

PROCESS AND SYSTEM FOR TREATING AN EXHAUST GAS COMPRISING N₂O AND NO_x**Field of the Invention**

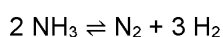
The present invention relates to processes and systems for catalytically treating a gas stream. More specifically, the present invention relates to processes and systems for catalytically decomposing nitrous oxide (N₂O) and nitric oxide and nitrogen dioxide (NO_x) produced from an ammonia cracking reactor.

Background of the Invention

- 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:

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- The ammonia cracking reaction is endothermic and may usefully be achieved by passing ammonia over a suitable catalyst in 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 and are referred to herein as ammonia cracking reactors.

- In industrial processes used for the catalytic cracking of ammonia, a fuel is combusted in the ammonia cracking reactor to provide heat energy to the catalyst containing reaction tubes.
- The fuel may be a hydrocarbon fuel, however, typically, the fuel may comprise ammonia and/or hydrogen. For instance, the fuel may be a portion of the ammonia which is to be cracked, or a waste gas stream. Waste gas streams are typically produced from the

purification of the hydrogen stream (e.g. by pressure swing adsorption) following the ammonia cracking reaction. In certain cases, nitrogen gas (N_2) may also be present in the fuel.

- 5 However, combustion of fuels comprising ammonia produce nitrogen oxygen gases, such as N_2O and NO_x . Moreover, the heat of combustion of hydrogen may be sufficient to produce N_2O and NO_x by reaction of nitrogen gas (N_2) with oxygen (O_2).

- The emission of N_2O and NO_x (e.g. NO and NO_2) are tightly controlled for numerous well
10 known environmental and health reasons. For example, N_2O is a powerful greenhouse gas, whilst NO_x is associated with smog and acid rain formation.

- Methods of treating N_2O and NO_x in exhaust gas streams are known in industrial process such as in the production of nitric acid. However, the nature and composition of the exhaust
15 gas streams formed during production of nitric acid are vastly different to those found in exhaust gases from ammonia cracking reactors. As a consequence, known N_2O and NO_x treatment systems may not be suitable for treating exhaust gases from ammonia cracking reactors.

- 20 There is a need for processes and systems capable of treating exhaust gas streams from ammonia cracking reactors used in the decomposition of ammonia to produce hydrogen.

Summary of the Invention

- Accordingly, in a first aspect of the invention there is provided a process for treating an
25 exhaust gas comprising N_2O and NO_x from an ammonia cracking reactor, the process comprising the steps of:

- i) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
- ii) combining the N_2O depleted exhaust gas with a reducing agent; and
- 30 iii) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas.

- The present invention provides a process for treating an exhaust gas comprising N_2O and
35 NO_x from an ammonia cracking reactor. The exhaust gas produced from the ammonia cracking reactor of the process of the invention are different to those produced in the production of (for example) nitric acid, both in terms of composition and physical properties

(e.g. temperature). For example, the exhaust gas comprising N_2O and NO_x produced from an ammonia cracking reactor has a higher water content and a higher temperature than the exhaust gas found in a nitric acid plant. Accordingly, it is unlikely that a process which may be suitable for decomposing N_2O and/or NO_x in an exhaust gas from a nitric acid production process would be suitable for treating the exhaust gas from an ammonia cracking reactor. It has surprisingly been found that the process and system of the present invention, which comprises a first iron containing zeolitic catalyst, may be used to decompose N_2O and NO_x in an exhaust gas produced by an ammonia cracking reactor. Moreover, processes and systems of the present invention have been found to decompose N_2O and NO_x over an extended period of time, providing a commercially attractive solution to treating the exhaust gas produced by an ammonia cracking reactor.

In a second aspect of the invention there is provided an exhaust gas system for treating an exhaust gas comprising N_2O and NO_x from an ammonia cracking reactor, the system comprising an exhaust gas pathway comprising a first iron containing zeolitic catalyst configured to decompose N_2O at a first temperature and to produce an N_2O depleted exhaust gas, an injection device configured to mix a reducing agent with the N_2O depleted exhaust gas, and a first selective catalytic reduction catalyst configured to decompose NO_x at a second temperature and to produce a purified exhaust gas.

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Brief Description of the Drawings

Figure 1 shows the effect of water content of an exhaust gas on the N_2O and NO conversion.

Figure 2 shows NO and N_2O conversion in an exhaust gas as a function of temperature for a series of iron containing zeolitic catalyst.

Figure 3 show NO and N_2O conversion in an exhaust gas as a function of temperature for a series of activated and non-activated iron containing zeolitic catalyst.

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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.

The process of the invention provides a process for treating an exhaust gas comprising N_2O and NO_x from an ammonia cracking reactor.

5 In the context of the present application, NO_x will be understood to refer to compounds including NO and NO_2 .

Ammonia cracking reactors are known and typically 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 depleted air, oxygen enriched air, oxygen, and/or
10 oxygen and an inert gas such as nitrogen are fed. The radiant section may comprise one or more catalyst containing reaction tubes through which an ammonia stream is passed. Combustion of the 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, hundreds, or thousands of catalyst
15 containing reaction tubes in the radiant section. The ammonia stream is decomposed, or cracked, in the one or more reaction tubes to form a cracked gas stream comprising hydrogen (H_2), nitrogen (N_2), and residual ammonia (NH_3). 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 invention.

20 As will be understood, the exhaust gas comprising N_2O and NO_x from the ammonia cracking reactor is the exhaust gas produced from the combustion of the one or more fuel streams in the presence of oxygen in the ammonia cracking reactor.

25 Accordingly, the process of the invention may comprise the step of combusting one or more fuel streams in the presence of oxygen in the ammonia cracking reactor to provide heat energy and to produce the exhaust gas comprising N_2O and NO_x .

The one or more fuel streams may comprise hydrogen (H_2). The one or more fuel streams
30 may comprise ammonia (NH_3). The one or more fuel streams may comprise hydrogen (H_2), nitrogen (N_2), and/or ammonia (NH_3), and optionally a hydrocarbon fuel, such as methane.

The oxygen used to combust the one or more tail gas streams may suitably be, or comprise, air, compressed air, oxygen depleted air, oxygen enriched air, oxygen, and/or oxygen and an
35 inert gas such as nitrogen.

As used herein, the unit “ppm” refers to parts per million by volume unless otherwise specified.

5 The exhaust gas may comprise N_2O in an amount of 0.05 ppm or more, 1 ppm or more, 5 ppm or more, or 10 ppm or more. The exhaust gas may comprise N_2O in an amount of 500 ppm or less, 400 ppm or less, 300 ppm or less, or 200 ppm or less. For example, the exhaust gas may comprise N_2O in an amount of from 0.05 ppm to 500 ppm, from 1 ppm to 400 ppm, from 5 ppm to 300 ppm, or from 10 to 200 ppm, such as 75 ppm, 100 ppm, or 150 ppm.

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The exhaust gas may comprise NO_x in an amount of 1 ppm or more, 5 ppm or more, 10 ppm or more, or 15 ppm or more. The exhaust gas may comprise NO_x in an amount of 2,000 ppm or less, 1,500 ppm or less, 1,200 ppm or less, or 1,000 ppm or less. For example, the exhaust gas may comprise NO_x in an amount of from 1 ppm to 2,000 ppm, from 5 ppm to 1,500 ppm, from 10 ppm to 1,200 ppm, or from 15 ppm to 1,000 ppm, such as 400 ppm, 500 ppm, 600 ppm, or 700 ppm.

20 The exhaust gas may comprise nitrogen (N_2). The exhaust gas may comprise nitrogen (N_2) in an amount of 50 vol% or more, 55 vol% or more, or 60 vol% or more. The exhaust gas may comprise nitrogen (N_2) in an amount of 90 vol% or less, 85 vol% or less, 80 vol% or less. For example, the exhaust gas may comprise nitrogen (N_2) in an amount of from 50 vol% to 90 vol%, from 55 vol% to 85 vol%, or from 60 vol% to 80 vol%, such as 65 vol%, 70 vol%, or 75 vol%.

25 The exhaust gas may comprise oxygen (O_2). The exhaust gas may comprise oxygen (O_2) in an amount of 0.1 vol% or more, 0.2 mol% or more, 0.5 mol% or more, or 0.75 mol% or more. The exhaust gas may comprise oxygen (O_2) in an amount of 25 vol% or less, 20 vol% or less, 18 vol % or less, or 15 vol% or less. For example, the exhaust gas may comprise oxygen (O_2) in an amount of from 0.1 vol% to 25 vol%, from 0.2 vol% to 20 vol%, from 0.5 vol% to 18 vol%, or from 0.75 vol% to 15 vol%, such as about 5 vol% or 10 vol%.

35 As will be understood, the amount of N_2O and NO_x present in the exhaust gas will depend upon how the ammonia cracking reactor is operated. The composition of the exhaust gas described hereinabove are compositions of the exhaust gas under typical operating conditions of the ammonia cracking reactor, such as when the ammonia cracking reactor is operating under steady state conditions to produce the cracked gas stream. Where the ammonia cracking reactor is operated under certain exceptional conditions the amount of

N₂O and/or NO_x in the exhaust gas may increase considerably. For example, during a “turndown” of the ammonia cracking reactor NO_x levels in the exhaust gas may be as high as 10,000 ppm or more and N₂O levels in the exhaust gas may be as high as 1500 ppm or more. A “turndown” of the ammonia cracking reactor may include conditions where the rate of supply of the one or more fuel streams is decreased relative to the supply rate of the oxygen feed gas. Here, the higher oxygen concentration, relative to the one or more fuel streams, is believed to produce higher N₂O and NO_x.

It has been found by the present applicant that the presence of high concentrations of water in an exhaust gas inhibits the performance of iron containing zeolitic catalysts in the decomposition of N₂O. In comparison to exhaust gas from an ammonia cracking reactor, which typically comprise high concentrations of water, exhaust gas from a nitric acid production process typically comprises less than 2 vol% water (more typically less than 1 vol% or 0.5 vol%).

It is therefore a surprising advantage of the process of the invention that the first iron containing zeolitic catalyst may decompose N₂O and NO_x in the exhaust gas despite its high water content.

Accordingly, the exhaust gas of the process of the invention may comprise water (H₂O) in an amount of 5 vol% or more, 6 vol% or more, 7 vol% or more, or 8 vol% or more. The exhaust gas may comprise water (H₂O) in an amount of 40 vol% or less, 37 vol% or less, 35 vol% or less, or 32 vol% or less. For example, the exhaust gas may comprise water (H₂O) in an amount of from 5 vol% to 40 vol%, from 6 vol% to 37 vol%, from 7 vol% to 35 vol%, or from 8 vol% to 32 vol%, such as 10 vol%, 15 vol%, 25 vol%, or 30 vol%.

In certain processes of the invention, the exhaust gas may be a turndown exhaust gas.

The turndown exhaust gas may be produced by a turndown of the ammonia cracking reactor. Accordingly, in certain processes of the invention, the process may comprise the step of turning-down the ammonia cracking reactor and producing an exhaust gas which is a turndown exhaust gas. The step of turning-down the ammonia cracking reactor may comprise decreasing the rate of supply of the one or more fuel streams to the ammonia cracking reactor. The step of turning-down the ammonia cracking reactor may comprise decreasing the rate of supply of the one or more fuel streams to the ammonia cracking reactor relative to the supply rate of the oxygen feed gas.

The exhaust gas which is the turndown exhaust gas may then be contacted with the first iron containing zeolitic catalyst of the process of the invention.

5 The turndown exhaust gas may comprise N_2O in an amount of 300 ppm or more, 400 ppm or more, 500 ppm or more, or 600 ppm or more. The turndown exhaust gas may comprise N_2O in an amount of 4,000 ppm or less, 3,000 ppm or less, 2,500 ppm or less, or 2,000 ppm or less. For example, the turndown exhaust gas may comprise N_2O in an amount of from 300 ppm to 4,000 ppm, from 400 ppm to 3,000 ppm, from 500 ppm to 2,500 ppm, or from 600 to 2,000 ppm, such as about 1,000 ppm or 1,800 ppm.

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The turndown exhaust gas may comprise NO_x in an amount of 2,000 ppm or more, 3,000 ppm or more, 4,000 ppm or more, or 5,000 ppm or more. The turndown exhaust gas may comprise NO_x in an amount of 20,000 ppm or less, 15,000 ppm or less, 12,000 ppm or less, or 10,000 ppm or less. For example, the turndown exhaust gas may comprise NO_x in an amount of from 2,000 ppm to 20,000 ppm, from 3,000 ppm to 15,000 ppm, from 4,000 ppm to 12,000 ppm, or from 5,000 ppm to 10,000 ppm.

20 The turndown exhaust gas may comprise nitrogen (N_2). The turndown exhaust gas may comprise nitrogen (N_2) in an amount of 50 vol% or more, 55 vol% or more, or 60 vol% or more. The turndown exhaust gas may comprise nitrogen (N_2) in an amount of 90 vol% or less, 85 vol% or less, 80 vol% or less. For example, the turndown exhaust gas may comprise nitrogen (N_2) in an amount of from 50 vol% to 90 vol%, from 55 vol% to 85 vol%, or from 60 vol% to 80 vol%, such as 65 vol%, 70 vol%, or 75 vol%.

25 The turndown exhaust gas may comprise oxygen (O_2). The turndown exhaust gas may comprise oxygen (O_2) in an amount of 0.1 vol% or more, 0.2 mol% or more, 0.5 mol% or more, or 0.75 mol% or more. The turndown exhaust gas may comprise oxygen (O_2) in an amount of 25 vol% or less, 20 vol% or less, 18 vol % or less, or 15 vol% or less. For example, the turndown exhaust gas may comprise oxygen (O_2) in an amount of from 0.1 vol% to 25 vol%, from 0.2 vol% to 20 vol%, from 0.5 vol% to 18 vol%, or from 0.75 vol% to 15 vol%, such as about 5 vol% or 10 vol%.

35 The turndown exhaust gas of the process of the invention may comprise water (H_2O). The turndown exhaust gas of the process of the invention may comprise water (H_2O) in an amount of 5 vol% or more, 6 vol% or more, 7 vol% or more, or 8 vol% or more. The turndown exhaust gas may comprise water (H_2O) in an amount of 40 vol% or less, 37 vol% or less, 35 vol% or less, or 32 vol% or less. For example, the turndown exhaust gas may

comprise water (H₂O) in an amount of from 5 vol% to 40 vol%, from 6 vol% to 37 vol%, from 7 vol% to 35 vol%, or from 8 vol% to 32 vol%, such as 10 vol%, 15 vol%, 25 vol%, or 30 vol%.

- 5 The process of the invention comprises the step of contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N₂O and to produce an N₂O depleted exhaust gas.

10 The first iron containing zeolitic catalyst preferably comprises iron in the pore structure of the zeolite of the first iron containing zeolitic catalyst. For example, the iron may be ion-exchanged with hydrogen ions (H⁺) or sodium ions (Na⁺) in the pore structure of the zeolite of the first iron containing zeolitic catalyst to replace H⁺ or Na⁺ with an iron ion.

15 Preferably, the zeolite of the first iron containing zeolitic catalyst may have a BEA, FER, ZSM-5, CHA, AEI, or MFI framework (i.e. Fe-BEA, Fe-FER, Fe-ZSM-5, FeCHA, FeAEI, or Fe-MFI). More preferably, the zeolite of the first iron containing zeolitic catalyst may have a BEA framework (i.e. Fe-BEA) or a FER framework (i.e. Fe-FER).

20 The first iron containing zeolitic catalyst may contain iron in an amount of 1 weight% or more, 1.5 weight% or more, 2 weight% or more, or 2.5 weight% or more relative to the total weight of the first iron containing zeolitic catalyst. The first iron containing zeolitic catalyst may contain iron in an amount of 10 weight % or less, 8 weight % or less, 7 weight% or less, or 6 weight% or less relative to the total weight of the first iron containing zeolitic catalyst. For example, the first iron containing zeolitic catalyst may contain iron in an amount of from 25 1 weight% to 10 weight%, from 1.5 weight% to 8 weight %, from 2 weight% to 7 weight%, or from 2.5 weight% to 6 weight % relative to the total weight of the first iron containing zeolitic catalyst, such as 3 weight%, 4 weight%, or 5 weight% relative to the total weight of the first iron containing zeolitic catalyst.

30 Advantageously, where the first iron containing zeolitic catalyst may be present in an activated form. The first iron containing zeolitic catalyst may be activated by heating it to an elevated temperature (for example 600 °C or more, 700 °C or more, or 750 °C or more) in an inert atmosphere (e.g. N₂ or Ar gas with less than 1 volume% O₂) to reduce the iron to Fe(0). Accordingly, it may be preferred that the first iron containing zeolitic catalyst is an activated 35 first iron containing zeolitic catalyst. Accordingly, it may be preferred that the first iron containing zeolitic catalyst comprises iron as Fe(0).

Without being bound by any kind of theory, it is believed that where the first iron containing zeolitic catalyst is an activated first iron containing zeolitic catalyst that a high number of isolated iron exchange sites are present, and fewer oligonuclear Fe_2O_3 sites exist. The enhanced number of isolated Fe(0) exchange sites are believed to give rise to improved catalytic activity.

The first iron containing zeolitic catalyst may have a silica to alumina ratio (SAR) of from 100:1 to 5:1, such as from 50:1 to 10:1 or from 40:1 to 15:1.

The first iron containing zeolitic catalyst may be present in the process of the invention as a coating on a structured support or as an extrudate.

The structured support may comprise an inorganic oxide, such as an alumina, a silica-alumina, cordierite, or a titania. Alternatively, the structured support may be metallic. The structured support may be present in any of a number of shapes. For example, the structured support may be a shaped particle (e.g. a quadralobe, or a sphere), or a flow-through monolith, such as a so called "honeycomb" monolith. Preferably, the structured support may be a flow-through monolith. As will be understood a flow-through monolith refers to a structured support which comprises a plurality of channels which allow gas to pass through. The first iron containing zeolitic catalyst may be applied to the structured support as a coating by any means known in the art, such as by depositing it as a washcoat.

It has surprisingly been found that the first iron containing zeolitic catalyst has improved durability in the process of the invention where it is present as a coating on a structured support. Without being bound by any sort of theory it is believed that where the first iron containing zeolitic catalyst is present as a coating on a structured support that it is capable of withstanding the chemical and physical conditions of the exhaust gas from the ammonia cracking reactor (e.g. the elevated water content).

Alternatively, the first iron containing zeolitic catalyst may be present in the process of the invention as an extrudate. Here, the first iron containing zeolitic catalyst may be extruded into any desired shape, but may preferably be an extruded flow-through monolith. Where the catalyst is an extrudate it will be understood that the extrudate itself is catalytically active.

The first iron containing zeolitic catalyst may suitably be prepared according to the methods disclosed in any one of WO2016/020806A1, WO2011/064666A2, and WO2012/075400A1.

The process of the invention comprises the step of contacting the exhaust gas with the first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas.

- 5 The first temperature may be a temperature of 450 °C or more, 500 °C or more, 525 °C or more, 540 °C or more, or 550 °C or more. The first temperature may be a temperature of 750 °C or less, 700 °C or less, 650 °C or less, or 620 °C or less. For example, the first temperature may be a temperate of from 450 °C to 750 °C, from 500 °C to 700 °C, from 525 °C to 650 °C, or from 550 °C to 620 °C.

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- It is an advantage of the process of the invention that the exhaust gas from the ammonia cracking reactor may be at or above the first temperature before it is contacted with the first iron containing zeolitic catalyst. As a consequence, the exhaust gas may not require further energy input to heat it to the first temperature. Accordingly, the process of the invention
- 15 utilises energy already present in an ammonia cracking process and may be provided as a so-called "passive" exhaust gas treatment system to which no further energy is supplied. A passive exhaust gas treatment system is particularly advantageous in a plant for the cracking of ammonia due to the endothermic nature of the ammonia cracking reaction, which requires the input of energy to maintain the cracking reaction, and the consequential need
- 20 for careful energy management.

It may be preferred that the first iron containing zeolitic catalyst may be present in a flue duct of the ammonia cracking reactor.

- 25 The first iron containing zeolitic catalyst may decompose N_2O to nitrogen (N_2) and oxygen (O_2). The first iron containing zeolitic catalyst may decompose N_2O to nitrogen (N_2) and oxygen (O_2) without the addition of a reducing agent. The first iron containing zeolitic catalyst may be a thermal decomposition catalyst which thermally decomposes N_2O to nitrogen (N_2) and oxygen (O_2) in the absence of a reducing agent. As will be understood, a thermal
- 30 decomposition catalyst does not require the addition of a reducing agent to affect the decomposition of N_2O and catalyses the decomposition of N_2O by the action of heat alone.

- The N_2O depleted exhaust gas may comprise 20 ppm or less N_2O , 18 ppm or less N_2O , 15 ppm or less N_2O , 12 ppm or less N_2O , 10 ppm or less N_2O , or 8 ppm or less N_2O . In all other
- 35 respects, the N_2O depleted exhaust gas may comprise the same composition as the exhaust gas. That is to say that the amount of N_2 , O_2 , H_2O , and NO_x in the exhaust gas remain substantially unchanged following contact with the first iron containing zeolitic catalyst.

The process of the invention comprises the step of combining the N₂O depleted exhaust gas with a reducing agent.

- 5 The reducing agent may be mixed with the N₂O depleted exhaust gas in the gas phase. Accordingly, it may be preferred that the reducing agent is present as a gas prior to combination with the N₂O depleted exhaust gas. Suitably, the reducing agents may be selected from the group consisting of ammonia (NH₃), urea, or a hydrocarbon (e.g. methane). Preferably, the reducing agent may be ammonia (NH₃) or urea. Most preferably,
10 the reducing agent may be ammonia (NH₃).

The combining of the N₂O depleted exhaust gas with the reducing agent may be accomplished in any suitable way. Typically, the N₂O depleted exhaust gas and the reducing agent are mixed to provide a homogenous mixture.

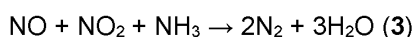
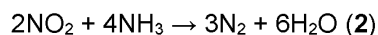
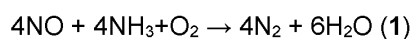
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The process of the invention comprises the step of contacting the N₂O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas.

- 20 Selective catalytic reduction catalysts of the invention function to decompose NO_x by catalysing a reaction with the reducing agent. Selective catalytic reduction catalysts of the invention may function to decompose NO_x by catalysing a reaction with the reducing agent to form nitrogen (N₂) and water (H₂O).

- 25 As will be understood a selective catalytic reduction catalyst is a catalyst which may reduce (i.e. decompose) NO_x in the presence of a reductant (e.g. ammonia) and oxygen to produce nitrogen (N₂) and water (H₂O). Equations 1-3 represent reactions of NO_x with a reductant (e.g. ammonia) which may be catalysed by a selective catalytic reduction catalyst:

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- 35 The first selective catalytic reduction catalyst may comprise, or consist essentially of, a metal oxide based SCR catalyst formulation. The metal oxide based SCR catalyst formulation may comprise vanadium and/or tungsten supported on a refractory oxide. The refractory oxide

may be selected from the group consisting of alumina, silica, titania, zirconia, ceria and combinations thereof.

5 The metal oxide based SCR catalyst formulation may comprise, or consist essentially of, an oxide of vanadium (e.g. V_2O_5) and/or an oxide of tungsten (e.g. WO_3) supported on a refractory oxide selected from the group consisting of titania (e.g. TiO_2), ceria (e.g. CeO_2), and a mixed or composite oxide of cerium and zirconium (e.g. $Ce_xZr(1-x)O_2$, wherein $x = 0.1$ to 0.9, preferably $x = 0.2$ to 0.5).

10 Preferably, the metal oxide based SCR catalyst formulation may comprise, or consist essentially of, an oxide of vanadium (e.g. V_2O_5) and optionally an oxide of tungsten (e.g. WO_3), supported on titania (e.g. TiO_2). Preferably, the concentration of the oxide of vanadium is from 0.5 to 6 wt.%, from 1 to 5 wt%, or from 1.5 to 3 wt% (e.g. of the metal oxide based SCR formulation) and/or the concentration of the oxide of tungsten (e.g. WO_3)
15 is from 5 to 20 wt.%.

A particularly preferred selective catalytic reduction catalyst may be any of those sold under the brand name SINO_x, available from Johnson Matthey PLC.

20 Alternatively, the first selective catalytic reduction catalyst may comprise, or consist essentially of, a molecular sieve based SCR catalyst formulation. The molecular sieve based SCR catalyst formulation comprises a molecular sieve, which is optionally a transition metal exchanged molecular sieve. It may be preferred that the SCR catalyst formulation comprises a transition metal exchanged molecular sieve.

25 In general, the molecular sieve based SCR catalyst formulation may comprise a molecular sieve having an aluminosilicate framework (e.g. zeolite), an aluminophosphate framework (e.g. AIPO), a silicoaluminophosphate framework (e.g. SAPO), a heteroatom-containing aluminosilicate framework, a heteroatom-containing aluminophosphate framework (e.g. MeAIPO, where Me is a metal), or a heteroatom-containing silicoaluminophosphate
30 framework (e.g. MeAPSO, where Me is a metal). The heteroatom (*i.e.* in a heteroatom-containing framework) may be selected from the group consisting of boron (B), gallium (Ga), titanium (Ti), zirconium (Zr), zinc (Zn), iron (Fe), vanadium (V) and combinations of any two or more thereof. It is preferred that the heteroatom is a metal (e.g. each of the above
35 heteroatom-containing frameworks may be a metal-containing framework).

It is preferable that the molecular sieve based SCR catalyst formulation comprises, or consist essentially of, a molecular sieve having an aluminosilicate framework (e.g. zeolite) or a silicoaluminophosphate framework (e.g. SAPO).

- 5 When the molecular sieve has an aluminosilicate framework (e.g. the molecular sieve is a zeolite), then typically the molecular sieve has a silica to alumina molar ratio (SAR) of from 5 to 200 (e.g. 10 to 200), preferably 10 to 100 (e.g. 10 to 30 or 20 to 80), such as 12 to 40, more preferably 15 to 30.
- 10 Typically, the molecular sieve is microporous. A microporous molecular sieve has pores with a diameter of less than 2 nm (e.g. in accordance with the IUPAC definition of "microporous" [see Pure & Appl. Chem., 66(8), (1994), 1739-1758])).

- The molecular sieve based SCR catalyst formulation may comprise a small pore molecular sieve (e.g. a molecular sieve having a maximum ring size of eight tetrahedral atoms), a medium pore molecular sieve (e.g. a molecular sieve having a maximum ring size of ten tetrahedral atoms) or a large pore molecular sieve (e.g. a molecular sieve having a maximum ring size of twelve tetrahedral atoms) or a combination of two or more thereof.
- 20 When the molecular sieve is a small pore molecular sieve, then the small pore molecular sieve may have a framework structure represented by a Framework Type Code (FTC) selected from the group consisting of ACO, AEI, AEN, AFN, AFT, AFX, ANA, APC, APD, ATT, CDO, CHA, DDR, DFT, EAB, EDI, EPI, ERI, GIS, GOO, IHW, ITE, ITW, LEV, KFI, MER, MON, NSI, OWE, PAU, PHI, RHO, RTH, SAT, SAV, SIV, THO, TSC, UEI, UFI, VNI, YUG and ZON, or a mixture and/or an intergrowth of two or more thereof. Preferably, the small pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of CHA, LEV, AEI, AFX, ERI, SFW, KFI, DDR and ITE. More preferably, the small pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of CHA and AEI. The small pore molecular sieve may have a framework structure represented by the FTC CHA. The small pore molecular sieve may have a framework structure represented by the FTC AEI. When the small pore molecular sieve is a zeolite and has a framework represented by the FTC CHA, then the zeolite may be chabazite.
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- 35 When the molecular sieve is a medium pore molecular sieve, then the medium pore molecular sieve may have a framework structure represented by a Framework Type Code (FTC) selected from the group consisting of AEL, AFO, AHT, BOF, BOZ, CGF, CGS, CHI,

DAC, EUO, FER, HEU, IMF, ITH, ITR, JRY, JSR, JST, LAU, LOV, MEL, MFI, MFS, MRE, MTT, MVY, MWW, NAB, NAT, NES, OBW, -PAR, PCR, PON, PUN, RRO, RSN, SFF, SFG, STF, STI, STT, STW, -SVR, SZR, TER, TON, TUN, UOS, VSV, WEI and WEN, or a mixture and/or an intergrowth of two or more thereof. Preferably, the medium pore molecular sieve

5 has a framework structure represented by a FTC selected from the group consisting of FER, MEL, MFI, and STT. More preferably, the medium pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of FER and MFI, particularly MFI. When the medium pore molecular sieve is a zeolite and has a framework represented by the FTC FER or MFI, then the zeolite may be ferrierite, silicalite or ZSM-5.

10

When the molecular sieve is a large pore molecular sieve, then the large pore molecular sieve may have a framework structure represented by a Framework Type Code (FTC) selected from the group consisting of AFI, AFR, AFS, AFY, ASV, ATO, ATS, BEA, BEC, BOG, BPH, BSV, CAN, CON, CZP, DFO, EMT, EON, EZT, FAU, GME, GON, IFR, ISV, ITG,

15 IWR, IWS, IWW, JSR, LTF, LTL, MAZ, MEI, MOR, MOZ, MSE, MTW, NPO, OFF, OKO, OSI, -RON, RWY, SAF, SAO, SBE, SBS, SBT, SEW, SFE, SFO, SFS, SFV, SOF, SOS, STO, SSF, SSY, USI, UWY, and VET, or a mixture and/or an intergrowth of two or more thereof. Preferably, the large pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of AFI, BEA, MAZ, MOR, and

20 OFF. More preferably, the large pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of BEA, MOR and MFI. When the large pore molecular sieve is a zeolite and has a framework represented by the FTC BEA, FAU or MOR, then the zeolite may be a beta zeolite, faujasite, zeolite Y, zeolite X or mordenite.

25 The molecular sieve based SCR catalyst formulation preferably comprises a transition metal exchanged molecular sieve, for example the molecular sieve based SCR catalyst formulation preferably comprises iron.

30 The transition metal may be present on an extra-framework site on the external surface of the molecular sieve or within a channel, cavity, or cage of the molecular sieve.

Typically, the transition metal exchanged molecular sieve comprises an amount of 0.10 to 10 % by weight of the transition metal exchanged molecular, preferably an amount of 0.2 to 5 % by weight.

35

The first selective catalytic reduction catalyst may be present in the process of the invention as an extrudate or as a coating on a structured support. In either case, the first selective catalytic reduction catalyst preferably takes the form of at least one flow-through monolith.

- 5 The first selective catalytic reduction catalyst may be prepared according to known methods, such as those disclosed in US11590482B1, WO2021/245375A1, US6054408A.

- The second temperature may be a temperature of 250 °C or more, 275 °C or more, 300 ° or more, or 310 °C or more. The second temperature may be a temperature of 450 °C or less,
10 400 °C or less, 375 °C or less, or 360 °C or less. For example, the second temperature may be a temperature of from 250 °C to 450 °C, from 275 °C to 400 °C, from 300 °C to 375 °C, or from 300 °C to 360 °C, such as 320 °C, 330 °C, or 340 °C.

- The process of the invention may comprise the step of cooling the N₂O depleted exhaust
15 gas to a temperature at or above the second temperature. The step of cooling the N₂O depleted exhaust gas to a temperature at or above the second temperature may be carried out after the step of i) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N₂O and to produce an N₂O depleted exhaust gas and before the step of iii) contacting the N₂O depleted exhaust gas and the reducing agent with
20 the first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas. The step of cooling the N₂O depleted exhaust gas may be carried out before or after the step of ii) combining the N₂O depleted exhaust gas with the reducing agent.

- 25 In certain processes of the invention, the process may comprise the step of combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas. As will be understood, the step of contacting the purified exhaust gas with the second selective catalytic reduction catalyst at
30 a third temperature may occur after the purified exhaust gas is contacted with the first selective catalytic reduction catalyst. The further purified exhaust gas from this step may be further processed as described hereinbelow.

- The second selective catalytic reduction catalyst may be the same or different as the first
35 selective catalytic reduction catalyst. The second selective catalytic reduction catalyst may be a high temperature selective catalytic reduction catalyst. For instance, the second selective catalytic reduction catalyst may comprise, or consist essentially of, a molecular

sieve based SCR catalyst formulation comprising, or consisting essentially of, a copper zeolite (e.g. a Cu-CHA) or an iron zeolite (e.g. an Fe-BEA).

- 5 The additional reducing agent may be combined with the purified exhaust gas in much the same way as the reducing agent may be combined with the N₂O depleted exhaust gas, as described hereinabove. The additional reducing agent may suitably be selected from the group consisting of ammonia (NH₃), urea, or a hydrocarbon (e.g. methane). Preferably, the additional reducing agent may be ammonia (NH₃).
- 10 The step of combining the purified exhaust gas with the additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second selective catalytic reduction catalyst at a third temperature is able to accommodate situations where the exhaust gas comprises particularly high levels of NO_x (e.g. 2,000 ppm or more), such as during “turndown” of the ammonia cracking reactor. The selective catalytic reduction
- 15 of NO_x is an exothermic reaction. Thus, where high levels of NO_x (e.g. 2,000 ppm or more) are present, the purified exhaust gas may have a temperature which is higher than the second temperature following contact with the first selective catalytic reduction catalyst.

- Accordingly, the third temperature may be a temperature of 350 °C or more, 400 °C or more,
- 20 450 °C or more, or 500 °C or more. The third temperature may be a temperature of 700 °C or less, 650 °C or less, 625 °C or less, or 600 °C or less. For example, the third temperature may be a temperature of from 350 °C to 700 °C, from 400 °C to 650 °C, from 450 °C to 625 °C, or from 500 °C to 600 °C.

- 25 In view of the above, it may therefore be advantageous that the second selective catalytic reduction catalyst is a high temperature selective catalytic reduction catalyst, such as one described hereinabove. High temperature selective catalytic reduction catalysts are, in particular, those which may be capable of decomposing NO_x at the third temperature. It has surprisingly been found that processes which comprise a second selective catalytic
- 30 reduction catalyst are better able to accommodate and decompose NO_x than systems which attempt to decompose NO_x in a single NO_x decomposition step.

- It may be preferred that the first selective catalytic reduction catalyst and/or the second selective catalytic reduction catalyst may be present in a flue duct of the ammonia cracking
- 35 reactor.

The process of the invention produces a purified exhaust gas.

The purified exhaust gas (or further purified exhaust gas) may comprise N_2O in an amount of 20 ppm or less, 18 ppm or less, 15 ppm or less, or 12 ppm or less.

- 5 The purified exhaust gas(or further purified exhaust gas) may comprise NO_x in an amount of 100 ppm or less, 75 ppm or less, 65 ppm or less, or 55 ppm or less. The purified exhaust gas (or further purified exhaust gas) may comprise NO_x in an amount of 0 ppm or more, 2 ppm or more, 4 ppm or more, or 5 ppm or more. For example, the purified exhaust gas (or further purified exhaust gas) may comprise NO_x in an amount of from 0 ppm to 100 ppm,
10 from 2 ppm to 75 ppm, from 4 ppm to 65 ppm, or from 5 ppm to 55 ppm.

- The process of the invention may comprise the step of recovering heat energy from the purified exhaust gas (or further purified exhaust gas). For example, the process of the invention may comprise the step of recovering heat energy from the purified exhaust gas (or
15 further purified exhaust gas) using a steam generator, or by heat exchange of the purified exhaust gas with another process fluid (e.g. the ammonia stream).

- The process of the invention may comprise the step of discharging the purified exhaust gas (or further purified exhaust gas). The process of the invention may comprise the step of
20 discharging the purified exhaust gas (or further purified exhaust gas) to atmosphere. The process of the invention may comprise the step of discharging the purified exhaust gas (or further purified exhaust gas) to a further treatment system, such as to a flare system, an afterburner system, or a scrubbing system (e.g. a scrubbing system to remove residual ammonia).

- 25 The process of the invention may comprise the step of contacting the purified exhaust gas (or further purified exhaust gas) with an ammonia slip catalyst. As will be understood, an ammonia slip catalyst functions to decompose ammonia (NH_3) into nitrogen (N_2) and water (H_2O), thereby preventing the emission of ammonia in the purified exhaust gas (or further
30 purified exhaust gas). Suitable ammonia slip catalysts are known in the art and may suitably take the form of a flow through monolith, as described hereinabove. Typically, ammonia slip catalysts comprise a platinum group metal (e.g. platinum) on a zeolitic or alumina support. Suitable ammonia slip catalyst compositions may also be described in WO2012138405A1, WO2017134454A1, WO2018178627A1, WO2019186121A1 and EP2885514A1. Suitable
35 ammonia slip catalysts include Johnson Matthey's advanced Ammonia Slip Catalyst (ASC).

The process of the invention may comprise the step of supplying an ammonia stream to one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor.

5 The ammonia stream comprises ammonia (NH₃). The ammonia stream may be derived from any source. In preferred processes of the invention, the ammonia stream is produced by the catalytic combination of hydrogen and nitrogen, for example the ammonia stream may be produced from a Haber-Bosch ammonia synthesis process. In preferred processes of the invention the ammonia stream may be produced in an ammonia production facility located upstream of the ammonia cracking reactor. Alternatively, the ammonia stream may be
10 provided from an ammonia gas storage facility, an ammonia storage unit, an ammonia storage tank, or an ammonia gas pipeline.

In preferred processes of the invention the ammonia stream may be pre-heated prior to being supplied to the one or more catalyst containing reaction tubes. Accordingly, the
15 process of the invention may comprise the step of pre-heating the ammonia stream. The ammonia stream 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 stream 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 stream may be pre-heated
20 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.

The catalyst in the catalyst containing reaction tubes may be any ammonia cracking catalyst. For instance, nickel catalysts and/or ruthenium catalysts may be used. Preferred catalysts
25 are nickel catalysts. 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
30 from Johnson Matthey PLC, which comprises 12% nickel, expressed as NiO, on a cylindrical pellet formed from a high surface area calcium aluminate support. A further particularly preferred catalyst is KATALCO^{RTM} 27-200MQ available from Johnson Matthey PLC, which comprises 16 wt% NiO on a quadralobe shaped calcium aluminate support.

35 The one or more catalyst containing reaction tubes may suitably be formed of an iron based alloy, a nickel based alloy, or a cobalt based alloy. The iron based alloy may be an iron-chromium based alloy such as a stainless steel, preferably 316 stainless steel, or a high

nickel steel such as those described by WO03/051771A1. Preferably, the one or more catalyst containing reaction tubes are formed of a nickel based alloy or a cobalt based alloy. More preferably, the one or more catalyst containing reaction tubes are formed of a cobalt based alloy.

5

The process of the invention may comprise the step of cracking the ammonia in the ammonia stream in the one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream.

- 10 The temperature of the ammonia stream 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 775 °C, such as from 550 °C to 750 °C. The temperature of the cracked gas 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
- 15 950°C. Preferably, the temperature of the cracked gas stream exiting the one or more catalyst containing reaction tubes may be at, or above, the first temperature, as defined hereinabove.

- The pressure inlet to the one or more catalyst containing reaction tubes will be set by the
- 20 flowsheet design and may be in the range 1 to 100 bar absolute, preferably 10 to 90 bar absolute, such as 31 to 51 bar absolute.

- The ammonia cracking reaction produces a cracked gas stream. The cracked gas stream contains H₂. The cracked gas stream also contains nitrogen, and may further contain
- 25 residual ammonia (e.g. unreacted ammonia).

- The cracked gas stream may comprise 60 mol% or more H₂, 65 mol% or more H₂, 70 mol% or more H₂, 72 mol% or more H₂, or 73 mol% or more H₂. The cracked gas stream may comprise up to 75 mol% or less H₂. For example, the cracked gas stream may comprise
- 30 from 60 mol% to 75 mol% H₂. Preferably, the cracked gas stream comprises from 70 mol% to 75 mol% H₂, such as 72 mol% to 75 mol% H₂.

- The cracked gas stream may comprise 20 mol% or more N₂, 21 mol% or more N₂, 22 mol% or more N₂, or 23 mol% N₂ or more. The cracked gas stream may comprise up to 25 mol% or less N₂. For example, the cracked gas stream may comprise from 20 mol% to 25 mol% N₂. Preferably the cracked gas stream comprises from 22 mol% to 25 mol% N₂, such as
- 35 from 23 mol% to 25 mol% N₂.

The cracked gas stream may comprise less than 20 mol% NH_3 , less than 15 mol% NH_3 , less than 10 mol% NH_3 , less than 5 mol% NH_3 , less than 1 mol% NH_3 , or less than 0.1 mol% NH_3 . Preferably, the cracked gas stream comprises less than 4 mol% NH_3 , less than 2 mol% NH_3 , less than 1 mol% NH_3 , or less than 0.1 mol% NH_3 .

Preferably, the cracked gas stream may comprise an equilibrium mixture of ammonia, hydrogen, and nitrogen. In other words, the cracked gas stream may comprise a mixture of ammonia, hydrogen, and nitrogen at partial pressures such that no further hydrogen and nitrogen may be produced from further cracking reaction. An equilibrium mixture may comprise from 72 mol% to 75 mol% H_2 , from 23 mol% to 25 mol% N_2 , and less than 4 mol% NH_3 (e.g. less than 1 mol% or less than 0.1 mol% NH_3).

In preferred processes of the invention, the cracked gas stream may be fed to a purification unit, such as a pressure swing adsorption unit, to increase the H_2 content by separating H_2 from the other components. The purification unit therefore produces an enriched hydrogen stream and a tail gas stream. Accordingly, the process of the invention preferably comprises the step of feeding the cracked gas stream to a purification unit to produce an enriched hydrogen stream and a tail gas stream.

The enriched hydrogen stream may comprise 70 mol% or more H_2 , 75 mol% or more H_2 , 80 mol% or more H_2 , 85 mol% H_2 or more, or 90 mol% H_2 or more. The enriched hydrogen stream may comprise up to 100 mol% or less H_2 . For example, the enriched hydrogen stream may comprise from 70 mol% to 100 mol% H_2 , from 75 mol% to 100 mol% H_2 , from 80 mol% to 100 mol% H_2 , from 85 mol% to 100 mol% H_2 , or from 90 mol% to 100 mol% H_2 . Preferably, the enriched hydrogen stream may comprise greater than 90 mol% H_2 , greater than 95 mol% H_2 , greater than 98 mol% H_2 , or greater than 99 mol% H_2 . More preferably, the enriched hydrogen stream may comprise greater than 99.9% mol% H_2 , greater than 99.95 mol% H_2 , or about 100 mol% H_2 . Most preferably, the enriched hydrogen containing stream may comprise greater than 99.95 mol% H_2 or about 100 mol% H_2 .

The tail gas stream may comprise nitrogen (N_2), ammonia, and hydrogen (H_2).

The tail gas stream may comprise from 20 mol% to 95 mol% N_2 , from 45 mol% to 85 mol% N_2 , or from 65 mol% to 80 mol% N_2 .

The tail gas stream may comprise from 2 mol% to 10 mol% ammonia, from 2.5 mol% to 7 mol% ammonia, or from 3 mol% to 5 mol% ammonia.

Typically, the tail gas stream may comprise from 10 mol% to 70 mol% H₂, such as from 20 mol% to 50 mol% H₂. It may be preferred that the tail gas stream comprises from 15 mol% to 40 mol% H₂, from 20 mol% H₂ to 35 mol% H₂, or from 22 mol% H₂ to 30 mol% H₂.

The one or more fuel streams may comprise a portion of the cracked gas stream. The one or more fuel stream may comprise a portion of the tail gas stream. The one or more fuel streams may comprise a portion of the enriched hydrogen stream. The one or more fuel streams may comprise a portion of the ammonia stream. The one or more fuel streams may comprise a portion of the cracked gas stream, the ammonia stream, the tail gas stream, the enriched hydrogen stream, or mixtures thereof.

Accordingly, the process of the invention may comprise the step of providing one or more fuel streams comprising a portion of one or more of the cracked gas stream, the ammonia stream, the tail gas stream, and/or the enriched hydrogen stream to the ammonia cracking reactor and combusting the one or more fuel streams in the presence of oxygen in the ammonia cracking reactor to provide heat energy to support the cracking of the ammonia in the ammonia cracking reactor and to produce the exhaust gas comprising N₂O and NO_x.

In certain processes of the invention, the process may comprise the steps of:

- i) supplying an ammonia stream to one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor;
- ii) cracking the ammonia in the ammonia stream in one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream;
- iii) providing one or more fuel streams comprising a portion of the cracked gas stream and/or the ammonia stream to the ammonia cracking reactor;
- iv) combusting the one or more fuel streams comprising ammonia, hydrogen, and/or nitrogen in the presence of oxygen in the ammonia cracking reactor to provide heat energy to support the cracking of the ammonia in the ammonia cracking reactor and to produce the exhaust gas comprising N₂O and NO_x;
- v) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N₂O and to produce an N₂O depleted exhaust gas;
- vi) combining the N₂O depleted exhaust gas with a reducing agent;

- vii) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas; and
- viii) optionally, combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas.

In certain processes of the invention, the process may comprise the steps of:

- i) supplying an ammonia stream to one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor;
- ii) cracking the ammonia in the ammonia stream in one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream;
- iii) feeding the cracked gas stream to a purification unit to produce an enriched hydrogen stream and a tail gas stream;
- iv) providing one or more fuel streams comprising a portion of one or more of the cracked gas stream, the ammonia stream, the tail gas stream, and/or the enriched hydrogen stream to the ammonia cracking reactor;
- v) combusting the one or more fuel streams comprising ammonia, hydrogen, and/or nitrogen in the presence of oxygen in the ammonia cracking reactor to provide heat energy to support the cracking of the ammonia in the ammonia cracking reactor and to produce the exhaust gas comprising N_2O and NO_x ;
- vi) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
- vii) combining the N_2O depleted exhaust gas with a reducing agent;
- viii) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas; and
- ix) optionally, combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas.

In certain processes of the invention, the process may comprise the steps of:

- i) turning-down the ammonia cracking reactor and producing an exhaust gas which is a turndown exhaust gas;

- ii) contacting the turndown exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
- iii) combining the N_2O depleted exhaust gas with a reducing agent;
- 5 iv) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas; and
- v) optionally, combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a
- 10 second selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas.

In certain processes of the invention, the process may comprise the steps of:

- i) supplying an ammonia stream to one or more catalyst containing reaction tubes
- 15 disposed within the ammonia cracking reactor;
- ii) cracking the ammonia in the ammonia stream in one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream;
- iii) feeding the cracked gas stream to a purification unit to produce an enriched
- 20 hydrogen stream and a tail gas stream;
- iv) providing one or more fuel streams comprising a portion of one or more of the cracked gas stream, the ammonia stream, the tail gas stream, and/or the enriched hydrogen stream to the ammonia cracking reactor;
- v) combusting the one or more fuel streams comprising ammonia, hydrogen, and/or
- 25 nitrogen in the presence of oxygen in the ammonia cracking reactor to provide heat energy to support the cracking of the ammonia in the ammonia cracking reactor and to produce the exhaust gas comprising N_2O and NO_x ;
- vi) turning-down the ammonia cracking reactor and producing an exhaust gas which is a turndown exhaust gas;
- 30 vii) contacting the turndown exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
- viii) combining the N_2O depleted exhaust gas with a reducing agent;
- ix) contacting the N_2O depleted exhaust gas and the reducing agent with a first
- 35 selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas; and

- x) optionally, combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas.

5

In a second aspect of the invention there is provided an exhaust gas system for treating an exhaust gas comprising N_2O and NO_x from an ammonia cracking reactor, the system comprising an exhaust gas pathway comprising a first iron containing zeolitic catalyst configured to decompose N_2O at a first temperature and produce an N_2O depleted exhaust gas, an injection device configured to mix a reducing agent with the N_2O depleted exhaust gas, and a first selective catalytic reduction catalyst configured to decompose NO_x at a second temperature and to produce a purified exhaust gas.

The system of the invention may be configured in such a way so as to carry out the process as defined in relation to the first aspect of the invention. Accordingly, features which have been described in relation to the process of the first aspect of the invention may be incorporated into the system of the second aspect of the invention.

Examples

Experimental tests were conducted on four different iron containing zeolitic catalysts. The catalysts are summarised in Table 1.

Examples	Fe loading (%)	Zeolite	SAR	Calcination	Cells per square inch (CPSI)	Form
Fe-BEA	5	BEA	24	Air	600	Coated
Fe-FER	5	FER	17	Air	600	Coated
Fe-FER (Activated)	3	FER	20	N_2	400	Coated
Fe-MFI	3.6	MFI	27	Air	200	Extruded

Table 1

25 Example 1 – Effect of water on N_2O decomposition

Example 1 investigated N_2O and NO decomposition performance of a fresh Fe-BEA catalyst (a first iron containing zeolitic catalyst) at different water concentrations. The Fe-BEA type

catalyst was 1"x 2.73" in size. Catalytic activity tests were carried out at 410 °C at a space velocity of 4,800h⁻¹. The gas mixture comprised 50 ppm N₂O, 1500 ppm NO, 1% O₂ and varying amounts of H₂O ranging from 0 to 25%.

- 5 The data, as shown in **Figure 1**, was analysed using a Fourier Transform Infrared Spectroscopy (FTIR) analyser.

As shown in the **Figure 1**, water was found to inhibit the N₂O activity of the Fe-BEA catalyst. The declining impact on N₂O activity is predominantly observed when
10 increasing water concentrations from 0 to 15%. However, no further effect on N₂O conversion is observed above 15% H₂O. Under the conditions tested, NO conversion was found not to be significantly affected by water and remained comparatively low over the water contents tested.

15

Example 2 – The effect of temperature on N₂O decomposition

Example 2 shows the N₂O and NO decomposition performance of a fresh Fe-BEA, Fe-FER and Fe-MFI catalysts at 5 different furnace temperatures: 350 °C, 400 °C, 450 °C, 500 °C and 550 °C. The catalysts were 1"x 2.73" in size and were tested at a space velocity of
20 4,800h⁻¹. The gas mixture comprised 50 ppm N₂O, 1500 ppm NO, 1% O₂ and 17% H₂O. The temperatures explored range from 350 °C to 550 °C. A temperature ramp rate of 5 °C/min was set up for each temperature followed by a dwell of 45min.

The data, as shown in Figure 2, was analysed using a Fourier Transform Infrared
25 Spectroscopy (FTIR) analyser.

Figure 2 shows that all catalysts decompose N₂O at temperatures above 400 °C. Full conversion is achieved at temperatures of 550 °C, with N₂ formed as the major product.

30 The results demonstrate the capacity of these catalysts to convert N₂O at medium-high temperatures, in the presence of oxygen and high water content. The catalysts are also able to oxidise NO to NO₂ promoting the decomposition of NO_x over the selective catalytic reduction catalyst placed downstream the N₂O catalyst. In the presence of NO₂, the SCR process can run according to equation 3 (known as the "Fast SCR reaction"),
35 which occurs, inherently, at a higher rate than that of equation 1.

Example 3 – Effect of calcination

Example 3 shows the results of N₂O and NO decomposition tests over an activated catalyst and non-activated catalyst. The catalyst was activated by calcination under nitrogen (N₂), or
5 provided in a non-activated form by calcination under air. Calcinations were carried out at five different temperatures (350, 400, 450, 500 and 550 °C).

In this Example 3, the catalyst was an Fe-FER catalyst. The catalysts were 1"x 2.73" in size and were tested at a space velocity of 4,800h⁻¹ in a gas mixture including 50 ppm N₂O,
10 1500 ppm NO, 1% O₂ and 17% H₂O. The temperatures explored ranged from 350 °C to 550 °C. A ramp rate of 5 °C/min was set up for each temperature followed by a dwell of 45min. The data were analysed using a Fourier Transform Infrared Spectroscopy (FTIR) analyser.

15 The results, shown in Figure 3, demonstrate that the "activated" Fe-FER type catalyst is more active than the "non-activated" Fe-FER catalyst below 550 °C. Moreover, the activated Fe-FER catalyst remains fully active for N₂O removal at 550 °C in the presence of oxygen and high water levels. The enhanced performance of the "activated" catalyst at low temperatures has been assigned to the presence of a large proportion of low
20 coordinated and isolated Fe sites (reported to be the active sites for N₂O removal) instead of Fe₂O₃-clusters. At low temperatures, NO conversion is also promoted over the "activated" catalysts while at high temperatures the reaction is believed to be controlled by thermodynamics.

25

Claims

1. A process for treating an exhaust gas comprising N_2O and NO_x from an ammonia cracking reactor, the process comprising the steps of:
 - 5 i) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
 - ii) combining the N_2O depleted exhaust gas with a reducing agent; and
 - iii) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x
10 and to produce a purified exhaust gas.
2. A process according to claim 1, wherein the process comprises the step of combusting one or more fuel streams in the presence of oxygen in the ammonia cracking reactor to provide heat energy to support the cracking of ammonia in the ammonia cracking
15 reactor and to produce the exhaust gas comprising N_2O and NO_x .
3. A process according to claim 2, wherein the one or more fuel streams comprise hydrogen (H_2), nitrogen (N_2), and/or ammonia (NH_3).
- 20 4. A process according to any one of the preceding claims, wherein the exhaust gas comprises N_2O in an amount of 0.05 ppm to 500 ppm, from 1 ppm to 400 ppm, from 5 ppm to 300 ppm, or from 10 to 200 ppm.
5. A process according to any one of the preceding claims, wherein the exhaust gas
25 comprises NO_x in an amount of from 1 ppm to 2,000 ppm, from 5 ppm to 1,500 ppm, from 10 ppm to 1,200 ppm.
6. A process according to any one of the preceding claims, wherein the exhaust gas comprises water (H_2O) in an amount of from 5 vol% to 40 vol%, from 6 vol% to 37 vol%,
30 from 7 vol% to 35 vol%, or from 8 vol% to 32 vol%.
7. A process according to any one of the preceding claims, wherein the zeolite of the first iron containing zeolitic catalyst has a BEA, FER, ZSM-5, CHA, AEI, or MFI framework.
- 35 8. A process according to any one of the preceding claims, wherein the first iron containing zeolitic catalyst contains iron in an amount of from 1 weight% to 10 weight%, from 1.5 weight% to 8 weight %, from 2 weight% to 7 weight%, or from 2.5

weight% to 6 weight % relative to the total weight of the first iron containing zeolitic catalyst.

9. A process according to any one of the preceding claims, wherein the first iron
5 containing zeolitic catalyst has a silica to alumina ratio (SAR) of from 100:1 to 5:1, from 50:1 to 10:1, or from 40:1 to 15:1.
10. A process according to any one of the preceding claims, wherein the first iron
10 containing zeolitic catalyst is present as a coating on a structured support or as an extrudate.
11. A process according to any one of the preceding claims, wherein the first temperature
is a temperature of from 450 °C to 750 °C, from 500 °C to 700 °C, from 525 °C to 650
15 °C, or from 550 °C to 620 °C.
12. A process according to any one of the preceding claims, wherein the N₂O depleted
exhaust gas comprises 20 ppm or less N₂O, 18 ppm or less N₂O, 15 ppm or less N₂O,
12 ppm or less N₂O, 10 ppm or less N₂O, or 8 ppm or less N₂O.
- 20 13. A process according to any one of the preceding claims, wherein the reducing agents
is selected from the group consisting of ammonia (NH₃), urea, or a hydrocarbon (e.g.
methane).
- 25 14. A process according to any one of the preceding claims, wherein the first selective
catalytic reduction catalyst comprises, or consist essentially of, a metal oxide based
SCR catalyst formulation.
- 30 15. A process according to claim 14, wherein the metal oxide based SCR catalyst
formulation comprises, or consist essentially of, an oxide of vanadium and/or an oxide
of tungsten supported on a refractory oxide selected from the group consisting of
titania, ceria, and a mixed or composite oxide of cerium and zirconium.
- 35 16. A process according to any one of the preceding claims, wherein the second
temperature is a temperature of from 250 °C to 450 °C, from 275 °C to 400 °C, from
300 °C to 375 °C, or from 300 °C to 360 °C.

17. A process according to any one of the preceding claims, wherein the process comprises the step of supplying an ammonia stream to one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor, and cracking the ammonia in the ammonia stream in the one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream.
18. A process according to claim 17, wherein the one or more fuel streams comprises a portion of the cracked gas stream, and/or a portion of the ammonia stream.
19. A process according to claim 17 or claim 18, wherein the process comprises the step of feeding the cracked gas stream to a purification unit to produce an enriched hydrogen stream and a tail gas stream.
20. A process according to claim 19, wherein the one or more fuel streams comprises a portion of one or more of the cracked gas stream, the ammonia stream, the tail gas stream, and/or the enriched hydrogen stream.
21. A process according to any one of claims 1 to 16, wherein the process comprises the steps of:
- i) supplying an ammonia stream to one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor;
 - ii) cracking the ammonia in the ammonia stream in one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream;
 - iii) providing one or more fuel streams comprising a portion of the cracked gas stream and/or the ammonia stream to the ammonia cracking reactor;
 - iv) combusting the one or more fuel streams comprising ammonia, hydrogen, and/or nitrogen in the presence of oxygen in the ammonia cracking reactor to provide heat energy to support the cracking of the ammonia in the ammonia cracking reactor and to produce the exhaust gas comprising N_2O and NO_x ;
 - v) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
 - vi) combining the N_2O depleted exhaust gas with a reducing agent;
 - vii) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas; and

- viii) optionally, combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas.

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22. A process according to any one of claims 1 to 16, wherein the process comprises the steps of:

- i) supplying an ammonia stream to one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor;
- 10 ii) cracking the ammonia in the ammonia stream in one or more catalyst containing reaction tubes disposed within the ammonia cracking reactor to produce a cracked gas stream;
- iii) feeding the cracked gas stream to a purification unit to produce an enriched hydrogen stream and a tail gas stream;
- 15 iv) providing one or more fuel streams comprising a portion of one or more of the cracked gas stream, the ammonia stream, the tail gas stream, and/or the enriched hydrogen stream to the ammonia cracking reactor;
- v) combusting the one or more fuel streams comprising ammonia, hydrogen, and/or nitrogen in the presence of oxygen in the ammonia cracking reactor to provide heat
- 20 energy to support the cracking of the ammonia in the ammonia cracking reactor and to produce the exhaust gas comprising N_2O and NO_x ;
- vi) contacting the exhaust gas with a first iron containing zeolitic catalyst at a first temperature to decompose N_2O and to produce an N_2O depleted exhaust gas;
- vii) combining the N_2O depleted exhaust gas with a reducing agent;
- 25 viii) contacting the N_2O depleted exhaust gas and the reducing agent with a first selective catalytic reduction catalyst at a second temperature to decompose NO_x and to produce a purified exhaust gas; and
- ix) optionally, combining the purified exhaust gas with an additional reducing agent and contacting the purified exhaust gas and the additional reducing agent with a second
- 30 selective catalytic reduction catalyst at a third temperature to produce a further purified exhaust gas.

23. A process according to any one of the preceding claims, wherein the process comprises the steps of turning-down the ammonia cracking reactor and producing an

35 exhaust gas which is a turndown exhaust gas.

24. An exhaust gas system for treating an exhaust gas comprising N_2O and NO_x from an ammonia cracking reactor, the system comprising an exhaust gas pathway comprising a first iron containing zeolitic catalyst configured to decompose N_2O at a first temperature and to produce an N_2O depleted exhaust gas, an injection device
5 configured to mix a reducing agent with the N_2O depleted exhaust gas, and a first selective catalytic reduction catalyst configured to decompose NO_x at a second temperature and to produce a purified exhaust gas.
25. An exhaust gas system according to claim 24, wherein the exhaust gas system is
10 configured to carry out the process as defined in any one of claims 1 to 23.