

REACTOR FOR THE GENERATION OF HYDROGEN

Description

- 5 The invention relates to a reactor for generating hydrogen and at least one other product from at least one reactant.

Many areas of chemical process engineering employ reactors, catalysts, heat exchangers, and evaporators to crack or to
10 synthesize substances. The basic principle of such installations is based on the spatial separation of two substance flows and the transfer of heat energy through the reactor structure. Often, high temperatures, if necessary increased pressures, and the presence of a catalyst are required for ac-
15 tivating these processes. Two examples of such chemical processes are steam reforming and ammonia cracking (dehydration) to produce hydrogen (H_2) from hydrocarbons such as, for example, methane (CH_4) and ammonia (NH_3).

20 In ammonia cracking, ammonia is evaporated, heated and cracked into hydrogen and nitrogen in a reactor (cracker) at a temperature of up to 950 °C and a pressure higher than 1 bar using a nickel catalyst. Heat energy for activating and maintaining the endothermal process has to be supplied via electrical
25 heating or a burner. A particular challenge herein is the corrosion attack of the starting media (hydrocarbons, water vapor, ammonia) and the reaction products (hydrogen, carbon, nitrogen) on the corrosion resistance of the reactor materials used. The insufficient corrosion resistance of metal-based
30 systems (stainless steel and nickel-based alloys) in ammonia, hydrogen, and oxygen atmospheres is the main limitation for attaining high conversion rates.

If heat is not supplied via electrical heating, heating using a burner results in an additional requirement of resistance against the oxidizing atmosphere.

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The main challenge is attaining an adapted heat transfer performance with an efficiency that is as high as possible and a flow resistance or a loss of pressure that is as low as possible. There are further essential construction- and process-related requirements regarding the design and nature of a reactor. High efficiency is promoted by high heat conductivity of the reactor material and a large internal heat exchanger surface (heat transfer) with an outer surface that is as small as possible (heat losses through radiation and convection) as well as the demand for heat losses via the outflowing reaction products being as low as possible.

Installations for ammonia cracking are currently only available in the performance range $< 100 \text{ kg H}_2/\text{h}$ and are of a structure similar to a steam reformer.

Metal-based installation concepts for steam reforming are generally operated using beds of usually extruded ceramic profiles (pellets) that are coated or vapor-coated with the catalyst material.

It is an object of the invention to ensure an improvement of the corrosion resistance of a reactor for the generation of hydrogen and thus an increased service life of the reactor.

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According to the invention, the object is achieved by a reactor for generating hydrogen and at least one other product

from at least one reactant, the reactor comprising a tubular reactor vessel which contains a catalyst in the form of a bed, wherein the reactor vessel is formed from silicon-infiltrated silicon carbide (SiSiC).

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Improved corrosion resistance against a variety of media (especially against the impact of water vapor, ammonia, hydrogen, and nitrogen) and thus an increased service life of the reactor is achieved by producing the reactor vessel, therefore the main component of the reactor, from a ceramic material. The ceramic material is gas-tight to ensure a material separation of the heat and substance flows.

In the case of, for example, ammonia cracking at high temperatures, high corrosion of metallic reactor materials, caused by the hydrogen and oxygen atmosphere, occurs. The use of ceramic materials that are resistant to corrosion and high temperatures solves this problem, allows high conversion rates (> 99.8 %), and offers the potential for significant increases of component service life. The ceramic tubular vessel achieves, with a view to chemical resistance for ammonia cracking, high corrosion resistance to the medium ammonia that is to be converted and to the reaction products, especially to hydrogen and nitrogen in the temperature range of 300 - 950 °C and at pressures of 1 to 40 bar.

According to the invention, the ceramic material of which the reactor vessel consists is silicon-infiltrated silicon carbide (SiSiC). This material stands out due to a number of advantages regarding its mechanical, thermal and chemical properties. It meets the strength requirements in the temperature range from room temperature to 1100 °C as a result of the high

stationary and non-stationary thermal gradients. Additionally, it has high oxidation and corrosion resistance, high heat conductivity as well as high thermal shock resistance. Another advantage lies in the rapid heating behavior due to the thermal-mechanical material properties of SiSiC and therefore a short turn-on delay (this allows the use in cyclically operated installations). The low weight when using SiSiC also allows the use in non-stationary applications.

Preferably, the catalyst bed is also formed from a ceramic material, especially from silicon-infiltrated silicon carbide (SiSiC), and coated with a catalytic material. In case of ammonia cracking taking place in the reactor, the catalytic coating is, for example, nickel. For other chemical reactions, however, the material of the coating is a different one, depending on requirements. The advantages of silicon-infiltrated silicon carbide already listed in regard to the reactor vessel can be transferred to the catalyst bed. As nickel (Ni) is a preferred and economically acceptable catalyst material for the production of hydrogen (H_2) by cracking, for example, ammonia (NH_3), the ceramic material has to be coatable or wettable with nickel. Silicon-infiltrated silicon carbide also has this property.

The size and form of the catalyst particle depend on the flow channel in question. The most important geometrical factor in regard to the activity of the catalytically coated bed is the ratio of the geometrical surface of the particles to their volume. In order to attain a high reactor surface, the aim has to be a particle size that is as small as possible. However, this is contrary to the requirement of a loss of pressure or a

flow resistance that is as low as possible, which requires a preferably large particle size.

Advantageously, cylindrical structures with one or more longitudinal bores and with grooves on the outer faces are used as catalyst particles to increase the surface area. For smaller flow cross-sections, simple geometrical structures such as spheres and solid cylinders are also suitable. The particle size depends on the flow channel in question. By way of example, particles with a diameter of 1 to 20 mm with a length-to-diameter-ratio of 0.5 to 1.5 are provided, depending on the size of the flow channel. The ratio of reactor diameter to particle diameter usually is 3 to 10.

According to a first preferred embodiment,

- the tubular reactor vessel is built from a cylindrical pipe,
- the pipe has a feed opening for the at least one reactant at one end and a discharge opening for the at least one product at the other end, and

- the catalyst is located in a middle area of the pipe and is held in place by a fixing element through which a flow can pass. This is a simple embodiment of the reactor. Here, a cylindrical pipe is understood to mean a substantially straight pipe without any significant bends. The fixing element is of a porous design so that the reactant flow and/or the product flow can flow through it. The fixing element preferably also consists of SiSiC (silicon-infiltrated silicon carbide) or another ceramic material, as it is arranged in the area with the highest process temperatures. Here, the pores of the fixing element are smaller than the diameter of the particles of the catalyst bed. If the pipe is oriented in a vertical arrangement, only one fixing element is needed that supports the cat-

alyst bed from below. In a, for example, horizontal arrangement of the pipe, two fixing elements on each side of the catalyst bed may be required.

5 Advantageously, the fixing element is attached to the cylindrical pipe via a positive and/or non-positive joint. Such a joint is suitable for use at high temperatures as occur during operation of the reactor. In principle, a material-fitting joint is also suitable. When using a standard pipe geometry, a
10 positive joint is particularly advantageous, from a constructional point of view. In its simplest embodiment, it can be realized with a preferably ceramic support rod that holds the fixing element in place. In alternative embodiments, the fixing element can be held by a neck attached in the pipe, a step
15 or a conic internal pipe geometry.

According to a second preferred embodiment,

- the tubular reactor vessel is formed from a u-shaped pipe with an apex,
- 20 - the pipe is oriented with both its ends upwards and has a feed opening for the reactant at a first end and a discharge opening for the products at a second end, and
- the catalyst is located in the area of the apex of the pipe. In this embodiment, there is no fixing element, as the
25 catalyst bed is held in the area of the apex of the pipe by the form of the curved pipe and the gravitational forces in the bottom area.

According to a third preferred embodiment,

- 30 - the tubular reactor vessel is formed from a w-shaped pipe or pipe with multiple w-shapes, wherein the pipe has two or more bottom apices,

- the pipe is oriented with both its ends upwards and has a feed opening for the reactant at a first end and a discharge opening for the products at a second end, and

- the catalyst is located in the area of the bottom apices of the pipe. Here, at least two catalyst beds are provided. With this embodiment, no fixing element is needed for the catalyst bed, either. Furthermore, the w-shaped embodiment of the ceramic pipe offers the advantage of a longer path for the reactants in the reactor or a longer retention time.

According to a fourth preferred embodiment,

- the tubular reactor vessel comprises a cylindrical internal pipe and a cylindrical external pipe,

- the internal pipe and the external pipe extend vertically,

- the internal pipe is arranged in the external pipe, especially concentrically, and the diameter of the internal pipe is smaller than the diameter of the external pipe, so that a flow channel is formed around the internal pipe,

- the bottom end of the internal pipe lies higher than the bottom end of the external pipe, so that a gap is formed in the area of the bottom end of the external pipe,

- the external pipe has a feed opening for the reactant at its upper end and its bottom end is closed,

- the internal pipe has a discharge opening for the product at its upper end and its bottom end is open, and

- the gap is filled with the catalyst, wherein the bottom end of the internal pipe extends into the catalyst. This way, the at least one reactant and the products are transported in opposite directions. The main advantage of this embodiment is that a heat exchange takes place between the internal pipe and the external pipe. Here, the products in the internal pipe that are on a high temperature level, release their heat to

the reactants flowing in the opposite direction in the flow channel of the external pipe. These are heated by this, so that the amount of heat that has to be supplied externally is lower. A high efficiency is achieved through the integration of heat exchanger and reactor and by reducing the heat loss as a result of the smaller external surface.

To achieve the temperature level required in the reactor for the reaction to proceed, the tubular reactor vessel is preferably arranged in a heating device. Here, the tubular reactor vessel can be completely encased by the heating device or it may be sufficient if only the area of the pipe in which the catalyst is located and the chemical reaction occurs is surrounded by the heating device. Here, the heating device can be an electric heating device, can contain a burner or may be based on a different heating principle.

Exemplary embodiments of the invention are explained with reference to a drawing. Here, the individual figures show schematically:

- FIG. 1 a first embodiment of a catalytic reactor;
- FIG. 2 a second embodiment of a catalytic reactor; and
- FIG. 3 a third embodiment of a catalytic reactor.

Identical references in the figures have the same meaning.

FIG. 1 shows a first catalytic reactor 2, i.e., a reactor for the catalytic conversion of at least one reactant, in this case ammonia NH_3 , into hydrogen H_2 and nitrogen N_2 . The reactor 2 comprises a tubular reactor vessel 4 which contains a catalyst 6 in the form of a bed. The reactor vessel 4 is

formed from a ceramic material, in this case silicon-infiltrated silicon carbide (SiSiC). The bed 6 of catalytically coated particles preferably also consists of a ceramic material, given the higher corrosion resistance. Commercially available catalyst carriers (beds) are based on aluminum oxide (Al_2O_3) or steatite (magnesium silicate). In the exemplary embodiment shown, however, the catalyst 6 is formed of silicon-infiltrated silicon carbide (SiSiC). Furthermore, the catalyst particles are coated with a catalytic coating of nickel.

In the exemplary embodiment shown, the tubular reactor vessel 4 is formed from a straight cylindrical pipe 3. The pipe comprises connecting flanges 8 at one or at both ends. The pipe 3 is oriented vertically and has a feed opening 10 for the ammonia stream NH_3 at the upper end and a discharge opening 12 for discharging the product gases hydrogen H_2 and nitrogen N_2 at the bottom end. The catalyst 6 is located in a middle area of the pipe 4 and is held in place by a fixing element 14 through which a flow can pass. Here, the fixing element 14 is especially designed to be porous or as a honeycomb and lets the product gases flow through you.

The process gas flows through the pipe in a longitudinal direction and is heated in the inlet area, near the feed opening 10, by a heat flow $\dot{Q}$ supplied externally, to the temperature level of 700 to 950 °C (for high gas mass flows and required high conversion rates/purities also up to 1000 °C) required for the subsequent cracking reaction. The required temperature level depends on the required purity of the process gases after cracking and on the gas mass flow. A partial cracking already starts to occur from a temperature of 600 °C. The technical advantage of the SiSiC pipe reactor compared to

a metallic solution, however, is especially the corrosion resistance under the atmospheres described above and at high temperatures. The conversion rate, that is the degree of conversion of ammonia NH_3 into hydrogen H_2 and nitrogen N_2 , results depending on the gas temperature, the catalyst parameters and the gas mass flow.

The reactor according to FIG. 2 differs from the first embodiment in regard to the form of the reactor vessel 4. The ceramic pipe 16 is based on a u-shaped pipe geometry of the SiSiC pipe. This design variant allows for feeding the reactant gas and for discharging the product gas from the same side. In this design variant, there is no fixing element 14 through which a flow can pass in accordance with FIG 1, as the catalytically coated bed is located in the apex of the u-pipe 16 that lies at the bottom. Furthermore, a heating device 18 is shown, into which the reactor vessel 4 is integrated, through which the heat to start and maintain the reaction is fed, which is indicated by $\dot{Q}$.

According to FIG. 3, the reactor 2 consists of an external pipe 18 with a closed bottom and an internal pipe 20 that is concentrically guided in the external pipe 18. The internal pipe 20 does not reach the bottom of the external pipe 18, so that a distance is created in the bottom area between the internal pipe 20 and the external pipe 18 which defines a gap 22. The bottom area of the external pipe 18 is filled with the ceramic catalytically coated bed 6. The internal pipe 20 extends into this catalytic bed 6. The reactant gas that flows into a flow channel 24 in the area of the annular gap between the external pipe 18 and the internal pipe 20 flows in the direction of the external pipe bottom and flows through the cat-

alytically coated bed 6 within which the cracking into hydrogen H_2 and nitrogen N_2 takes place. The resulting product gas flows through the empty space 22 into the internal pipe and against the flow direction of the inflowing ammonia NH_3 in the
5 direction of the discharge opening of the internal pipe 20 and under release of heat to the inflowing ammonia NH_3 via the wall of the internal pipe 20.

In all three figures, the heat flows that are supplied externally to the reactor vessel 4 and that are generated by a
10 heating device (18 in FIG. 2) are designated with $\dot{Q}$ (FIG. 1 and FIG. 3 without representation of the heating device). These heat flows are, for example, generated in an oven space, either by heating with electric resistive heating elements or
15 by gas flames. The oven is a conventional high-temperature oven, such as is used, for example, for ceramic firing or heat treatment and into which the ceramic reactor pipe, including the feed and discharge openings through the oven wall or walls,
is integrated.

Claims

1. A reactor (2) for generating hydrogen and at least one other product from at least one reactant, the reactor comprising a tubular reactor vessel (4) which contains a catalyst (6) in the form of a bed, wherein the reactor vessel (4) is formed from silicon-infiltrated silicon carbide (SiSiC).
2. The reactor (2) according to claim 1, wherein the catalyst bed is formed from another ceramic material, especially from silicon-infiltrated silicon carbide (SiSiC), and is coated with a catalytic material.
3. The reactor (2) according to claim 1 or 2, wherein
 - the tubular reactor vessel (4) is built from a cylindrical pipe (3),
 - the pipe (3) has a feed opening (10) for the at least one reactant at one end and a discharge opening (12) for the at least one product at the other end, and
 - the catalyst (6) is located in a middle area of the pipe (3) and is held in place by a fixing element (14) through which a flow can pass.
4. The reactor (2) according to claim 3, wherein the fixing element (14) is attached to the cylindrical pipe (3) via a positive and/or non-positive joint.
5. The reactor (2) according to any one of claim 1 or 2, wherein
 - the tubular reactor vessel (4) is formed from a u-shaped pipe (16) with an apex,

- the pipe (16) is oriented with both its ends upwards and has a feed opening (10) for the reactant at a first end and a discharge opening (12) for the products at a second end, and
- the catalyst (6) is located in the area of the apex of the pipe (16).

6. The reactor (2) according to any one of claim 1 or 2, wherein

- the tubular reactor vessel (4) is formed from a w-shaped pipe or a pipe with multiple w-shapes, wherein the pipe has two or more bottom apices,
- the pipe is oriented with both its ends upwards and has a feed opening (10) for the reactant at a first end and a discharge opening (12) for the products at a second end, and
- the catalyst (6) is located in the area of the bottom apices of the pipe.

7. The reactor according to any one of claims 1 or 2, wherein

- the tubular reactor vessel (4) comprises a cylindrical internal pipe (20) and a cylindrical external pipe (18),
- the internal pipe (20) and the external pipe (18) extend vertically,
- the internal pipe (20) is arranged in the external pipe (18), especially concentrically, and the diameter of the internal pipe (20) is smaller than the diameter of the external pipe (18), so that a flow channel is formed around the internal pipe (20),
- the bottom end of the internal pipe (20) lies higher than the bottom end of the external pipe (18), so that a gap (22) is formed in the area of the bottom end of the external pipe (18),

- the external pipe (18) has a feed opening (10) for the reactant at its upper end and its bottom end is closed,
- the internal pipe (20) has a discharge opening (12) for the product at its upper end and its bottom end is open, and
- 5 - the gap (22) is filled with the catalyst (6), wherein the bottom end of the internal pipe (20) extends into the catalyst (6).

8. The reactor (2) according to any one of the preceding
10 claims, wherein the tubular reactor vessel (4) is arranged in a heating device (18).