PROCESS FOR CRACKING AMMONIA

Field

The present invention relates to a process for catalytically cracking ammonia. The present invention further relates to a reaction vessel, optionally a tubular reaction vessel, for use in the catalytic cracking of ammonia.

Background

There is renewed interest in using hydrogen as a green, carbon free, fuel in a variety of industrial settings. Hydrogen may be combusted to produce heat energy or electricity. Alternatively, hydrogen may be used to produce electrochemical energy in, for example, a fuel cell.

Ammonia has received interest as a possible compound to enable the storage and transport of hydrogen. Liquid ammonia has a higher hydrogen density than liquid hydrogen and may be transported using existing infrastructure which is already in use for this purpose, such as that used for the transportation of ammonia in the agrochemical fertiliser industry.

Once the liquid ammonia has been transported it may be combusted directly or converted to hydrogen by the process of cracking.

The catalytic cracking of ammonia into hydrogen and nitrogen has been known for many years. The reaction may be depicted as follows:

$$2\ NH_3 \rightleftharpoons N_2 + 3\ H_2$$

The ammonia cracking reaction is endothermic and may usefully be achieved by passing ammonia over a suitable catalyst in heated catalyst-containing reaction vessels such as externally heated catalyst-containing reaction tubes disposed in a furnace. Such furnaces are known, for example, for the steam reforming of natural gas or naphtha feedstocks.

However, the heated catalyst-containing reaction tubes disposed in the furnace may react with the ammonia containing gas forming unwanted metal nitrides within the tube material. This unwanted material damage mechanism, known as nitriding or nitridation, may cause the accelerated failure of the reaction tubes, in particular, at a location within the reaction tubes where nitriding potential is highest (e.g., location of highest partial pressure of ammonia/

nitrogen, location of highest temperature, and/or location where a combination of ammonia/ nitrogen partial pressure and temperature results in the highest nitriding potential).

Reaction tube failures require a complete shutdown of the ammonia cracking reactor, and result in significant plant down time. Moreover, nitriding, and failure, of the reaction tubes presents a serious safety hazard.

It is an aim of the present specification to address the aforementioned problem of nitriding and provide a process for the catalytic cracking of ammonia with improved operability and increased safety.

Summary

One option for addressing the problem of nitriding in a process for catalytically cracking ammonia is to construct the reaction vessels/tubes from a material (e.g., an alloy) which is resistant to nitriding. However, most alloys which are resistant to nitriding do not have the thermal and/or mechanical characteristics required to maintain mechanical integrity when exposed for extended time periods to high pressures and temperatures. Since previous ammonia cracking processes are typically not performed at high pressures for extended time periods, this has not been such a problem in these lower pressure ammonia cracking processes. That is, most ammonia cracking reactions have been conducted at low pressure and at a moderate scale where high temperature, high pressure mechanical properties and economics of use of nitride resisting alloys has been more acceptable. Ammonia cracking at the scale required for hydrogen production for the energy sector requires high pressures, therefore higher required creep strength, but also will be highly influenced by the most economic metallurgy/ design.

The present applicant has developed a high pressure, high temperature ammonia cracking process and has identified that the reaction vessels/tubes must be formed of a material (e.g., an alloy) which has good thermal and mechanical stability over extended operating periods at such elevated pressures and temperatures. Deformation of the catalyst-containing reaction tubes can occur which may result in the eventual failure of the reaction tubes. Heat-resisting materials have resistance to attack by the hot gases, but also possess suitable mechanical properties at high temperatures under long-term loading. This property is known as creep strength. However, while alloys which have a high creep strength are known, many of these are susceptible to nitriding.

The present applicant has therefore identified that for a high pressure, higher temperature ammonia cracking process, the reaction vessels must be formed of an alloy which has both good nitriding resistance and good thermal and mechanical stability over extended operating periods at such elevated pressures and temperatures.

According to the present specification there is provided a process for the catalytic cracking of ammonia, the process comprising:

supplying an ammonia feed gas to one or more heated catalyst containing reaction vessels disposed within an ammonia cracking reactor; and

cracking the ammonia in the ammonia feed gas in the one or more catalyst containing reaction vessels to produce a hydrogen containing stream,

wherein the ammonia feed gas is fed into the or each reaction vessel at a pressure of at least 10 bar,

wherein the or each reaction vessel is heated to a temperature of at least 500°C, and

wherein the or each of the reaction vessels has a wall comprising or consisting of an alloy selected to be resistant to both nitriding and creep deformation at said temperature and pressure over an operating period of at least 1000 hours, 5000 hours, 10,000 hours, 50,000 hours, or 100,000 hours without failure.

The ammonia feed gas may be fed into the or each reaction vessel at a pressure of: at least 20 bar, 30 bar, 40 bar, or 50 bar; no more than 1000 bar, 500 bar, 100 bar, or 75 bar; or within a range defined by any combination of the aforementioned lower and upper limits.

The or each reaction vessel may be heated to a temperature of: at least 550°C, 600°C, 650°C, or 700°C; no more than 1500°C,1000°C, 950°C, 900°C, or 850°C; or within a range defined by any combination of the aforementioned lower and upper limits.

The or each reaction vessel may be in the form of a reaction tube in which catalyst is disposed. The or each reactor vessel/tube wall may have a thickness of: at least 3 mm, 5 mm, 8 mm, or 10 mm; no more than 50 mm, 20 mm, 15 mm, or 14 mm; or within a range defined by any combination of the aforementioned lower and upper limits. An example thickness range is 8 to 14 mm, optionally 10 to 14 mm.

Selection of a suitable alloy to meet the criteria of the invention requires knowledge of the operating conditions of the high pressure, high temperature ammonia cracking process, an understanding of the combined effects of nitriding and creep deformation in such a process, and an understanding of the nitriding and creep deformation properties of alloys in order to

select a suitable alloy to meet all the operational requirements of the process. Only a small subset of metallic alloy compositions fulfils the required criteria as selected using specialist knowledge of both alloys, their properties and interactions with the high pressure, high temperature ammonia cracking environment, and thermal, mechanical, and nitriding resistance requirements. Thus, the present specification involves the application of specialist materials knowledge to the field of ammonia cracking at high pressures.

Suitable alloys may comprise nickel and/or cobalt in an amount greater than 11 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, or 75 wt%. The total nickel + cobalt (if present) content of the alloy is preferably > 40 wt%. Optionally, the alloy may also comprise one or more of Cr, Si or Al. For example, the alloy may comprise at least 10 wt%, 14 wt%, 15 wt%, 20%, or 30% chromium, such as at least 40%. Additionally, the alloy may comprise at least 1 wt%, 3 wt%, or 4 wt% aluminium, e.g., in a range 1 – 5 wt %.

The alloy may also have an oxide layer disposed on the surface thereof. Such an oxide layer may be an aluminium oxide layer formed from aluminium in the alloy, but may also be a silicon or chrome oxide, or a combination of two or more of these. The alloy may undergo a pre-oxidation treatment to form the oxide layer. The ammonia feed gas may comprise oxidizing species, such as oxygen and/or water, to ensure oxidizing conditions in the reaction vessels and aid in maintaining the oxide layer. These oxidizing species may be natural present in the ammonia feed gas or deliberately added. Maintaining water in the process flow gas is preferred in the context of high pressure, high temperature nitriding in ammonia as it shows a large advantage over the other means of oxide formation and ensures good healing of the oxide through the operating period if damaged.

The alloy may be selected from the list consisting of alloy 600, alloy 601, alloy 602ca, alloy 617, alloy 625, alloy 690, alloy 693, alloy 699, VDM® ALLOY 699 XA, alloy 214, alloy 230, alloy 233, alloy MA47P, alloy X, alloy S, alloy 160, S+C® G 4879, G 4878 Micro, ET 45 Micro, ET 45 LC, HT E, ET 35 Co, Paralloy® OPTIM-AL, 35/45 Microalloy, 22H, Manurite® 40XO, XAl4, XTM Low C, 40X, XTM, 50W, Manauré 2, Kubota SCH42, KHR48N, KHR48NCo, KHRSA, KHR45A, UCX, Alloy 800/H/HT, Cast grades HT, HU, HW, HX, HP15Nb, HP, HPNb, HPNbS, CT15C, Kanthal® A-1, APM, AF, D, and NIKROTHAL 40, 60, 70, 80, Alloy 120, and INCOLOY® Alloy HX, 803, 890. Alloys 600, and 625 are favoured due to their balance of desirable properties and good creep data availability and cost. Alternatively, alloys 214, MA47P, 233, 699, and VDM® ALLOY 699 XA are favoured due to having sufficient aluminium to provide a tenacious oxide scale for nitriding resistance. Some of the other listed alloys are less favoured due to cost and/or availability.

Without being bound by any sort of theory it is believed that chromium containing alloys are advantageous due to their ability to react with nitrogen containing species on the surface of the alloy. In doing so, it is believed that a protective layer may be formed which functions to protect the bulk of the alloy from further nitriding.

In relation to the above list of suitable alloys, it may be noted that all the alloys contain either cobalt or nickel and some contain both. Suitable alloys typically contain at least nickel, but a cobalt-based alloy can also be used. Those containing cobalt tend to have enhanced mechanical properties at the most extreme temperatures but will come at a higher cost. As such, while a cobalt-based alloy would be of use, in practice this may not be economically favourable. For the present process, the total nickel + cobalt (if present) content of the alloy is preferably > 40 wt%, with increasing amounts adding greater advantage.

Some of the listed alloys contain aluminium. This can give an added advantage through a less nitrogen permeable oxide layer, and an ability to form under lower trace oxygen containing environments than chrome oxides. For the alloys which do contain aluminium for oxide layer formation, advantageously these should have sufficient aluminium content for good oxide layer formation. Greater amounts tend to offer greater advantage, until they start to cause mechanical property changes through excessive gamma prime precipitation at elevated temperatures. Optionally, aluminium content may range between 1 - 5 wt%, with an optimum being 3 wt% with pre-oxidation treatment, and > 4wt% without a pre-oxidation.

All the listed alloys also contain chromium. A chromium content of >14 wt% is the minimum for most alloys for the present process. Strength is mainly important when used to enhance economics, e.g., thinner wall, less material used. Accordingly, strengthening elements need to be economic to add. For example, cobalt will add high temperature strength, but may be more costly to add and process the material than simply making the wall thicker with a non-Co containing alloy. The optimum composition for the alloy will depend on the specifics of the reactor design and process conditions. However, chromium will be present in most commercially available alloys which are suitable for the present process.

The process as described above provides a high pressure, high temperature process for the cracking of ammonia to produce hydrogen with improved operability, reduced downtime, and increased safety. The one or more reaction tubes/vessels used in the process are resistant to nitriding and to creep and/ or embrittlement damage under the high temperature, high pressure ammonia cracking process.

The present specification also provides a reaction vessel for use in the process as described above. The reaction vessel comprises an ammonia cracking catalyst and has a wall comprising or consisting of an alloy selected to be resistant to both nitriding and creep deformation at an operating pressure of at least 10 bar and an operating temperature of at least 500°C for an operating period of at least 1000 hours, 5000 hours, 10,000 hours, 50,000 hours, or 100,000 hours without failure. In other respects, the reaction vessel is as described in relation to the process for cracking ammonia. Also provided is an ammonia cracking reactor comprising one or more of these reaction vessels.

Brief Description of the Drawings

For a better understanding of the present invention and to show how the same may be carried into effect, certain embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:

Figure 1 shows a schematic of a reaction tube along its axial length x and in the plane x,y - a circular cross-section of the reaction tube may be seen in the y,z plane;

Figure 2 shows a schematic of the cross-section of a reaction tube in the plane y,z with “a” representing the thickness of the reaction tube and “o” representing an oxide layer on the interior surface of the tube; and

Figure 3 shows an illustration of an ammonia cracking reactor comprising catalyst filled reaction tubes and burners for providing heat energy to the reaction tubes.

Detailed Description

Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise.

A process of the present specification comprises the step of supplying an ammonia feed gas to one or more heated catalyst containing reaction tubes disposed within an ammonia cracking reactor. The ammonia feed gas may be derived from any source. The ammonia feed gas can be produced by the catalytic combination of hydrogen and nitrogen, for example the ammonia feed gas may be produced from a Haber-Bosch ammonia synthesis process. The ammonia

feed gas may be produced in an ammonia production facility located upstream of the ammonia cracking reactor. Alternatively, the ammonia feed gas may be provided from an ammonia gas storage facility, an ammonia storage unit, an ammonia storage tank, or an ammonia gas pipeline.

The ammonia feed gas may be pre-heated prior to being supplied to the one or more catalyst containing reaction tubes. Accordingly, the process may comprise the step of pre-heating the ammonia feed gas. The ammonia feed gas may be pre-heated to a temperature of greater than 350°C, greater than 400°C, greater than 450°C, greater than 500°C, or greater than 550°C. The ammonia feed gas may be pre-heated to a temperature of less than 1000°C, less than 950°C, less than 850°C, less than 750°C, or less than 700°C. The ammonia feed gas may be pre-heated to a temperature of from 350°C to 1000°C, from 400°C to 950°C, from 450°C to 850°C, or from 500°C to 750°C, such as from 550°C to 700°C.

Suitable ammonia cracking reactors are known and may comprise a fuel combustion zone having a radiant section comprising one or more burners to which one or more fuel streams and an oxygen feed gas, such as air, oxygen enriched air, or oxygen, are fed. The radiant section may comprise the one or more catalyst containing reaction tubes though which the ammonia feed gas is passed. Combustion of one or more fuel streams in the one or more burners of the fuel combustion zone, creates heat energy (e.g., radiant heat) for heating the one or more catalyst containing reaction tubes. There may be tens or hundreds of catalyst-containing reaction tubes in the radiant section. If desired, downstream of the radiant section, a flue gas from the combustion of the one or more fuel streams may be used to pre-heat one or more feed streams in a convection section. Reactors comprising a radiant section containing catalyst containing reaction tubes and a convection section for preheating feeds are known in steam methane reforming and may be applied to the present process for ammonia cracking.

Alternative ammonia cracking reactors may be used. For example, where the combustion of the one or more fuel streams in a fuel combustion zone is separate to the reactor comprising the catalyst containing reaction tubes. Such a reactor is the compact reformer available from Johnson Matthey Davy Technologies Limited. Other alternative forms of reactor include a plate or tubular exchanger heated by molten salts, a rotary heater such as by Coolbrook, or a printed circuit heat exchanger. In certain configurations the tubes may be fired and the region outside of the tubes contains the ammonia. Alternatively still, the tubes may be electrically heated, induction heated, or concentrated solar heating.

The catalyst may be any ammonia cracking catalyst. For instance, nickel catalysts and/or ruthenium catalysts may be used. The catalyst may comprise 3 to 30% by weight nickel, preferably 8 to 20% by weight nickel, expressed as NiO, on a suitable refractory support, such as alumina or a metal aluminate. The catalyst may be in the form of pelleted shaped units, which may comprise one or more through holes, or may be provided as a wash coat on a structured metal or ceramic catalyst. A particularly preferred catalyst is KATALCO^{RTM} 27-2 available from Johnson Matthey PLC, which comprises 12% nickel, expressed as NiO, on a cylindrical pellet formed from a high surface area calcium aluminate support.

The process of the invention comprises the step of cracking the ammonia in the ammonia feed gas in the one or more heated catalyst containing reaction tubes to produce a hydrogen containing stream.

The ammonia feed gas is fed into the or each reaction vessel/tube at a pressure of: at least 10 bar, 20 bar, 30 bar, 40 bar, or 50 bar; no more than 1000 bar, 500 bar, 100 bar, or 75 bar; or within a range defined by any combination of the aforementioned lower and upper limits.

The or each reaction vessel/tube is heated to a temperature of: at least 500°C, 550°C, 600°C, 650°C, or 700°C; no more than 1500°C,1000°C, 950°C, 900°C, or 850°C; or within a range defined by any combination of the aforementioned lower and upper limits.

The temperature of the ammonia feed gas at the inlet to the one or more catalyst containing reaction tubes may be in the range of 350 °C to 1000 °C, from 400 °C to 950 °C, from 450 °C to 850 °C, or from 500 °C to 750 °C, such as from 550 °C to 700 °C. The temperature of the hydrogen containing stream exiting the one or more catalyst containing reaction tubes will influence the equilibrium position of the cracking reaction, and may be in the range of 500 to 950°C. Where nickel catalysts are used in the one or more catalyst containing reaction tubes, the temperature of the hydrogen containing stream exiting the one or more catalyst containing reaction tubes may preferably be greater than about 700°C.

The ammonia cracking reaction produces a hydrogen containing stream. The hydrogen containing stream contains H_2. The hydrogen containing stream also contains nitrogen, and may further contain residual ammonia (e.g., unreacted ammonia).

The hydrogen containing stream may comprise 40 mol% or more H_2, 50 mol% or more H_2, or 60 mol% or more H_2. Optionally, the hydrogen containing stream may comprise 75 mol% or less H_2, 70 mol% or less H_2, or 65 mol% or less H_2. For example, the hydrogen containing

stream may comprise from 40 mol% to 75 mol% H_2, from 50 mol% to 70 mol% H_2, or from 60 mol% to 65 mol% H_2.

As described in the summary section, the process of the present specification uses catalyst containing reaction vessels (e.g. tubes) composed of an alloy selected to be resistant to both nitriding and creep deformation at the high operating temperatures and pressures of the present process over an operating period of at least 1000 hours, 5000 hours, 10,000 hours, 50,000 hours, or 100,000 hours without failure.

The reaction tube has an inlet side and an outlet side defining an axial length, x, of the reaction tube. It will be understood that catalyst for the ammonia cracking reaction is disposed inside of the reaction tube along the axial length, x. It will further be understood that the ammonia feed gas is passed from the inlet side of the reaction tube, over the ammonia cracking catalyst disposed therein, and that the hydrogen stream exits the reaction tube via the outlet side of the reaction tube. Figure 1 shows the axial length, x, of a reaction tube in the x,y plane.

The reaction tube has a cross-section in the plane perpendicular to the axial length in the y,z plane. The cross-section may take on any shape and is not particularly limited. For instance, the cross-section may be circular, elliptical, quadrilateral (e.g., square or rectangular), or triangular in shape. Typically, the cross-section is circular. Where the cross-section is circular, the reaction tube will be understood to be a cylindrical tube.

An example of a cross-section, in the y,z plane, of a reaction tube is shown in Figure 2 where the cross-section is circular in shape, and “a” represents the thickness of the alloy tube. The tube wall may have a thickness of: at least 3 mm, 5 mm, 8 mm, or 10 mm; no more than 50 mm, 20 mm, 15 mm, or 14 mm; or within a range defined by any combination of the aforementioned lower and upper limits. An example thickness range is 8 to 14 mm, optionally 10 to 14 mm. However, it is noted that these ranges are for standard fired reactor designs and thicknesses may vary for other types of reactor configuration.

Also indicated in Figure 2 is an oxide layer on the interior surface of the tube. This oxide layer may be formed by oxidation of a component of the alloy used to form the tube, e.g., aluminium forming an aluminium oxide scale. Such an oxide layer can reduce nitriding. It forms from reaction of the alloy with oxygen in the air when being fabricated. The oxide layer will also grow and heal in the process environment provided oxygen is available. Less oxygen partial pressure is required to form alumina in aluminium containing alloys. Controlling oxidizing species content (e.g., water and/or oxygen) in the process flow gas within the reaction tubes

during operation can ensure oxidizing conditions and aid in maintaining a protective oxide layer. Alternatively, naturally present oxidizing species in the process flow gas may fulfil this function. That said, maintaining water in the process flow gas is preferred in the context of high pressure, high temperature nitriding in ammonia as it shows a large advantage over the other means of oxide formation and ensures good healing of the oxide through the operating period if damaged. The oxide layer can provide a layer which protects the reaction tube from the nitriding effect of the ammonia feed gas.

As described in the summary section, moving from low pressure ammonia cracking processes to high pressure ammonia cracking processes has represented a challenge. Ammonia is known to cause nitriding of metallic alloys, especially when dissociated as is the case in the present process. The ammonia cracking section of the plant is conducted in metallic tubes that are externally fired to provide energy for the endothermic cracking reaction. Metallic tubes are required for good heat transfer, toughness, and because this is the proven method of driving such reactions, e.g., in steam methane reforming (SMR). Nitriding potential is a function of the ammonia/ nitrogen partial pressure with higher pressures increasing the rate of nitriding. Nitriding reduces the effective wall thickness and embrittles the reaction tubes. Furthermore, there are very few alloys that can provide good mechanical strength at high temperatures and pressures, as well as resist nitriding for extended periods, especially where data on the creep performance of the alloys over 100,000 hours is required for safe design.

Most elements will form nitrides at the temperatures and nitriding potentials of the ammonia cracking furnace. However, the formation of nitrides with Ni and Co is very un-favourable thermodynamically. Fortunately, Ni and Co are some of the few elements used for high temperature austenitic alloys for pressure applications, e.g., steam methane reformers (SMRs). Additionally, it has been found that aluminium when used as an oxide scale former in alloys has a high resistance to nitrogen transport through to the base material. Furthermore, alloys of Ni and Co can be alloyed to have better high temperature mechanical properties to allow better integrity, but also use less materials through thinner wall design. This is important with the rising prices of Ni and Co due to the battery market. Selection of these alloying elements is critical as when they form nitrides on the base alloy this needs to be in a controlled in a predictable way to provide a suitable life for the cracker without sudden failure due to catastrophic nitriding.

Suitable alloys may comprise nickel and/or cobalt in an amount greater than 11 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, or 75 wt%. The total nickel + cobalt (if present) content of the alloy is preferably > 40 wt%. Optionally, the alloy may also comprise one or more of Cr, Si or Al.

For example, the alloy may comprise at least 10 wt%, 14 wt%, 15 wt%, 20%, or 30% chromium. Additionally, the alloy may comprise at least 1 wt%, 3 wt%, or 4 wt% aluminium, e.g., in a range 1 – 5 wt %.

The alloy may be selected from the list consisting of alloy 600, alloy 601, alloy 602ca, alloy 617, alloy 625, alloy 690, alloy 693, alloy 699, alloy 214, alloy 230, alloy 233, alloy MA47P, alloy X, alloy S, alloy 160, S+C® G 4879, G 4878 Micro, ET 45 Micro, ET 45 LC, HT E, ET 35 Co, Paralloy® OPTIM-AL, 35/45 Microalloy, 22H, Manurite® 40XO, XAI4, XTM Low C, 40X, XTM, 50W, Manauré 2, Kubota SCH42, KHR48N, KHR48NCo, KHRSA, KHR45A, and UCX. Alloys 600, and 625 are favoured due to their balance of desirable properties and good creep data availability and cost. Alternatively, alloys 214, MA47P, 233 and 699 are favoured due to having sufficient aluminium to provide a tenacious oxide scale for nitriding resistance. Some of the other listed alloys are less favoured due to cost.

In relation to the above list of suitable alloys, it may be noted that all the alloys contain either cobalt or nickel and some contain both. Suitable alloys typically contain at least nickel, but a cobalt-based alloy can also be used. Those containing cobalt tend to have enhanced mechanical properties at the most extreme temperatures but will come at a higher cost. As such, while a cobalt-based alloy would be of use, in practice this may not be economically favourable. For the present process, the total nickel + cobalt (if present) content of the alloy is preferably > 40 wt%, with increasing amounts adding greater advantage.

Some of the listed alloys contain aluminium. This can give an added advantage through a longer incubation time for nitrogen to penetrate the material. For the alloys which do contain aluminium for oxide layer formation, advantageously these should have sufficient aluminium content for good oxide layer formation. Greater amounts tend to offer greater advantage, until they start to cause mechanical issues. Optionally, aluminium content may range between 1 - 5 wt%, with an optimum being 3 wt% with pre-oxidation treatment, and > 4wt% without a pre-oxidation.

All the listed alloys also contain chromium. A chromium content of, for example, >14 wt% is the minimum for most alloys for the present process. Strength is mainly important when used to enhance economics, e.g., thinner wall, less material used. Accordingly, strengthening elements need to be economic to add. For example, cobalt will add high temperature strength, but may be more costly to add and process the material than simply making the wall thicker with a non-Co containing alloy. The optimum composition for the alloy will depend on the

specifics of the reactor design and process conditions. However, chromium will be present in most commercially available alloys which are suitable for the present process.

In addition to the ammonia cracking process as described above, the present specification also provides a reaction vessel such as a reaction tube, for use in the catalytic cracking of ammonia, the reaction tube containing an ammonia cracking catalyst. The ammonia cracking catalyst is contained inside of the reaction tube. That is, the ammonia cracking catalyst is contained inside the reaction tube along its axial length. The ammonia cracking catalyst may be any catalyst known as suitable for catalysing the cracking of ammonia to hydrogen and nitrogen. It may be preferred that the catalyst is a nickel-based catalyst, such as nickel on an inert support (e.g. an alumina, silica, or another refractory oxide). For example, the catalyst may be KATALCO 27-2^{RTM}, available from Johnson Matthey PLC. Alternatively, it may be preferred that the catalyst is a noble metal catalyst, such a ruthenium based catalyst.

Also provided is an ammonia cracking reactor comprising one or more catalyst containing reaction vessels (e.g., reaction tubes) as described above. Figure 3 shows an illustration of an ammonia cracking reactor comprising catalyst filled reaction tubes and burners for providing heat energy to the reaction tubes.

New scaled ammonia cracking applications are pushing the boundaries of what is currently required in terms of reactor vessel alloys, and we are not aware that the concurrent issue of need for economically viable creep strength plus highly nitride resistance is required in other applications. Selection of materials for containment of a high pressure ammonia cracking reaction is challenging. This specification describes such materials and the small subset of metallic alloy compositions that fulfil the required criteria as selected using specialist knowledge of both alloys, their properties and interactions with the ammonia cracking environment and mechanical requirements. The specification allows the safe and cost effective utilisation of ammonia as an energy vector through use of carefully selected engineering alloys for the harshest chemical environment in an ammonium cracking process at elevated pressures.

While this invention has been particularly shown and described with reference to certain examples, it will be understood to those skilled in the art that various changes in form and detail may be made without departing from the scope of the invention as defined by the appended claims.

Claims

1. A process for the catalytic cracking of ammonia, the process comprising:

supplying an ammonia feed gas to one or more heated catalyst containing reaction vessels disposed within an ammonia cracking reactor; and

cracking the ammonia in the ammonia feed gas in the one or more catalyst containing reaction vessels to produce a hydrogen containing stream,

wherein the ammonia feed gas is fed into the or each reaction vessel at a pressure of at least 10 bar,

wherein the or each reaction vessel is heated to a temperature of at least 500°C, and

wherein the or each of the reaction vessels has a wall comprising or consisting of an alloy selected to be resistant to both nitriding and creep deformation at said temperature and pressure over an operating period of at least 1000 hours without failure.

2. A process according to claim 1, wherein the ammonia feed gas is fed into the or each reaction vessel at a pressure of: at least 20 bar, 30 bar, 40 bar, or 50 bar; no more than 1000 bar, 500 bar, 100 bar, or 75 bar; or within a range defined by any combination of the aforementioned lower and upper limits.

3. A process according to claim 1 or 2, wherein the or each reaction vessel is heated to a temperature of: at least 550°C, 600°C, 650°C, or 700°C; no more than 1500°C,1000°C, 950°C, 900°C, or 850°C; or within a range defined by any combination of the aforementioned lower and upper limits.

4. A process according to any preceding claim, wherein the or each reaction vessel is in the form of a reaction tube in which catalyst is disposed.

5. A process according to any preceding claim, wherein the alloy comprises nickel and/or cobalt in an amount greater than 11 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, or 75 wt%.

6. A process according to claim 5, wherein the alloy comprises a total nickel + cobalt content > 40 wt%.

7. A process according to any preceding claim, wherein the alloy comprises one or more of Cr, Si or Al.

8. A process according to any preceding claim, wherein the alloy comprises at least 10 wt%, 14 wt%, 15 wt%, 20%, or 30% chromium, such as at least 40% chromium.

9. A process according to any preceding claim, wherein the alloy comprises at least 1 wt%, 3%, or 4% aluminium, optionally no more than 5 wt%.

10. A process according to any preceding claim, wherein the alloy has an oxide layer disposed on the surface thereof.

11. A process according to claim 10, wherein the oxide layer is an aluminium oxide layer formed from aluminium in the alloy.

12. A process according to claim 10 or claim 11, wherein the ammonia feed gas comprises oxidizing species during operation to ensure oxidizing conditions and aid in maintaining the oxide layer.

13. A process according to any preceding claim, wherein the alloy is selected from the list consisting of alloy 600, alloy 601, alloy 602ca, alloy 617, alloy 625, alloy 690, alloy 693, alloy 699, VDM® ALLOY 699 XA, alloy 214, alloy 230, alloy 233, alloy MA47P, alloy X, alloy S, alloy 160, S+C® G 4879, G 4878 Micro, ET 45 Micro, ET 45 LC, HT E, ET 35 Co, Paralloy® OPTIM-AL, 35/45 Microalloy, 22H, Manurite® 40XO, XAl4, XTM Low C, 40X, XTM, 50W, Manauré 2, Kubota SCH42, KHR48N, KHR48NCo, KHRSA, KHR45A, UCX, Alloy 800/H/HT, Cast grades HT, HU, HW, HX, HP15Nb, HP, HPNb, HPNbS, CT15C, Kanthal® A-1, APM, AF, D, and NIKROTHAL 40, 60, 70, 80, Alloy 120, and INCOLOY® Alloy HX, 803, 890.

14. A process according to claim 13, wherein the alloy is alloy 600 or alloy 625.

15. A process according to claim 13, wherein the alloy is alloy 214, alloy MA47P, alloy 233, alloy 699, or VDM® ALLOY 699 XA.

16. A process according to any preceding claim, wherein the or each reactor vessel wall has a thickness of: at least 3 mm, 5 mm, 8 mm, or 10 mm; no more than 50 mm, 20 mm, 15 mm, or 14 mm; or within a range defined by any combination of the aforementioned lower and upper limits.

17. A process according to any preceding claim, wherein the alloy is selected to be resistant to both nitriding and creep deformation at the operating temperature and pressure

over an operating period of at least at least 5000 hours, 10,000 hours, 50,000 hours, or 100,000 hours without failure.

18. A reaction vessel for use in the process according to any preceding claim, wherein the reaction vessel comprises an ammonia cracking catalyst and has a wall comprising or consisting of an alloy selected to be resistant to both nitriding and creep deformation at an operating pressure of at least 10 bar and an operating temperature of at least 500°C for an operating period of at least 1000 hours, 5000 hours, 10,000 hours, 50,000 hours, or 100,000 hours without failure.

19. An ammonia cracking reactor comprising one or more reaction vessels according to claim 18.