting appropriate feeder (2) and quencher (3) and by selecting appropriate valves installed into a standard lock-hopper system (for disengaging and storing product).

**[0046]** [Reactor System] The invention further provides for a solar thermochemical system comprising a feeding system (2); a solar thermochemical reactor (1) (particularly as defined herein); a quenching system (3); a vacuum generating system (4); optionally a work-up system (5); and optionally a sunlight collecting system (c.f. fig. 1).

**[0047]** In a further embodiment, the invention provides for a solar thermochemical system comprising a cavity-receiver for capturing and distributing concentrated solar energy to a solar thermochemical reactor (1), a feeder (2) (to continuously supply starting materials), a quencher (3) (for cooling of the reaction products), and a vacuum generating system (4) (for generating an environment of reduced pressure in the feeder, solar thermochemical reactor and quencher). This system is adapted and suited for carrying out the thermal reduction of metal oxides with or without reducing agents.

**[0048]** [Feeding system (2)] Feeding systems are commercially available items and may be adapted to the specific requirements by the skilled person. Suitable are, for example, feed hoppers equipped with conveying screws.

**[0049]** [Quenching system (3)] Cooling devices are commercially available items and may be adapted to the specific requirements by the skilled person. Suitable quenchers are adapted to operate under reduced pressure and at temperatures adapted to the reaction conditions.

In one embodiment, the cooling device ensures rapid cooling of the products to avoid further side reactions.

In one further embodiment, the quencher design may be optimized to partially allow recombination reactions. For example, by recombining apart of the Zn and  $O_2$  produced by the thermal reduction of ZnO, a mixture of Zn and ZnO is produced that allows for the conversion of Zn in the oxidation step of the  $CO_2$  and/or  $H_2O$  splitting cycle that is substantially higher than the one achieved when using the pure Zn.

In one further embodiment, product quenching is accomplished by contacting a cold solid surface using a commercial ash cooler, such as Holo Scru®. The vapors are forced to condense and solidify on a moving surface provided by the equipment itself and/or by moving cold condensed product. Advantageously, this solid surface is designed to transfer the resulting solids into a storage bin via disengaging lock-hoppers.

**[0050]** [Vacuum generating system (4)] Vacuum generating systems are commercially available items and may be adapted to the specific requirements by the skilled person.

**[0051]** [Work-up system (5)] The work-up system is adapted to the aimed overall-process. In case of thermal or carbothermal reduction of metal oxides, it is designed to purify or further process products obtained. In case of thermochemical redox cycle, it is designed to recycle and optionally purify products to complete the catalytic cycle. Such work-up systems are commercially available items and may be adapted to the specific requirements by the skilled person.

**[0052]** In one embodiment, the product may be further refined in a subsequent process step to recover desired material. For example, an  $Al_4C_3/Al_2O_3$  mixture, resulting from the carbothermal reduction of alumina, may be slagged in a separate step to recover the aluminum metal (e.g. as disclosed in US 6440193, incorporated by reference).

In one further embodiment, the product may be oxidized to produce a fuel. For example, (a) Zn as a product of the thermal reduction of ZnO or (b) a Zn/C containing mixture as a product of the carbothermal reduction of ZnO may be oxidized by a  $H_2O/CO_2$  mixture to produce clean syngas (a  $H_2/CO$  mixture).

**[0053]** [Sunlight collecting system (6)] Solar collectors are known in the field and may be adapted to the specific reaction by the skilled person.

**[0054]** [Operating the system] The reactor is fed by solid starting materials comprising metal oxides as defined herein optionally combined with reducing agents (Red) and further components (Add) as defined herein. The reducing agent may be in the solid, liquid, or gas phase. The feed is entrained into the hot reactor zone under vacuum and reacted in either entrained-flow or moving-bed mode, depending on a residence time required for the reaction. The vacuum conditions allow for the occurrence of the desired forward reaction at temperatures lower than those needed if the reaction is to be carried out at ambient pressure (Le Chatelier's principle). The product mixture may contain the metal in liquid and gas phases, oxygen containing gaseous products ( $O_2$ ,  $CO_2$ , CO, etc.), solid side-products ( $Me_{x2}O_{y2}$ , metal carbides, etc.) and starting materials. In order to precipitate the metal before it recombines into the oxide or other undesired products, the product mixture is rapidly quenched, e.g. by intimate contact with a cold inert gas and/or solid surface, and/or by expansion through a de Laval nozzle. The cold solid product is purged with an inert gas (e.g. by using a disengaging lock-hopper), pressurized to the ambient pressure, and discharged (e.g. to a product storage bin).

**[0055]** To further illustrate the invention, the following examples are provided. These examples are provided with no intent to limit the scope of the invention.

**[0056]** The performance of carbothermal reductions of  $Al_2O_3$  and ZnO under reduced pressure according to the proposed invention was evaluated against their counterparts at standard pressure through four examples summarized in Table 1 using the experimental setup shown in Figure 3.

**[0057]** The setup comprises three major parts: a powder feeder within a vacuum-tight steel box (2), a graphite reactor tube within a quartz tube enclosure sealed to the vacuum box (1), and a cooler/condenser unit sealed to the quartz tube (3).

**[0058]** The custom made cylindrical vacuum box (1) was fabricated out of a 550 mm long and 250 mm ID steel tube having a wall thickness of 2 mm. A powder feeder (Lambda Doser, Lambda Laboratory Instruments, Brno, Czech Republic) is placed inside the vacuum box and positioned to discharge particles directly into a graphite tube having 26.3 mm OD and wall thickness of 1.6 mm. The graphite tube was placed inside a transparent quartz glass tube that was connected to the condenser/quencher unit. This assembly was connected to a vacuum pump (Adixen ACP 15, Pfeiffer Vacuum GmbH, Asslar, Germany) which was used to pull vacuum and to pump the product gases out of the reactor. The system pressure was measured in the vacuum box by a piezoresistive absolute pressure sensor (Type 4045A2, Kistler Group, Winterthur, Switzerland). In the experiments performed at atmospheric pressure, the entire system was first evacuated and then filled and purged with argon.

**[0059]** The graphite tube was heated by concentrated radiation generated via the high flux solar simulator described in the by Furler et al which is cited above and incorporated by reference (particularly section 2, and fig. 1). The concentrated radiation was capable of creating a ~25 mm long hot zone located 3-4 cm above the top end of the condenser. The temperature of the inside reactor wall in the middle of the hot zone was measured by a type C thermocouple in the absence of a reaction in order to eliminate effects of fouling by the falling particles. This temperature was correlated to the outside graphite tube temperature T3 measured 165 mm from its top end. It has been found that T3 temperature of 480°C corresponded to the hot zone temperatures of 1750°C.

**[0060]** The particle size distributions of the reactants used in the Examples were measured by Horiba LA-950 as follows:

- C: Carbon Black (Black Pearls 2000, CABOT Corporation, Billerica, US; particle size: D10=4.9 μm, D50= 15.9 μm, D90=124.3μm, feedstock: gas or liquid hydrocarbons)
- A1203: (particle size: D10=48 μm, D50= 79 μm, D90=113μm)
- ZnO: (Sigma Aldrich Inc., St. Louis, US; D10=0.73 μm, D50= 1.05 μm, D90=2.70 μm)

**[0061]** The reactants were mechanically blended in stoichiometric ratios (see Table 1) and loaded into the powder feeder inside the vacuum box. After sealing and evacuating the system to a desired pressure, the reactor was heated to a setpoint temperature T3 via a high-flux solar simulator. The reactants were then commenced from the feeder and entrained into the graphite tube using a small amount of argon. During reaction, argon was also flown through the quartz enclosure. Due to both product condensation on the filter before the vacuum pump and increase in the system temperature, the pressure was increasing during the reaction; therefore, Table 1 reports both the initial and final pressures of the experiments.

**[0062]** The feeding rate of the powder feeder was set equal for each Example. However, the resulting powder feeding rate was not accurately reproducible and therefore the feeding time and the total mass fed are shown in table 1. The amount of reactants fed was determined by weighing the retainer in the feeder after the reaction.

**[0063]** The products of the reaction are quenched rapidly in the condenser unit with intention to minimize backward and side reactions. It should be mentioned that no special attention has been made to optimize the performance of the quencher thus the intention of the examples summarized in Table 1 was only to compare relative performance of the system under different conditions.

**[0064]** The reaction product gases were analyzed by using a gas-phase chromatograph (GC) (Varian 490 Micro GC, Varian, Middleburg, The Netherlands), an IR gas analyzer (Ultramat 23, Siemens, Munich, Germany) and a thermal conductivity gas analyzer (Calomat 6, Siemens, Munich, Germany). H2 was detected because of moisture content in the graphite tube and in the reactants. In the hot zone of the reactor the moisture reacts with carbon and forms an equimolar mixture of H2 and CO according to the reaction:



**[0065]** Therefore, the amount of CO produced from a reaction of metal oxide and carbon was estimated as the difference between the total amounts of CO and H2 produced during the experiment. This value is in Table 1 designated H2 corrected CO.

**[0066]** The oxygen conversion is a measure of the reaction efficiency based on the CO production. It is defined as the ratio of the molar amount of oxygen contained in the produced CO (H2 corrected CO) and the molar amount of oxygen contained in the amount of metal oxide fed. If MA1203=101.96 g mol<sup>-1</sup>, MC=12.01 g mol<sup>-1</sup>, and MZnO=81.41 g mol<sup>-1</sup> are the molar masses of A1203, C, and ZnO respectively, the Oxygen conversion is calculated as follows:

(a) for the system A1203+3C,

$$\text{Oxygen conversion} = \frac{(H_2 \text{ corrected CO})}{3 \cdot (\text{amount } Al_2O_3 \text{ fed})} \text{ where } \text{amount } Al_2O_3 \text{ fed} = \frac{(\text{total mass fed})}{(M_{Al_2O_3} + 3M_C)}$$

(b) for the system ZnO+C,

$$(\text{Oxygen conversion}) = \frac{(H_2 \text{ corrected CO})}{(\text{amount ZnO fed})} \text{ where } (\text{amount ZnO fed}) = \frac{(\text{total mass fed})}{(M_{ZnO} + M_C)}$$

Table 1: Summary of all parameters and outputs of all experimental runs

|                                                   | Example 1<br>(inventive)           | Example 2<br>(comparative)         | Example 3<br>(inventive) | Example 4<br>(comparative) |
|---------------------------------------------------|------------------------------------|------------------------------------|--------------------------|----------------------------|
| chemistry / stoichiometry                         | Al <sub>2</sub> O <sub>3</sub> +3C | Al <sub>2</sub> O <sub>3</sub> +3C | ZnO+C                    | ZnO+C                      |
| graphite tube length [mm]                         | 430                                | 430                                | 450                      | 450                        |
| hot zone length [mm]                              | 25                                 | 25                                 | 25                       | 25                         |
| initial pressure [mbar]                           | 18                                 | ~1000                              | 20                       | ~1000                      |
| final pressure [mbar]                             | 238                                | ~1000                              | 400                      | ~1000                      |
| ref. temp. T3 [°C]                                | 481                                | 524                                | 528                      | 527                        |
| feeding time [min]                                | 9.3                                | 15                                 | 20.1                     | 12.4                       |
| total mass fed [g]                                | 1.80                               | 2.77                               | 4.93                     | 3.30                       |
| Ar carrier gas flow rate<br>[l <sub>n</sub> /min] | 1.00                               | 1.00                               | 1.00                     | 1.00                       |
| CO gas produced [mmol]                            | 11.40                              | 9.77                               | 31.80                    | 15.30                      |
| H <sub>2</sub> gas produced [mmol]                | 4.50                               | 4.66                               | 4.45                     | 2.14                       |
| H <sub>2</sub> corrected CO [mmol]                | 6.90                               | 5.11                               | 27.36                    | 13.16                      |
| Oxygen conversion [%]                             | 17.6                               | 8.5                                | 51.9                     | 37.3                       |

[0067] The results shown in Table 1 indicate higher Oxygen conversions achieved under reduced pressure in Examples 1 and 3 compared to Examples 2 and 4 completed at atmospheric pressure.

## Claims

1. A method for reducing metal oxide particles, comprising the steps of:

- providing (i) metal oxide particles (Me<sub>x</sub>O<sub>y</sub>) (ii) optionally reducing agents (Red) and optionally further components (Add);
  - subjecting the starting materials to a reduction reaction;
  - quenching the obtained reaction mixture;
  - optionally further processing the cooled reaction mixture;
- whereby step (b) is performed by providing the required heat at high temperatures for the endothermic transformation with a source of concentrated solar energy; and  
whereby step (b) is performed under a reduced pressure between 1 - 500 mbar.

2. The method of claim 1, wherein in step a)

- said metal oxide particles (Me<sub>x</sub>O<sub>y</sub>) are selected from the group consisting of the oxides of zinc, aluminum, iron, magnesium, silicon, manganese, titanium, copper, and calcium; and / or

- said metal oxide particles are mixed oxides  $(\text{Me}^I\text{Me}^{II})_x\text{O}_y$ , particularly perovskites.
- said reducing agents (Red) are selected from the group consisting of carbonaceous materials; and /or
- said further components (Add) are selected from the group consisting of natural gas, methane, and hydrogen; and / or
- said further components (Add) are selected from the group consisting of nitrogen and nitrogen containing gases.

3. The method of claim 1, wherein in step c) quenching from the reaction temperature to the condensation temperature of the desired product is effected within a time period of 5 sec or less.

4. The method according to any of the preceding claims, wherein the method provides

- pure metals (Me); and / or
- metal alloys; and /or
- mixed metal oxides  $(\text{Me}^I\text{Me}^{II})_x\text{D}_y$ , particularly perovskites.
- metal oxides  $(\text{Me}_{x2}\text{O}_{y2})$  with a reduced oxidation state of the metal ( $y/x > y2/x2$ ); and / or
- metal carbides; and /or
- metal nitrides.

5. The method according to any of the preceding claims, wherein steps a), b) and c) are performed continuously.

6. The method according to any of the preceding claims, wherein in step a) the starting materials are supplied by conveyer screw.

7. The method according to any of the preceding claims, wherein in step b) reaction times  $\tau$  are within the range of 0.1 - 10 sec and reaction pressure is in the range of 10 - 250 mbar.

8. The method according to any of the preceding claims, wherein in step c) the product is quenched by

- contacting a cold solid surface, preferably a cold solid moving surface, and/or
- by diluting with nitrogen, and/or
- by diluting with inert gas, and/or
- by expanding through a de Laval nozzle.

9. The method according to any of the preceding claims, wherein in step d) the solid products obtained are

- further purified and/or further processed (in case of the production of metals), or
- recycled (in case of the production of fuels).

10. The method according to any of the preceding claims, wherein no reducing agent (Red) is provided.

11. The method according to any of the preceding claims, wherein

- a) the metal oxide particles are Zinc oxide particles, no reducing agent is provided and the solid reaction product is Zinc; or
- b) the metal oxide particles are aluminum oxide particles, the reducing agent is graphite and the solid reaction product is aluminum; or
- c) the metal oxide particles are aluminum oxide particles, the reducing agent is methane and the solid reaction product is aluminum; or
- d) the metal oxide particles are copper oxide particles, and the solid reaction product is copper or a reduced copper oxide for use in a thermochemical redox cycle to separate oxygen from a gas mixture containing oxygen; or
- e) the metal oxide particles are aluminum oxide particles, the reducing agent is a carbonaceous source, the Additive is nitrogen and the solid reaction product is aluminum nitride.

12. Use of a method according to any of the preceding claims

- a) for manufacturing aluminum or aluminum alloys or aluminum carbides, preferably aluminum or aluminum carbides ; or
- b) in a redox cycle for transferring oxygen, particularly for manufacturing carbon monoxide and / or hydrogen

and/or hydrocarbons, and or ammonia; or

c) in a redox cycle for separating oxygen from a gas mixture containing oxygen.

**13.** A solar thermochemical reactor (1) which is adapted to operate under reduced pressure comprising:

- one or more reaction tubes (11) equipped with vacuum-proof inlet (12) for receiving starting materials and a vacuum proof outlet (13) for releasing products and
- a housing (14) which is optionally equipped with inlet (15) and outlet (16) for purge gas and a transparent window (17).

**14.** The reactor of claim 12 comprising

- one or more reaction tubes (11) equipped with vacuum-proof inlet (12) and outlet (13) and
- a housing (14) which is equipped with inlet (15) and outlet (16) for purge gas and with a transparent window (17) and
- whereby the transparent window is not in direct contact with the reactants.

**15.** The reactor of claim 13 or 14, wherein said tubes (11) are made of

- a) graphite, which is optionally coated; or
- b) a material selected from the group consisting of alumina, zirconia, silicon carbide and sapphire.

**16.** The reactor according to any of claims 13 - 15 comprising

- one or more reaction tubes (11) and
- a housing (14) in the form of a cylindrical quartz envelope
- whereby the space between the tubes (11) and the quartz cylinder (14) is either under vacuum or filled with an inert gas or purged with an inert gas.

**17.** A reactor system comprising

- a feeding system (2);
- a reactor (1) as defined in any of claims 12 to 16;
- a quenching system (3);
- a vacuum generating system (4)
- optionally a work-up system (5);
- optionally a solar concentrating system.

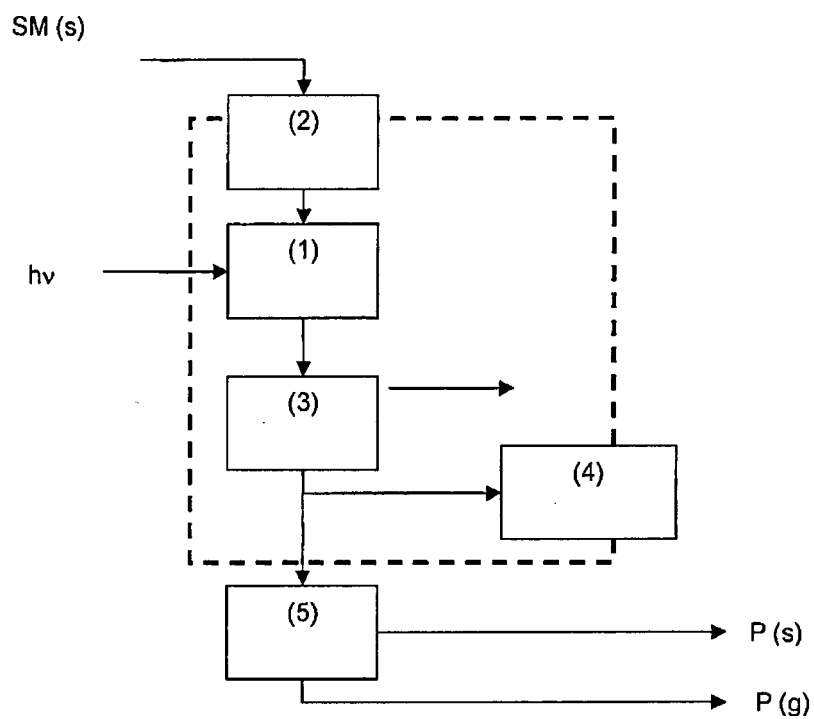


Fig. 1

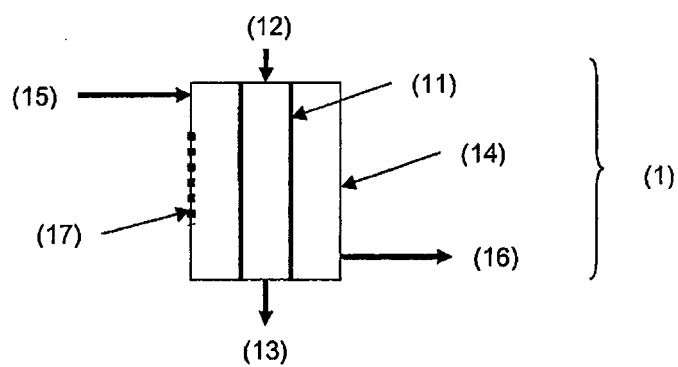


Fig. 2

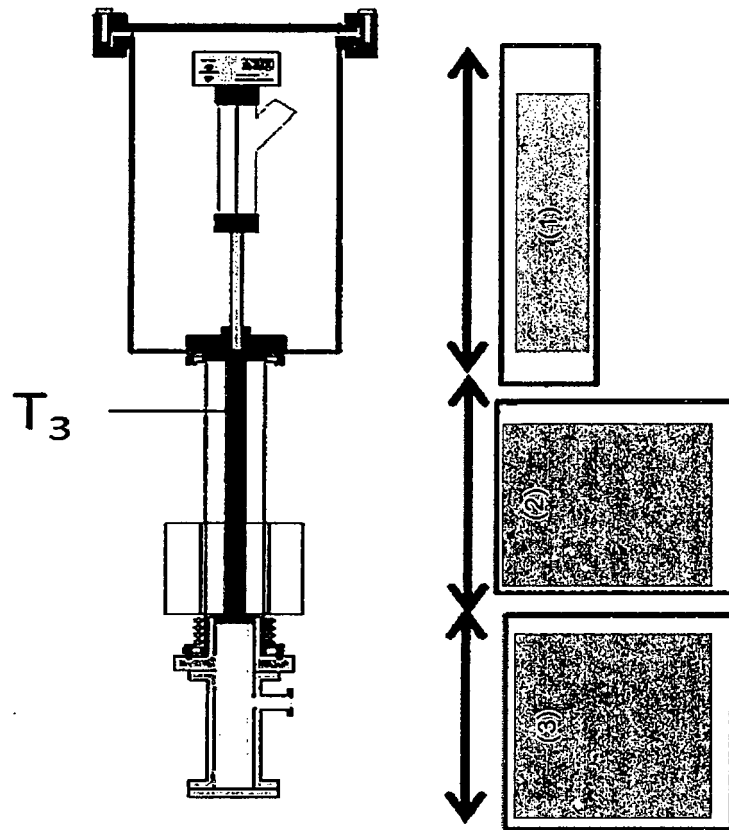


Fig. 3



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