



## Methods for removing nox from a gas stream containing more than one gaseous compound

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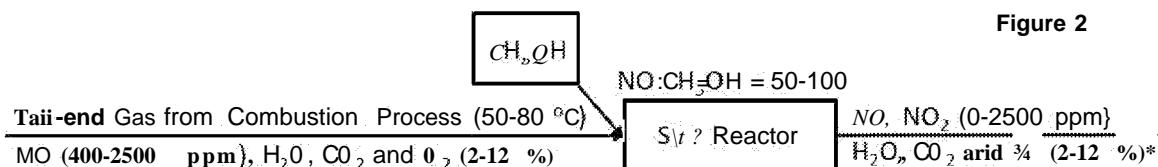


Figure 2

(57) Abstract: The invention relates to an efficient process for removing NO<sub>x</sub>, and specifically the most abundant NO<sub>x</sub> component NO, from flue gasses from e.g. large stationary sources. Said process comprises a method for converting nitric oxide (NO) from a gas stream, where the gas stream contains more than one gaseous compound. Said method comprises two steps, a) pre-mixing the gas stream with at least one low molecular mass alcohol, and b) oxidizing said NO to nitrogen dioxide (NO<sub>2</sub>) and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species in the presence of the low molecular mass alcohol present in the gas stream, by use of a supported ionic liquid phase catalyst at relatively low temperatures.



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**Methods for removing NO<sub>x</sub> from a gas stream containing more than one gaseous compound.**

**Technical Field**

5 The invention relates to an efficient process for removing NO<sub>x</sub>, and specifically the most abundant NO<sub>x</sub> component NO, from flue gases from large stationary sources like, e.g. power or incineration plants, or from mobile emission sources like, e.g. commercial marine vessels.

10 **Background art**

*Origin of NO<sub>x</sub>*

NO<sub>x</sub> is a generic term used for a mixture of nitrogen oxides. Nitrogen oxides are believed to aggravate asthmatic conditions, react with the oxygen in the air to produce ozone, which is also an irritant, and eventually form nitric acid when dissolved in  
15 water. When dissolved in atmospheric moisture the result can be acid rain, which can damage both trees and entire forest ecosystems. Consequently, the sources of NO<sub>x</sub> emissions are now being subjected to more stringent standards. In atmospheric chemistry the term NO<sub>x</sub> means the total concentration of NO, NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub>. A main source of NO<sub>x</sub> is generated by combustion processes.

20

*Methods of Nitrogen Oxides Removal*

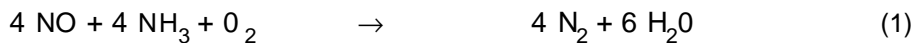
The numerous possibilities to reduce NO<sub>x</sub> from combustion processes can be divided into three categories: Pre-combustion, combustion modifications, and post-combustion [C. S. Latta, Plant Engineering, vol. 52 (10), pp. 105-110, 1998]. The pre-combustion strategy implies using alternative fuels with a lower content of nitrogen  
25 species [G. Busca et al., Catal. Today, vol. 107-108, pp. 139-148, 2005]. During combustion different types of modifications can be utilized, of which the most used are: Low NO<sub>x</sub>-burners, reburning, and staged air combustion (thermal oxidation) [Latta]. A variety of other methods is also possible in the combustion modification:  
30 Burners out-of-service, derating, burner system modification, trim, and diluent injection; all described by Latta. Several post-combustion approaches are applied to reduce NO<sub>x</sub>: selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), adsorption, NO<sub>x</sub> recycle, direct decomposition [Latta], photocatalytic oxidation [J. Dalton, et al Environmental Pollution, vol. 120, pp. 415-422, 2002],

multifunctional filter (removal of fly-ash and NO<sub>x</sub>) [D. Fino et al. Chem. Eng. Sci., vol. 59, pp. 5329-5336, 2004], and pulse intense electron beam irradiation.

5 One of the most widespread technologies for removing NO<sub>x</sub> from flue gases is the selective catalytic reduction (SCR) process. The selective catalytic reduction is considered a useful approach for removing nitrogen oxides generated from stationary sources in view of economic and technological efficiency. A wide number of catalysts have been reported for the effective removal of nitric oxide by using ammonia as the reducing agent. All the catalysts can broadly be classified into three types namely  
10 noble metals, metal oxides, and zeolites. Noble metals are very active for the reduction of NO<sub>x</sub>, but do not reduce selectively to N<sub>2</sub> because of ammonia oxidation. Side products like N<sub>2</sub>O might also be formed. Accordingly, noble metal catalysts have been replaced by metal oxide catalysts for conventional SCR and by zeolites for high temperature SCR applications because of their thermal stability.

15

The SCR process for removing nitrogen oxides is based on the reaction between NO<sub>x</sub> and ammonia:



NO<sub>x</sub> formed in combustion processes is typically composed of more than 90% NO and reaction (1) therefore dominates. Reaction (2) is the so called fast SCR reaction. Expressed in terms of a first order rate law, the ratio of the two rate constants, <sup>k(2)/k(1)</sup>  
25 (k(2) over k(1)) is at least 10 at temperatures above 200 degrees centigrade and might be even higher for temperatures below 200 degrees centigrade.

30

A reactant such as NH<sub>4</sub>NO<sub>3</sub>, which will generate NO<sub>2</sub> upon thermal decomposition, can be injected into the flue gas stream to facilitate the fast SCR reaction (2).

In a typical application, ammonia is injected into the NO<sub>x</sub>-containing gas and the mixture is passed through a flow distribution system and one or several catalyst layers. The main components of an SCR DeNO<sub>x</sub> system include a reactor with catalyst and an ammonia storage and injection system.

Many different supports and catalytic metals are utilized for the SCR process, but the vanadium/titanium catalyst is traditionally applied because of its thermal stability and resistance towards sulfur poisoning [N. Topsøe et al., J. Catal., vol. 151, pp. 226-240, 5 1995].

The ammonia source can be either anhydrous ammonia, ammonia water, or a solution of urea. Because of its better performance ammonia is often utilized, but due its poisonous character and difficult handling, urea can be used, although not quite as 10 effectively as ammonia.

The ammonia is evaporated and subsequently diluted with air or a flue gas side stream before it is injected into the flue gas duct upstream of the SCR reactor. Direct injection of ammonia water or a urea solution is also possible. The SCR process 15 requires precise control of the ammonia injection rate and a homogeneous mixing into the flue gas to ensure efficient  $\text{NO}_x$  conversion without an undesirable release of unconverted ammonia referred to as ammonia slip. The SCR process typically requires a temperature of about 350 to 400 degrees centigrade.

20 Urea is often used in mobile units, where e.g. the ammonia slip would be avoided. Besides urea as an alternative to ammonia in the SCR process, it is also possible to use hydrocarbons. The possibility for reducing NO with hydrocarbons such as olefins and higher alkanes was first proposed in 1990 [Busca]. Hydrocarbon-SCR systems use hydrocarbons as the reductant. The hydrocarbon may be present in the exhaust 25 gas or it may be added to the exhaust gas. This has the advantage that no additional reductant source (e.g. urea) needs to be carried on-board, but these systems cannot offer the performance of the ammonia-SCR systems. In stationary plants, methane is the preferred choice for  $\text{NO}_x$  removal from flue gases from power stations because it is already present, at least in methane fueled plants (natural gas plants).

30 Although the catalytic removal of  $\text{NO}_x$  (nitrogen oxides, covering NO,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ) from the flue gas is a very effective process, the overall high operating expenses of the SCR process and possibility of ammonia slip have motivated a search for other methods to abate emissions of nitrogen oxides.

A different concept is presented by wet scrubbing systems for removal of SO<sub>2</sub> and NO<sub>x</sub>. Some aqueous scrubbing systems have been developed for the simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> [C.-L. Yang et al., Environmental Progress, 17, 80-85, 1998].

5

The wet flue gas desulfurization (FGD) typically exhibits high SO<sub>2</sub> removal efficiencies, but the FGD can only remove a small amount of NO<sub>x</sub> because about 90-95% in a typical flue gas is present as insoluble NO and only the remaining 5-10% NO<sub>2</sub> is water soluble. Attempts to oxidize NO to water soluble NO<sub>2</sub> have been made by adding strong oxidizing additives, such as MnO<sub>4</sub><sup>-</sup> (permanganate) and H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide), but the treatment cost involved herein has been too high for practical utilization.

10

The above proposed technologies for NO removal are all associated with various challenges such as: low capacity, large installation footprint, poor reaction kinetics, hazardous stoichiometric reductants or oxidants, elevated reaction temperatures, or the requirement for specialized catalysts.

15

Many of the above proposed technologies are further based on liquids with a vapor pressure, which means that the solvent to some extent vaporizes during operation. One promising solution to this particular problem could be the use of a relatively new class of solvents referred to as ionic liquids (ILs). The expression 'ionic liquid' in principle encompasses any liquid entirely composed of ions (e.g. molten salts). However, within the context of this work the term will only be used to describe materials which are liquid in their pure state below 100 degrees centigrade. This class of solvents is often considered as 'green' solvents because of their immeasurably low vapor pressure. This feature gives the ILs an essential advantage over traditional solvents used for absorbing gases. Ionic liquids have already demonstrated promising behavior in a number of reactions where gaseous reactants enter the IL solution (such as hydrogenation, hydroformylation, and oxidations) despite low gas solubility of the gases in the IL at ambient conditions [J. L. Anthony et al., The Journal of Physical Chemistry B, 106. 7315-7320, 2002].

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Consequently, there is still a need for developing efficient processes for removing NO<sub>x</sub>, and specifically the most abundant NO<sub>x</sub> component NO, from flue gasses from not only large stationary sources like power or incineration plants, but also from mobile emission sources like, e.g. commercial marine vessels which require a small installation footprint, low energy consumption, and preferably no carrying of hazardous chemicals.

### Summary of the invention

One aspect the present invention provides a method for converting nitric oxide (NO) to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species from a gas stream, where the gas stream contains more than one gaseous compound, which method comprises:

- a) pre-mixing the gas stream with at least one low molecular mass alcohol,
- b) oxidizing said NO to nitrogen dioxide (NO<sub>2</sub>) and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species in the presence of the low molecular mass alcohol present in the gas stream, where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5, by use of a supported ionic liquid phase catalyst at temperatures from 0 to 160 degrees centigrade.

By injecting a low molecular mass alcohol into a gas stream before oxidation using a supported ionic liquid phase catalyst a promotion of the oxidation of NO is seen, hereby increasing or optimizing the conversion of NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species compared to if no alcohol is present in the gas stream. Hence by the present invention it is shown that a small molecular mass alcohol is a promoter for the oxidation of NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species.

In one or more embodiments of the present invention, the method further comprises:

- c) injecting an ammonia source or a hydrocarbon source into the oxidized gas mixture from step b upstream of a SCR reactor and performing a SCR reaction with a SCR catalyst at low temperatures, such as between 100 to 300 degrees centigrade, between 120 to 200 degrees centigrade, or between 120 to 150 degrees centigrade.

By performing the steps a and b before utilizing an SCR reaction; the reaction preference of the SCR reaction may be pushed more towards the fast SCR reaction

(2), without the need of injection of auxiliary reagent such as  $\text{NH}_4\text{NO}_3$  into the gas stream, e.g. the flue gas stream, as step a and b will convert some NO present in the gas into  $\text{NO}_2$  and other  $\text{H}_x\text{N}_y\text{O}_z$  species. The fast SCR may be promoted by in-situ formation of  $\text{NO}_2$  from the NO contained in the gas by oxidation with a supported ionic liquid phase catalyst according to the present invention. This technology enhances the SCR performance and allows thus a smaller  $\text{DeNO}_x$  unit, with a lower cost, to be applied in installations to obtain the same performance as obtained in units with traditional SCR. Similarly, the SCR process temperature can be lowered compared to traditional SCR operation conditions while maintaining the same SCR performance.

10

Another aspect the present invention is the use of at least one low molecular mass alcohol pre-mixed with a gas stream, where the gas stream contains more than one gaseous compound and a supported ionic liquid phase catalyst at temperatures from 0 to 160 degrees centigrade for oxidation of NO in the gas stream to  $\text{NO}_2$  and other  $\text{H}_x\text{N}_y\text{O}_z$ , where x, y, and z are integers in the ranges  $x=0-1$ ,  $y=1-2$ ,  $z=1-5$ .

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#### **Brief description of the drawings**

Figure 1 - Schematic overview of general experimental setup.

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Figure 2 - Schematic overview of one specific embodiment of the present invention.

Figure 3 - Schematic overview of another specific embodiment of the present invention.

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Figure 4 - Steady state NO conversions at varying methanol concentrations for a HS-SILP exposed to a gas containing 3,000 ppm NO, 12%  $\text{O}_2$  and balance  $\text{N}_2$  at 100% relative humidity (RH) with a space velocity (GHSV) of  $15,000\text{h}^{-1}$ , at 30 degrees centigrade. The highlighted point corresponds to methanol to NO of 1:75.

30 

Figure 5 - Steady-state NO conversions over different catalysts at 30 degrees centigrade with different alcohols added to the flue gas stream, 3,000 ppm NO, 130 ppm alcohol (1:23), 12%  $\text{O}_2$  and balance  $\text{N}_2$ , at 100% RH with GHSV of  $15,000\text{h}^{-1}$ .



Figure 6 - Steady state NO conversion for a HS-SILP (Hollow sphere silica-SILP) at temperatures ranging from 30 to 120 degrees centigrade given relative to the conversion observed at 30 degrees centigrade. 2,000 ppm NO, 800 ppm methanol (1:2.5 - methanol:NO), 12% O<sub>2</sub>, 4% H<sub>2</sub>O and balance N<sub>2</sub>, GHSV of 15,000 hr<sup>-1</sup>.

5

Figure 7 - Maximum obtained NO conversion after adding three drops of alcohol to the SILP (30% v/v [BMIM][NO<sub>3</sub>] on silica gel 100) reactor and then exposing it to a simulated flue gas containing 2,000 ppm NO, 1.5% H<sub>2</sub>O, 16% O<sub>2</sub>, balance N<sub>2</sub>, GHSV = 4500 h<sup>-1</sup>.

10

Figure 8 - Conversions for low concentration experiments at varying reactor volumes. The GHSV is varied from 15,000 to 96,000 hr<sup>-1</sup>. Gas composition: 500ppm NO, 17ppm methanol when present (MeOH:NO = 1:30), 4% H<sub>2</sub>O, 19% O<sub>2</sub> and balance N<sub>2</sub> at 30 degrees centigrade.

15

### Detailed description of the invention

In describing the aspects of the invention specific terminology will be resorted to for the sake of clarity. However, the invention is not intended to be limited to the specific terms so selected, and it is understood that each specific term includes all technical equivalents, which operate in a similar manner to accomplish a similar purpose.

20

One aspect the present invention provides a method for converting nitric oxide (NO) to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species from a gas stream, where the gas stream contains more than one gaseous compound, which method comprises:

25

- a) pre-mixing the gas stream with at least one low molecular mass alcohol,
- b) oxidizing said NO to nitrogen dioxide (NO<sub>2</sub>) and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species in the presence of the low molecular mass alcohol present in the gas stream, where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5, by use of a supported ionic liquid phase catalyst at temperatures from 0 to 160 degrees centigrade.

30

By injecting a low molecular mass alcohol into a gas stream before oxidation using a supported ionic liquid phase catalyst a promotion of the oxidation of NO is seen, hereby increasing or optimizing the conversion of NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub>

species compared to if no alcohol is present in the gas stream. Hence, by the present invention it is shown that a small molecular mass alcohol is a promoter for the oxidation of NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species.

5 It is hypothesized that two factors play a role when using a SILP catalyst for the oxidation of NO. The reaction rate of the oxidation is increasing with increased temperature while the gas solubility in the ionic liquid decreases at higher temperatures. The reaction temperature should therefore be kept relatively low. Furthermore, the temperature during the oxidation step should be below the  
10 decomposition temperature of the ionic composition used in the supported ionic liquid phase catalyst, thereby forming an oxidized gas mixture. The temperature is usually in a range within 0 to 160 degrees centigrade, such as from 30 to 120 degrees centigrade, such as from 30 to 100 degrees centigrade, such as from 50 to 80 degrees centigrade. For one of the preferred ionic liquids, [BMIM][N03], the temperature will  
15 range from 30 to 120 degrees centigrade.

In one or more embodiments of the present invention, the use of the supported ionic liquid phase catalyst is at temperatures from 30 to 120 degrees centigrade.

20 In one or more embodiments of the present invention, the use of the supported ionic liquid phase catalyst is at temperatures from 40 to 80 degrees centigrade.

Additionally, utilizing a supported ionic liquid phase catalyst the oxidation reaction is able to be performed at both low and high NO concentrations and in a gas stream  
25 containing water.

The gas stream, e.g. flue gas stream, may contain NO in an amount of at least 500 ppm. The gas stream, e.g. flue gas stream, may contain NO in an amount of at least 1000 ppm. The gas stream, e.g. flue gas stream, may contain NO in an amount of at  
30 least 2000 ppm. The gas stream, e.g. flue gas stream, may contain NO in an amount of at least 5000 ppm. Additionally, the gas stream containing more than one gaseous compound may contain at least NO, H<sub>2</sub>O, O<sub>2</sub>, and N<sub>2</sub>. Additionally, the gas stream may further at least comprise CO<sub>2</sub> and/or SO<sub>2</sub>.

The gas stream can be e.g. flue gas originating from either large stationary sources like power or incineration plants or cement production plants, or from mobile emission sources like e.g., commercial marine vessels or mobile incineration plants for incineration of e.g., domestic or industrial waste.

5

The method of low temperature oxidation of NO makes it possible for installation of a downstream SCR catalyst at the tail-end with low dust, which prolongs the life time of the SCR catalyst.

10 Throughout the present application, if not otherwise specified, 'incineration plant' shall mean any stationary or mobile technical unit and equipment dedicated to the thermal treatment of wastes with or without recovery of the combustion heat generated. This includes the incineration by oxidation of waste as well as other thermal treatment processes such as pyrolysis, gasification, or plasma processes, in so far as the  
15 substances resulting from the treatment are subsequently incinerated.

In one or more embodiments of the present invention, the gas stream is flue gas originating either from large stationary sources like power or incineration plants or cement production plants, or from mobile emission sources like e.g., commercial  
20 marine vessels or mobile incineration plants for incineration of e.g., domestic or industrial waste.

In one or more embodiments of the present invention, the gas stream is a flue gas originating from large stationary sources like power or incineration plants or cement  
25 production plants.

In one or more embodiments of the present invention, the gas stream is a flue gas originating from mobile emission sources like e.g., commercial marine vessels or mobile incineration plants for incineration of e.g., domestic or industrial waste, which  
30 typically require a small installation footprint, low energy consumption and preferably no carrying of hazardous chemicals.

In one or more embodiments of the present invention the gas stream is a flue gas originating from commercial marine vessels.

In one or more embodiments of the present invention, the at least one low molecular mass alcohol is mixed with water before pre-mixing with the gas stream.

- 5 In one or more embodiments of the present invention, the at least one low molecular mass alcohol is mixed with water before pre-mixing with the gas stream in a concentration between 1 and 10%, such as between 3 and 7%, such as 5%.

- 10 In one or more embodiments of the present invention the at least one low molecular mass alcohol mixed is with water before pre-mixing with the gas stream in a concentration of 5%.

In one or more embodiments of the present invention, the method further comprises:

- 15 c) injecting an ammonia source or a hydrocarbon source into the oxidized gas mixture from step b upstream of a SCR reactor and performing a SCR reaction with a SCR catalyst at low temperatures, such as between 100 to 300 degrees centigrade, between 120 to 200 degrees centigrade, or between 120 to 150 degrees centigrade.

- 20 By performing the steps a and b before utilizing an SCR reaction; the reaction preference of the SCR reaction may be pushed more towards the fast SCR reaction (2), without the need of injection of auxiliary reagent such as  $\text{NH}_4\text{NO}_3$  into the gas stream e.g. the flue gas stream, as step a and b will convert some NO present in the gas into  $\text{NO}_2$  and other  $\text{H}_x\text{N}_y\text{O}_z$  species. The fast SCR may be promoted by in-situ  
25 formation of  $\text{NO}_2$  from the NO contained in the gas by oxidation with a supported ionic liquid phase catalyst according to the present invention. This technology enhances the SCR performance and allows thus a smaller DeNOx unit, with a lower cost, to be applied in installations to obtain the same performance as obtained in units with traditional SCR. Similarly, the SCR process temperature can be lowered compared to  
30 traditional SCR operation conditions while maintaining the same SCR performance.

Another advantage of said method is that it may prolong the lifetime of the SCR catalyst, as the SCR catalyst can be installed at the tail-end with low dust.

In one or more embodiments of the present invention, the temperature is between 120 to 150 degrees centigrade when performing the SCR reaction.

5 The ammonia source used in the method further comprising the SCR reaction can be anhydrous ammonia, ammonia water, or a solution of urea. Because of its better performance ammonia is often utilized, but due to the poisonous character and difficult handling of ammonia, urea can alternatively be used, although not quite as effectively as ammonia.

10 The ammonia is evaporated and subsequently diluted with air or a gas side stream before it is injected into the gas duct upstream of the SCR reactor. Direct injection of ammonia-water or a urea solution is also possible. The SCR process requires precise control of the ammonia injection rate and a homogeneous mixing into the gas to ensure efficient NO<sub>x</sub> conversion without an undesirable release of unconverted  
15 ammonia referred to as ammonia slip.

Urea is often used in mobile units, where e.g. the ammonia slip would be avoided. Besides urea as an alternative to ammonia in the SCR process, it is also possible to use hydrocarbons. The possibility for reducing NO with hydrocarbons such as olefins  
20 and higher alkanes was first proposed in 1990 [Busca]. Hydrocarbon-SCR systems use hydrocarbons as the reductant. The hydrocarbon may be present in the exhaust gas or it may be added to the exhaust gas. This has the advantage that no additional reductant source (e.g. urea) needs to be carried on-board, but these systems cannot offer the performance of ammonia-SCR systems. In stationary plants, methane is the  
25 preferred choice for NO<sub>x</sub> removal from gases from power stations because it is already present, at least in methane fueled plants. However, other hydrocarbons may be used having relative activities, such as ethers > alcohols > aldehydes > esters > ketones > C<sub>3</sub>H<sub>8</sub>.

30 As the rate of NO<sub>x</sub> conversion in an SCR-reaction can be accelerated by use of a low molecular mass alcohol and an oxidation catalyst (the supported ionic liquid phase catalyst) upstream of the SCR unit, hereby pushing the reaction preference towards the fast SCR reaction (2), it enables that low temperature SCR installations operating at e.g. between 100 to 200 degrees centigrade can be sufficiently active for the

attractive end-of-pipe placement in e.g. waste incineration units or traditional and biomass fired power plants. The SCR reaction with a SCR catalyst can be performed at low temperatures such as between 100 to 300 degrees centigrade, between 100 to 200 degrees centigrade, between 120 to 200 degrees centigrade or between 120 to 150 degrees centigrade. The normal temperatures used during SCR reactions are much higher, normally between 350 to 400 degrees centigrade.

All conventional SCR catalysts can be used in step c. In one or more embodiments of the present invention, the SCR catalyst used in step c comprises one or more porous carrier material and one or more active catalytic components; the porous carrier material of the SCR catalyst is selected from  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{ZrO}_2$ , carbon, zeolite, a metal-organic framework, or mixtures thereof; and the active catalytic components supported by the porous carrier material are selected from either oxides of base metals such as vanadium, iron, copper, platinum, palladium, chromium, molybdenum, manganese, cerium and tungsten, zeolites, a metal-organic framework, metal-exchanged zeolites, or various precious metals, or mixtures thereof.

In one or more embodiments of the present invention, the active catalytic component of the SCR catalyst is vanadium ( $\text{V}_2\text{O}_5$ ) and the porous carrier material of the SCR catalyst is  $\text{TiO}_2$ .  $\text{V}_2\text{O}_5$  is traditionally used as the active material in SCR reactions.

In one or more embodiments of the present invention, the active catalytic component of the SCR catalyst is  $\text{V}_2\text{O}_5$  and the porous carrier material of the SCR catalyst is  $\text{ZrO}_2$ .

Base metal catalysts, such as the vanadium and tungsten, lack high thermal durability, but are less expensive and operate very well at the temperature ranges most commonly seen in industrial and utility boiler applications.

The two most common designs of SCR catalyst geometry used today are honeycomb and plate. The honeycomb form usually is an extruded ceramic applied homogeneously throughout the ceramic carrier or coated on the substrate. Like the various types of catalysts, their configuration also has advantages and disadvantages. Plate-type catalysts have lower pressure drops and are less

susceptible to plugging and fouling than the honeycomb types, but plate configurations are much larger and more expensive. Honeycomb configurations are smaller than plate types, but have higher pressure drops and plug much more easily. A third type is corrugated, comprising only about 10% of the market in power plant applications.

Also nano-sized particular (nanoparticulate) metal oxide catalysts such as vanadium oxide/anatase  $\text{TiO}_2$  catalysts can be used as SCR catalyst according to the present invention. The present invention therefore also concerns a method comprising SCR reactions of nitrogen oxides with ammonia or urea as reductant wherein nanoparticulate metal oxide catalysts are used. Nano-sized particular (nanoparticulate) metal oxide catalysts are disclosed in WO2010/055169 A1 which is hereby incorporated by reference in the present application. In one or more embodiment of the present invention, the SCR catalyst is a nanoparticulate metal oxide catalyst wherein the carrier metal oxide is anatase titanium dioxide or zirconium oxide and the catalyst metal oxide is  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ , or  $\text{CuO}$ . In one or more embodiment, the nanoparticulate metal oxide catalyst is further characterized by having a catalyst metal oxide content of up to 20 wt%  $\text{V}_2\text{O}_5$ . In another embodiment the nanoparticulate metal oxide catalyst is characterized by having a mean particle size between 6 and 16 nm. In yet another embodiment the nanoparticulate metal oxide catalyst is characterized by having an active surface area/BET surface area of between 64 and 250  $\text{m}^2/\text{g}$ . In yet another embodiment the nanoparticulate metal oxide catalyst is characterized by having an active surface area/BET surface area of between 130 and 250  $\text{m}^2/\text{g}$ . In yet another embodiment the nanoparticulate metal oxide catalyst is characterized by having an active surface area/BET surface area of between 130 and 219  $\text{m}^2/\text{g}$ .

In one or more embodiments of the present invention, the SCR catalyst is a nanoparticulate metal oxide catalyst wherein the carrier metal oxide is anatase  $\text{TiO}_2$  and the catalyst metal oxide is  $\text{V}_2\text{O}_5$ . The catalyst preferably has a vanadia loading up to 20 wt% of the total catalyst mass and has an average particle size down to 6 nm  $\pm$  2 nm with a narrow size distribution, and a relatively high-surface area (up to app. 250  $\text{m}^2/\text{g}$ ).

Since the method according to the invention allows for an accelerated conversion of NO<sub>x</sub> by use of an oxidation catalyst (supported ionic liquid phase catalyst) upstream of the SCR unit, the volume of needed SCR catalyst can be reduced considerably. If a traditional SCR catalyst is used, the volume of the SCR catalyst can be reduced 5  
5 to 10 times. This makes low-temperature SCR installations operating at temperatures between 100 to 300 degrees centigrade sufficiently active for the attractive end-of-pipe placement in e.g. waste incineration units or traditional and biomass fired power plants. An improvement of the activity (by a factor 5) of the traditional SCR catalysts is, according to the industry (LAB), adequate for making the installation economical  
10 feasible.

In one or more embodiments of the present invention, the at least one low molecular mass alcohol is present in a molar ratio of between 1:1 and 1:100 compared to the NO content of the gas stream (alcohol to NO), such as between 1:1 and 1:75, such  
15 as between 1:1 and 1:50 molar ratio, such as between 1:1 and 1:30, such as between 1:1 and 1:25, such as between 1:1 and 1:10, such as between 1:1 and 1:5.

The amount of low molecular mass alcohol is defined as being alcohol over NO content. E.g. if the gas contains 2,000 ppm NO, and 50 ppm alcohol is pre-mixed with  
20 the gas stream, the alcohol is in a molar ratio of 1:40 compared to the NO content.

In one or more embodiments of the present invention, the at least one low molecular mass alcohol is present in a molar ratio of between 1:10 and 1:50 compared to the NO content of the gas stream (alcohol to NO).  
25

A small amount of low molecular mass alcohol is desired, as this will decrease the amount of alcohol used in a commercial setup where NO is produced in ton scale per year in the gas stream.

30 In one or more embodiments of the present invention, the at least one low molecular mass alcohol is present in a molar ratio between 1:50 and 1:100 compared to the NO content of the gas stream.



In one or more embodiments of the present invention, the at least one low molecular mass alcohol is present in a molar ratio between 1:5 to 1:100 compared to the NO content of the gas stream.

- 5 In one or more embodiments of the present invention, the at least one low molecular mass alcohol is selected from  $C_1 - C_7$  linear or branched alcohols or mixtures thereof.

- In one or more embodiments of the present invention, the at least one low molecular mass alcohol is selected from methanol, ethanol, *tert*-butanol, *n*-propanol, *n*-butanol, 10 *n*-pentanol, *n*-hexanol, *n*-heptanol, allyl alcohol, or mixtures thereof.

In one or more embodiments of the present invention, the at least one low molecular mass alcohol is selected from methanol, ethanol, allyl alcohol, or mixtures thereof.

- 15 Considering an industrial application, methanol and ethanol would be preferred due to both being readily available, cost efficient, and globally produced on multimillion ton scale.

- In one or more embodiments of the present invention, a conversion of NO to NO<sub>2</sub> and 20 other  $H_xN_yO_z$  species is between 20 and 80% after the oxidation step b.

For applications wherein the gas stream, after step a and b, is not subjected to an SCR step, the conversion of NO may be preferred to be as high as possible.

- 25 In one or more embodiments of the present invention, a conversion of NO to NO<sub>2</sub> and other  $H_xN_yO_z$  species is between 40 to 60% after the oxidation step b.

- In one or more embodiments of the present invention, the amount of converted NO to NO<sub>2</sub> and other  $H_xN_yO_z$  species after the oxidation step b is controlled by varying 30 different parameters. Such parameters may be, but is not limited to, changing and/or adapting the temperature of the gas stream, varying the amount of added low molecular mass alcohol thereby changing the molar ratio of the at least one low molecular mass alcohol compared to the NO content of the gas stream, adjusting the gas-hourly space velocity hereby e.g. increasing or decreasing the contact time

between NO and the supported ionic liquid phase catalyst, increasing or decreasing the amount of supported ionic liquid phase catalyst, adjusting or regulating the supported ionic liquid phase catalyst reactor bed size and/or adding a damper before the bed reactor.

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The damper may function as a shutter, hereby controlling the access to the supported ionic liquid phase catalyst.

10 In one or more embodiments of the present invention, the amount of converted NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species after the oxidation step b is controlled by adjusting the temperature of the gas stream.

15 In one or more embodiments of the present invention, the amount of converted NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species after the oxidation step b is controlled by changing the molar ratio of the at least one low molecular mass alcohol compared to the NO content of the gas stream. The change in molar ratio may be performed continuously.

20 In one or more embodiments of the present invention, the amount of converted NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species after the oxidation step b is controlled by adjusting the gas-hourly space velocity. By adjusting the gas-hourly space velocity of the gas stream the contact time between NO and the supported ionic liquid phase catalyst may be increased or decreased.

25 In one or more embodiments of the present invention, the amount of converted NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species after the oxidation step b is controlled by increasing or decreasing the amount of supported ionic liquid phase catalyst and/or adjusting the supported ionic liquid phase catalyst reactor bed size.

30 If the gas stream is coupled to step c performing a SCR reaction with a SCR catalyst at low temperatures; a substantially equimolar ratio of NO to NO<sub>2</sub> is preferred, as if NO<sub>2</sub> fractions in excess of 50% of total NO<sub>x</sub> is produced, the excess NO<sub>x</sub> should be by-passed as NO<sub>2</sub> fractions in excess of 50% of total NO<sub>x</sub> should be avoided. This is because excess NO<sub>2</sub> with injected ammonia will form NH<sub>4</sub>NO<sub>3</sub> that deposits on the catalyst below 170 degrees centigrade (the decomposition temperature of the solid

nitrate). Also reduction of NO<sub>2</sub> demands two times the amount of ammonia injected compared to reduction of NO. With a substantially equimolar ratio is meant a ratio close to 1:1. However, ratios within the boundaries of 1.2:0.8 to 0.8:1.2 are also to be understood as being included in the expression 'substantially equimolar'.

5

In one or more embodiments of the present invention, a substantial equimolar ratio between NO and NO<sub>2</sub> in the gas stream after the oxidation step b is obtained by adjusting the gas-hourly space velocity. The gas-hourly space velocity (GHSV) is preferably adjusted to allow a conversion of NO to make the final gas substantially equimolar in NO and NO<sub>2</sub> if step c should be performed. This can be done by varying the volume of the catalyst and/or varying the gas flow. In one embodiment the supported ionic liquid phase catalyst is adjusted in volume to obtain a substantially equimolar ratio between NO and NO<sub>2</sub> in the oxidized gas stream before performing step c. In another embodiment the low molecular mass alcohol is adjusted in volume to obtain a substantially equimolar ratio between NO and NO<sub>2</sub> in the oxidized gas stream before performing step c.

In one or more embodiments of the present invention, the gas-hourly space velocity is between 15,000 h<sup>-1</sup> to 96,000 h<sup>-1</sup> of the gas stream before and/or after step b.

20

In one or more embodiments of the present invention, an ionic composition is an ionic liquid and is absorbed on a porous carrier (a support material in the supported ionic liquid phase catalyst) and used in the form of a supported ionic liquid phase (SILP) material. The solid carrier material is substantially or completely insoluble in water, it is porous, and it provides a medium to support the ionic composition. The solid carrier material in the supported ionic liquid phase catalyst can be any one of an inorganic, carbonaceous, and polymeric carrier material, having an acceptable porosity. In an embodiment of the invention, the porous solid support is selected from inorganic, carbonaceous, or polymeric solid carrier materials. In alternate embodiments of the present invention, porous synthetic foam, porous ceramic, activated carbon, diatomaceous earth, zeolites, kieselguhr, charcoal, porous alumina, porous titania, porous zirconia, or clay is employed. Mesoporous oxides of niobium, tantalum, cerium, and tin may also be employed. Other carbon materials or layered double hydroxides can also be used as a solid carrier material for the ionic composition. In

25  
30

one embodiment the porous carrier material is selected from all kinds of metal oxides, ceramics e.g., titanium oxide or carbon.

5 In one or more embodiments of the present invention, a support material in the supported ionic liquid phase catalyst is selected from **S102**, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeC<sub>2</sub>, ZrC<sub>2</sub>, carbon, or mixtures thereof.

**S102**, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeC<sub>2</sub>, ZrC<sub>2</sub> are mesoporous materials and highly porous. In one embodiment the porous carrier material is anatase TiO<sub>2</sub>.

10

The Supported Ionic Liquid Phase (SILP) materials used according to the present invention consist of an ionic liquid distributed in a porous support material with a high surface area. SILP materials are particularly practical for reactions involving gas phase reactants and may be used as catalysts, where the ionic liquid is the catalytically component itself or is used to dissolve catalytically components in the ionic liquid phase, or as gas absorbers. The SILP formulation eases diffusion, since the available surface area becomes much larger.

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In one or more embodiments of the present invention, a support material in the supported ionic liquid phase catalyst is selected from silica gel 100 or hollow-sphere silica.

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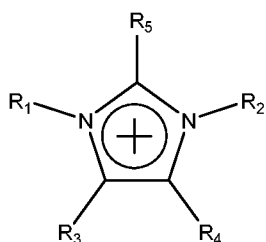
In one or more embodiments of the present invention, a support material in the supported ionic liquid phase catalyst is hollow-sphere silica.

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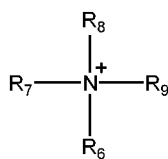
In one or more embodiments of the present invention, a support material in the supported ionic liquid phase catalyst is selected from, silica gel, silica, or hollow-sphere silica.

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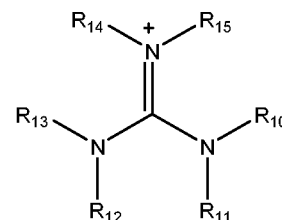
In one or more embodiments of the present invention, the supported ionic liquid phase catalyst comprises one or more organic cations selected from:



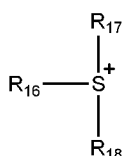
Imidazolium ion



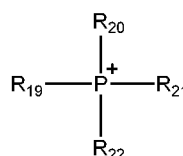
Ammonium ion



Guanidinium ion



Sulfonium ion



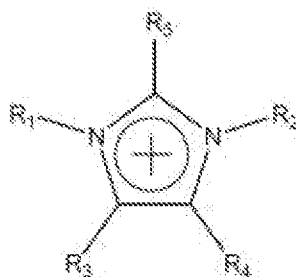
Phosphonium ion

wherein

- R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub>, R<sub>21</sub>, and R<sub>22</sub> can be, independently, hydrogen, alkyl, halogenated alkyl, aminoalkyl, hydroxyalkyl, alkoxyalkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl;
- the positively charged P, N, and S atoms may individually be part of heterocyclic or heteroaromatic structures by letting:
  - two of R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, e.g. R<sub>21</sub> and R<sub>22</sub> be fused such that a cyclic phosphonium ion is formed; or
  - two of R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> e.g. R<sub>6</sub> and R<sub>7</sub> be fused, such that a cyclic ammonium ion is formed, such as a pyridinium ion; or
  - two of R<sub>11</sub> and R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub>, R<sub>15</sub> and R<sub>10</sub>, e.g. R<sub>11</sub> and R<sub>12</sub> be fused, such that a cyclic guanidinium ion is formed; or
  - two of R<sub>16</sub>, R<sub>17</sub> and R<sub>18</sub> e.g. R<sub>16</sub> and R<sub>17</sub> be fused, such that a cyclic sulfonium ion is formed;
- one or more anions selected from C<sub>1</sub>-C<sub>6</sub> alkanoates such as acetate, arylcarboxylates such as benzoate, C<sub>1</sub>-C<sub>6</sub> alkylsulfates such as ethyl sulfate, C<sub>1</sub>-C<sub>6</sub> alkylsulfonates, C<sub>1</sub>-C<sub>6</sub> perfluoroalkylsulfonates such as triflate, C<sub>1</sub>-C<sub>6</sub> perfluoroalkanoates such as trifluoroacetate, C<sub>1</sub>-C<sub>6</sub> perfluoroalkylsulfonimides such as bis(trifluoromethylsulfonyl) imide (triflic imide), tetrafluoroborate, hexafluorophosphate, sulfate, hydrogen sulfate, nitrate, and halides such as chloride or bromide.

In one or more embodiments of the present invention, the supported ionic liquid phase catalyst further comprises one or more cations selected from  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ .

- 5 In one or more embodiments of the present invention, the supported ionic liquid phase catalyst comprises a cation having the following structure:



- wherein  $\text{R}_1$  and  $\text{R}_2$  are individually selected from  $\text{C}_1$ - $\text{C}_8$  alkyl groups or aryl groups, and wherein  $\text{R}_3$ ,  $\text{R}_4$ , and  $\text{R}_5$  are individually selected from hydrogens,  $\text{C}_1$ - $\text{C}_6$  alkyl groups, or aryl groups, or wherein  $\text{R}_3$  and  $\text{R}_4$  together with the imidazolium group may form a 4- to 6-membered saturated, unsaturated, or aromatic ring, which may further contain up to three hetero atoms selected from oxygen, nitrogen, and phosphorus.
- 10

- In a further specific embodiment,  $\text{R}_1$  and  $\text{R}_2$  are individually selected from  $\text{C}_1$ - $\text{C}_{16}$  alkyl groups or aryl groups. In another specific embodiment  $\text{R}_1$  and  $\text{R}_2$  are individually selected from  $\text{C}_1$ - $\text{C}_{12}$  alkyl groups or aryl groups. In a yet another specific embodiment  $\text{R}_1$  and  $\text{R}_2$  are individually selected from  $\text{C}_1$ - $\text{C}_6$  alkyl groups or aryl groups.
- 15

- In a further specific embodiment the cation is selected from 1-ethyl-3-methylimidazolium ( $[\text{EMIM}]^+$ ), 1-butyl-3-methylimidazolium ( $[\text{BMIM}]^+$ ), or 1-butyl-2,3-dimethyl-imidazolium ( $[\text{BDMIM}]^+$ ).
- 20

- Furthermore, in preferred embodiments of the invention the supported ionic liquid phase catalyst comprises one or more anions selected from  $\text{C}_1$ - $\text{C}_6$  alkanoates such as acetate, arylcarboxylates such as benzoate,  $\text{C}_1$ - $\text{C}_6$  alkylsulfates such as ethyl sulfate,  $\text{C}_1$ - $\text{C}_6$  alkylsulfonates,  $\text{C}_1$ - $\text{C}_6$  perfluoroalkylsulfonates such as triflate,  $\text{C}_1$ - $\text{C}_6$  perfluoroalkanoates such as trifluoroacetate,  $\text{C}_1$ - $\text{C}_6$  perfluoroalkylsulfonimides such
- 25

as bis(trifluoromethylsulfonyl) imide (triflic imide), tetrafluoroborate, hexafluorophosphate, sulphate, nitrate, and halides such as chloride or bromide.

In one embodiment the supported ionic liquid phase catalyst is selected from 1-ethyl-  
5 3-methylimidazolium ([EMIMf) acetate, 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>)  
acetate, 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>) triflate, 1-butyl-3-methylimidazolium  
([BMIM]<sup>+</sup>) triflate, 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>) nitrate, 1-butyl-3-  
methylimidazolium ([BMIM]<sup>+</sup>) nitrate, 1-butyl-2,3-dimethylimidazolium ([BDMIM]<sup>+</sup>)  
10 nitrate, choline chloride, choline acetate, and 1,1,3,3-tetramethylguanidinium  
chloride, or mixtures thereof.

In one embodiment the supported ionic liquid phase catalyst is selected from 1-ethyl-  
3-methylimidazolium ([EMIM]<sup>+</sup>) acetate, 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>)  
acetate, 1-butyl-3-methylimidazolium ([BMIMf) nitrate, 1-ethyl-3-methylimidazolium  
15 ([EMIM]<sup>+</sup>) triflate, 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>) triflate, 1-butyl-2,3-  
dimethylimidazolium ([BDMIM]<sup>+</sup>) nitrate, choline chloride, choline nitrate, or mixtures  
thereof.

In a particular embodiment the comprised anion is nitrate (NO<sub>3</sub><sup>-</sup>). In another particular  
20 embodiment the comprised anion is chloride (Cl<sup>-</sup>). In yet another particular  
embodiment the comprised anion is acetate (OAc). In yet another further embodiment  
the comprised anion is triflate (OTf). In yet another further embodiment the comprised  
anion is triflic imide (Tf<sub>2</sub>N<sup>-</sup>). In yet another particular embodiment the supported ionic  
liquid phase catalyst comprises [BMIM][NO<sub>3</sub>]. In yet another particular embodiment  
25 the supported ionic liquid phase catalyst comprises [BMIM][OTf]. In yet another  
particular embodiment the supported ionic liquid phase catalyst comprises  
[BMIM][OAc].

In one or more embodiments of the present invention, the supported ionic liquid phase  
30 catalyst is selected from 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>) acetate, 1-butyl-3-  
methylimidazolium ([BMIM]<sup>+</sup>) acetate, 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>) triflate,  
1-butyl-3-methylimidazolium ([BMIMf) triflate, 1-ethyl-3-methylimidazolium ([EMIMf)  
nitrate, 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>) nitrate, 1-butyl-2,3-  
dimethylimidazolium ([BMMIM]<sup>+</sup>) nitrate.

In one or more embodiments of the present invention, a wet scrubbing system for removal of SO<sub>2</sub> comprised in the gas stream is implemented before performing step a.

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The temperature during such wet scrubbing for removal of SO<sub>2</sub> from the gasses is usually in the range of from 80 to 90 degrees centigrade. Following the removal of SO<sub>2</sub> by a wet scrubbing system, the temperature may be increased a little to perform the oxidation step according to the present method.

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In one embodiment, as shown in Figure 2, the present invention is disclosing a method for capturing nitric oxide (NO) from a gas stream, where the gas stream contains NO (400 to 2,500 ppm), H<sub>2</sub>O, CO<sub>2</sub>, and O<sub>2</sub> (2 to 12%), which method comprises:

- 15 a) pre-mixing the gas stream with at least methanol, wherein said methanol is present in an amount of between 1:50 and 1:100 in molar ratio compared to the NO content of the gas stream (methanol:NO),
- b) oxidizing said NO to nitrogen dioxide (0 to 2,500 ppm) and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species in the presence of methanol present in the gas stream, where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5, by use of a supported  
20 ionic liquid phase catalyst at temperatures from 50 to 80 degrees centigrade.

In another embodiment, as shown in Figure 3, the present invention is disclosing a method for capturing nitric oxide (NO) from a gas stream, where the gas stream contains NO (400 to 2,500 ppm), H<sub>2</sub>O, CO<sub>2</sub>, and O<sub>2</sub> (2 to 12%), which method  
25 comprises:

- a) pre-mixing the gas stream with at least methanol, wherein said methanol is present in an amount of between 1:50 and 1:100 in molar ratio compared to the NO content of the gas stream (methanol:NO),
- b) oxidizing said NO to nitrogen dioxide (0 to 2,500 ppm) and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub>  
30 species in the presence of methanol present in the gas stream, where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5, by use of a supported ionic liquid phase catalyst at temperatures from 50 to 80 degrees centigrade.



c) injecting ammonia into the oxidized gas mixture from step b upstream of a SCR reactor and performing a SCR reaction with a SCR catalyst at a temperature of 150 degrees centigrade.

5 Another aspect the present invention is use of at least one low molecular mass alcohol pre-mixed with a gas stream, where the gas stream contains more than one gaseous compound and a supported ionic liquid phase catalyst at temperatures from 0 to 160 degrees centigrade for oxidation of NO in the gas stream to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub>, where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5.

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In one or more embodiments of the present invention, the at least one low molecular mass alcohol is mixed with water before pre-mixing with the gas stream.

15 In one or more embodiments the present invention is further used in combination with a downstream SCR reactor, which performs a SCR reaction with a SCR catalyst at low temperatures, such as between 100 to 300 degrees centigrade, between 120 to 200 degrees centigrade, or between 120 to 150 degrees centigrade.

20 In one or more embodiments of the present invention, the at least one low molecular mass alcohol is present in an amount between 1:1 and 1:100 in molar ratio compared to the NO content of the gas stream (alcohol to NO), such as between 1:1 and 1:75 in molar ratio, such as between 1:1 and 1:50 in molar ratio, such as between 1:1 and 1:30 in molar ratio, such as between 1:1 and 1:25 in molar ratio, such as between 1:1 and 1:10 in molar ratio, such as between 1:1 and 1:5 in molar ratio.

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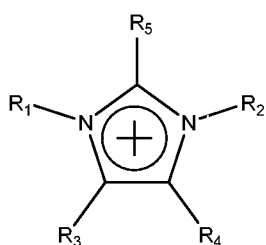
In one or more embodiments of the present invention, the at least one low molecular mass alcohol is selected from methanol, ethanol, te/f-butanol, n-propanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, allyl alcohol, or mixtures thereof.

30 In one or more embodiments of the present invention, a conversion of NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species is between 20 and 80% after the oxidation step b.

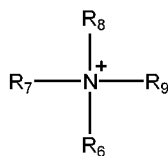
In one or more embodiments of the present invention, a support material in the supported ionic liquid phase catalyst is selected from SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeC<sub>2</sub>, ZrC<sub>2</sub>, carbon, or mixtures thereof.

- 5 In one or more embodiments of the present invention, a support material in the supported ionic liquid phase catalyst is selected from, silica gel, silica, or hollow-sphere silica.

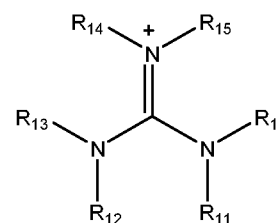
- 10 In one or more embodiments of the present invention, the supported ionic liquid phase catalyst comprises one or more organic cations selected from:



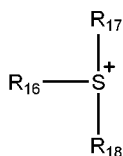
Imidazolium ion



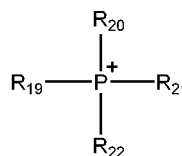
Ammonium ion



Guanidinium ion



Sulfonium ion



Phosphonium ion

wherein

- R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub>, R<sub>21</sub>, and R<sub>22</sub> can be, independently, hydrogen, alkyl, halogenated alkyl, aminoalkyl, hydroxyalkyl, alkoxyalkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl;
- the positively charged P, N, and S atoms may individually be part of heterocyclic or heteroaromatic structures by letting:
  - two of R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, e.g. R<sub>21</sub> and R<sub>22</sub> be fused such that a cyclic phosphonium ion is formed; or
  - two of R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> e.g. R<sub>6</sub> and R<sub>7</sub> be fused, such that a cyclic ammonium ion is formed, such as a pyridinium ion; or

- two of  $R_{11}$  and  $R_{12}$ ,  $R_{13}$  and  $R_{14}$ ,  $R_{15}$  and  $R_{10}$ , e.g.  $R_{11}$  and  $R_{12}$  be fused, such that a cyclic guanidinium ion is formed; or
  - two of  $R_{16}$ ,  $R_{17}$  and  $R_{18}$  e.g.  $R_{16}$  and  $R_{17}$  be fused, such that a cyclic sulfonium ion is formed;
- 5     • one or more anions selected from  $C_{1-C6}$  alkanoates such as acetate, arylcarboxylates such as benzoate,  $C_{1-C6}$  alkylsulfates such as ethyl sulfate,  $C_{1-C6}$  alkylsulfonates,  $C_{1-C6}$  perfluoroalkylsulfonates such as triflate,  $C_{1-C6}$  perfluoroalkanoates such as trifluoroacetate,  $C_{1-C6}$  perfluoroalkylsulfonimides such as bis(trifluoromethylsulfonyl) imide (triflic imide), tetrafluoroborate,
- 10     hexafluorophosphate, sulfate, hydrogen sulfate, nitrate, and halides such as chloride or bromide.

When describing the embodiments of the present invention, the combinations and permutations of all possible embodiments have not been explicitly described.

- 15     Nevertheless, the mere fact that certain measures are recited in mutually different dependent claims or described in different embodiments does not indicate that a combination of these measures cannot be used to advantages. The present invention envisages all possible combinations and permutations of the described embodiments.

## 20     **General experimental procedure**

The SILP was prepared by impregnating hollow-sphere silica (HS) or silica 100 with [BMIM][N03] (Io-Li-Tec) dissolved in methanol and drying by rotary evaporation at decreased pressure for 2 hours at 60 degrees centigrade. The materials were further dried at 120 degrees centigrade for 12 hours and stored in a desiccator until used.

- 25     The final material had a pore-filling degree of 30%. An amount of 0.8 g of the SILP material was placed on a glass frit in a vertical glass tube (diameter 1 cm) and heated to 30 degrees centigrade. The material was exposed to a gas stream containing NO (500-3,000 ppm),  $O_2$  (14-20%),  $H_2O$  (2-4%) and balance  $N_2$  at temperatures ranging from 30 to 120 degrees centigrade in a continuous flow setup using GE50A mass flow
- 30     controllers from MKS instruments, with total gas flow rates of 100 to 200 NmL/min. Gas bottles were supplied by AGA: 1% NO in He and pressurized air. A low molecular mass alcohol/water solution was injected into the gas stream prior to contact with the catalyst bed through a KDS 100 Legacy infusion pump at flow rates between 0.2 and 0.4 mL/h. The exit gas stream was continuously monitored by gas phase UV-Vis

spectroscopy and the NO partial pressure was obtained by comparing the area of the corresponding band with a reference curve constructed by feeding NO gas at different partial pressures to a stream bypassing the setup (see Figure 1). The setup was allowed to equilibrate for several hours; steady state was considered to have been achieved when there was no change in the NO partial pressure of the exit gas for 1.5 hours. To avoid an oxidation of NO by sunlight and the atmosphere all gas lines are made of steel.

## Examples

### 10 Example 1

Figure 4 show a steady state NO conversions at varying methanol concentrations for a HS-SILP exposed to a gas containing 3,000 ppm NO, 12% O<sub>2</sub> and balance N<sub>2</sub> at 100% relative humidity (RH) with a space velocity (GHSV) of 15,000h<sup>-1</sup>, at 30 degrees centigrade. The highlighted point corresponds to methanol:NO equal to 1:75.

15

Experimental example 1 investigates the ratio of NO to alcohol, wherein the alcohol was chosen herein to be methanol. The results from these experiments are presented in Figure 4. At low concentrations of methanol a noteworthy increase in the oxidation rate can be observed. The highlighted point in Figure 4 corresponds to a ratio of methanol:NO of 1:75, which corresponds to a methanol concentration in the gas phase of 40 ppm. The conversion with 1:75 is observed to be around 40% of the NO content. At this concentration the turn over number of methanol is more than 30, highly suggesting methanol to be a promoter for the oxidation of NO.

20

25 Additionally, as observed from Figure 4 a plateau is occurring at higher methanol concentration (around 1:20 methanol:NO - 150 ppm methanol), and the conversion of NO drops at even higher concentrations of methanol (around 1:12 - 250 ppm methanol).

### 30 Example 2

Figure 5 shows steady-state NO conversions over different catalysts at 30 degrees centigrade with different alcohols added to the flue gas stream. 3,000 ppm NO, 130 ppm alcohol (1:23), 12% O<sub>2</sub> and balance N<sub>2</sub>, at 100% RH with a GHSV of 15,000 h<sup>-1</sup> are used in the experimental procedure.

Experimental example 2 investigates the use of four different catalysts (HS-SILP, Silica-SILP, Silica, and no catalyst) and four different low molecular mass alcohols (methanol, ethanol, allyl alcohol, and no alcohol). From the data presented in Figure 5 it is observed that usage of a HS-SILP catalyst yields a higher conversion of NO than the other catalyst. Additionally, it is observed that methanol yields a higher conversion, when utilizing HS-SILP as catalyst compared to ethanol > allyl alcohol > no alcohol when using continuous flow.

### 10 **Example 3**

Figure 6 shows a steady state NO conversion for a HS-SILP where the temperature was varied from 30 to 120 degrees centigrade. The NO conversion is given relative to the conversion observed at 30 degrees centigrade (set to 1.00). The parameters used in this example are 2,000 ppm NO, 800 ppm methanol (methanol:NO - 1:2.5), 15 12% O<sub>2</sub>, 4% H<sub>2</sub>O, and balance N<sub>2</sub>, and GHSV of 15,000 h<sup>-1</sup>.

Experimental example 3 investigates the optimal temperature of the gas for maximum conversion of NO. From Figure 6 it is observed that a temperature around 60 degrees centigrade is the optimal temperature of the gas stream. However, all the investigated 20 gas temperatures give a relative conversion between 0.98 and 1.16 compared to the value at 30 degrees centigrade. This temperature dependence is different than what has previously been reported for low-temperature oxidation over carbonaceous materials and zeolites. For these catalysts, the oxidation rate decreases steadily with increasing temperature. It is hypothesized that two factors play a role when using a 25 SILP catalyst, the reaction rate is increasing with increased temperature, however, at higher temperatures the gas solubility in the ionic liquid becomes limiting.

### **Example 4**

The setup was additionally tested at high flow rates per gram of catalyst and low NO 30 content: NO: 500 ppm, methanol: 17 ppm (methanol to NO ratio of 1:30), 100% RH, 30 degrees centigrade and a GHSV of 96,000 h<sup>-1</sup>. The NO conversion under these conditions was found to be 40%, which corresponds to the conversion observed in experimental example 1 using 3,000 ppm NO, 12% O<sub>2</sub>, and balance N<sub>2</sub> at 100%

relative humidity (RH) with a GHSV of  $15,000\text{h}^{-1}$ , at 30 degrees centigrade and a methanol to NO ratio of 1:75.

### Example 5

- 5 Figure 7 shows maximum obtained NO conversion after adding three drops of alcohol to the SILP (30% v/v [BMIM][NO<sub>3</sub>] on silica gel 100) reactor and then exposing it to a simulated flue gas containing 2,000 ppm NO, 1.5% H<sub>2</sub>O, 16% O<sub>2</sub>, balance N<sub>2</sub>, GHSV =  $4500\text{h}^{-1}$ . In all cases, maximum conversion was obtained within the first 10 minutes.
- 10 Experimental example 5 investigates the maximum peak conversion (not the steady state conversion) using a silica-SILP with various low molecular mass alcohols. From Figure 7 it can be seen that the allyl alcohol is yielding the highest maximum conversion followed by methanol > ethanol > tert-butanol > n-propanol > n-butanol. From n-hexanol and up in molecular mass, an insignificant change in maximum
- 15 conversion is observed when comparing to using no alcohol. A strong correlation between the boiling point of the alcohol and the activity is observed. The only alcohol deviating from this trend is the allyl alcohol, however, this is the only unsaturated alcohol tested. Considering an industrial application, methanol and ethanol would be preferred due to both being readily available, cost efficient, and globally produced on
- 20 multimillion ton scale.

It is worth noting that there is a difference between which low molecular mass alcohol gives the highest maximum conversion (as investigated in experimental example 5) and which low molecular mass alcohol gives the highest steady state conversion (as

25 investigated in experimental example 2). Highest maximum conversion is found to be allyl alcohol, while highest steady state conversion is found to be methanol, however, all the low molecular mass alcohols seem to promote the oxidation of NO, hereby increasing the conversion compared to no alcohol present.

### 30 Example 6

Figure 8 shows conversions for low concentration experiments at varying reactor volumes. The GHSV is varied from 15,000 to  $96,000\text{h}^{-1}$ . The gas composition is: 500

ppm NO, 17 ppm methanol, when present, (MeOH:NO = 1:30), 4% H<sub>2</sub>O, 19% O<sub>2</sub> and balance N<sub>2</sub> at 30 degrees centigrade.

5 Experimental example 6 investigates the applications setup when the NO concentration is low (500 ppm). A NO concentration around 500 ppm is most likely in the low range of what is expected for exhaust gases. Additionally, experimental example 6 investigates the applications setup when the GHSV is at a high velocity (96,000 h<sup>-1</sup>), which is around the expected value required for the reaction to be successful in an industrial application. The results of these experiments can be found  
10 in Figure 8. From the results obtained it can be observed that oxidation is taking place at the lower NO concentration without great decrease in the conversion (around 55% when HS-SILP is used as the catalyst). However, the empty reactor oxidation rate is greatly decreased at a low NO concentration, as the reaction rate is largely dependent on the NO concentration.

15

Furthermore, a small drop in reaction rate is observed when increasing the GHSV to 96,000 h<sup>-1</sup>. This is a large increase in velocity. The corresponding volumetric rate of oxidation at 96,000 h<sup>-1</sup> is 2.51 E<sup>-4</sup> mol\*(L\*s)<sup>-1</sup>, which is 4 times higher than previous reported values using a zeolite catalyst. Previous values have been obtained at twice  
20 the NO concentration and in a flue gas without water, due to water being known as an inhibitor of the oxidation reaction.

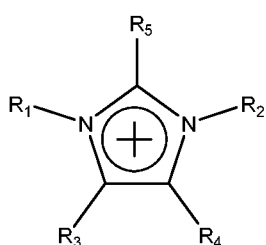
**Claims**

1. A method for converting nitric oxide (NO) to **NO<sub>2</sub>** and other  $H_xN_yO_z$  species from a gas stream, where the gas stream contains more than one gaseous compound, which method comprises:
  - a) pre-mixing the gas stream with at least one low molecular mass alcohol,
  - b) oxidizing said NO to nitrogen dioxide (**NO<sub>2</sub>**) and other  $H_xN_yO_z$  species in the presence of the low molecular mass alcohol present in the gas stream, where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5, by use of a supported ionic liquid phase catalyst at temperatures from 0 to 160 degrees centigrade.
2. The method according to any of the preceding claims, wherein the at least one low molecular mass alcohol is mixed with water before pre-mixing with the gas stream.
3. The method according to any of the preceding claims, wherein said method further comprises:
  - c) injecting an ammonia source or a hydrocarbon source into the oxidized gas mixture from step b upstream of a SCR reactor and performing a SCR reaction with a SCR catalyst at low temperatures, such as between 100 to 300 degrees centigrade, between 120 to 200 degrees centigrade, or between 120 to 150 degrees centigrade.
4. The method according to any of the preceding claims, wherein the at least one low molecular mass alcohol is present in a molar ratio of between 1:1 and 1:100 compared to the NO content of the gas stream (alcohol to NO), such as between 1:1 and 1:75, such as between 1:1 and 1:50, such as between 1:1 and 1:30, such as between 1:1 and 1:25, such as between 1:1 and 1:10, such as between 1:1 and 1:5.
5. The method according to any of the preceding claims, wherein the at least one low molecular mass alcohol is selected from methanol, ethanol, te/f-butanol, n-

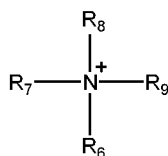


propanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, allyl alcohol, or mixtures thereof.

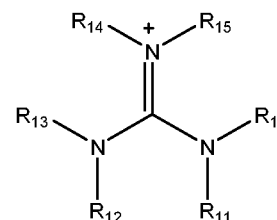
6. The method according to any of the preceding claims, wherein a conversion of NO to NO<sub>2</sub> and other H<sub>x</sub>N<sub>y</sub>O<sub>z</sub> species is between 20 and 80% after the oxidation step b.
7. The method according to any of the preceding claims, wherein a support material in the supported ionic liquid phase catalyst is selected from SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, carbon, or mixtures thereof.
8. The method according to any of the preceding claims, wherein a support material in the supported ionic liquid phase catalyst is selected from, silica gel, silica, or hollow-sphere silica.
9. The method according to any of the preceding claims, wherein the supported ionic liquid phase catalyst comprises one or more organic cations selected from:



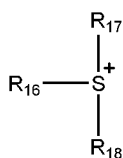
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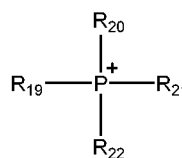
Ammonium ion



Guanidinium ion



Sulfonium ion



Phosphonium ion

20 wherein

- R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub>, R<sub>21</sub>, and R<sub>22</sub> can be, independently, hydrogen, alkyl, halogenated alkyl, aminoalkyl, hydroxyalkyl, alkoxyalkyl, alkenyl, alkynyl, aryl,

heteroaryl, cycloalkyl, cycloalkenyl, heterocycloalkyl, or heterocycloalkenyl;

- the positively charged P, N, and S atoms may individually be part of heterocyclic or heteroaromatic structures by letting:

5

- two of  $R_{20}$ ,  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ , e.g.  $R_{21}$  and  $R_{22}$  be fused such that a cyclic phosphonium ion is formed; or

- two of  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$  e.g.  $R_6$  and  $R_7$  be fused, such that a cyclic ammonium ion is formed, such as a pyridinium ion; or

10

- two of  $R_{11}$  and  $R_{12}$ ,  $R_{13}$  and  $R_{14}$ ,  $R_{15}$  and  $R_{10}$ , e.g.  $R_{11}$  and  $R_{12}$  be fused, such that a cyclic guanidinium ion is formed; or

- two of  $R_{16}$ ,  $R_{17}$  and  $R_{18}$  e.g.  $R_{16}$  and  $R_{17}$  be fused, such that a cyclic sulfonium ion is formed;

- one or more anions selected from  $C_{1-6}$  alkanooates such as acetate, arylcarboxylates such as benzoate,  $C_{1-6}$  alkylsulfates such as ethyl sulfate,  $C_{1-6}$  alkylsulfonates,  $C_{1-6}$  perfluoroalkylsulfonates such as triflate,  $C_{1-6}$  perfluoroalkanoates such as trifluoroacetate,  $C_{1-6}$  perfluoroalkylsulfonimides such as bis(trifluoromethylsulfonyl) imide (triflic imide), tetrafluoroborate, hexafluorophosphate, sulfate, hydrogen sulfate, nitrate, and halides such as chloride or bromide.

20

- Use of at least one low molecular mass alcohol pre-mixed with a gas stream, where the gas stream contains more than one gaseous compound and a supported ionic liquid phase catalyst at temperatures from 0 to 160 degrees centigrade for oxidation of NO in the gas stream to  $NO_2$  and other  $H_xN_yO_z$ , where x, y, and z are integers in the ranges x= 0-1, y=1-2, z=1-5.

25

Figure 1

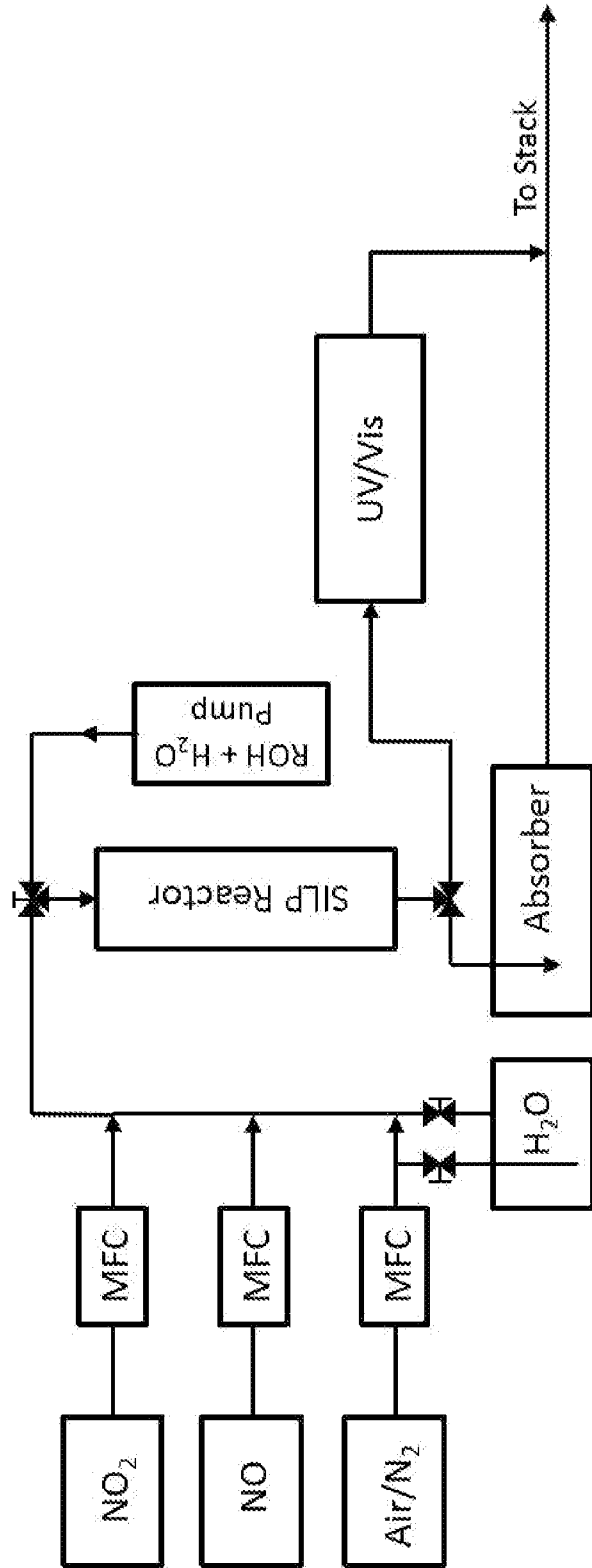


Figure 2

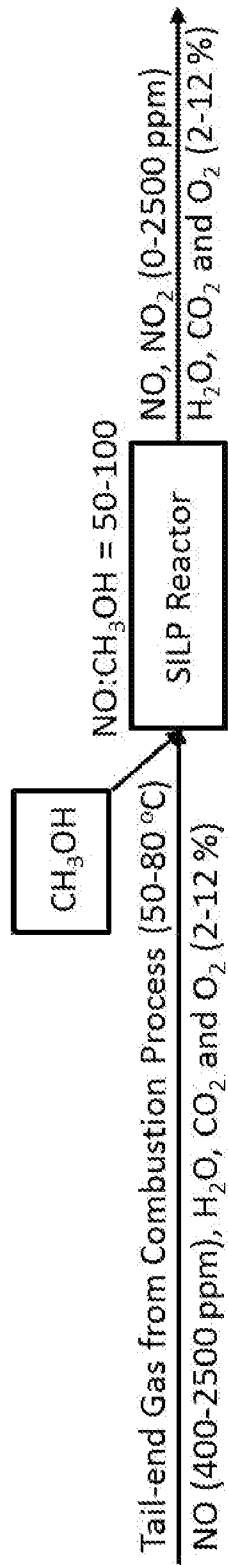
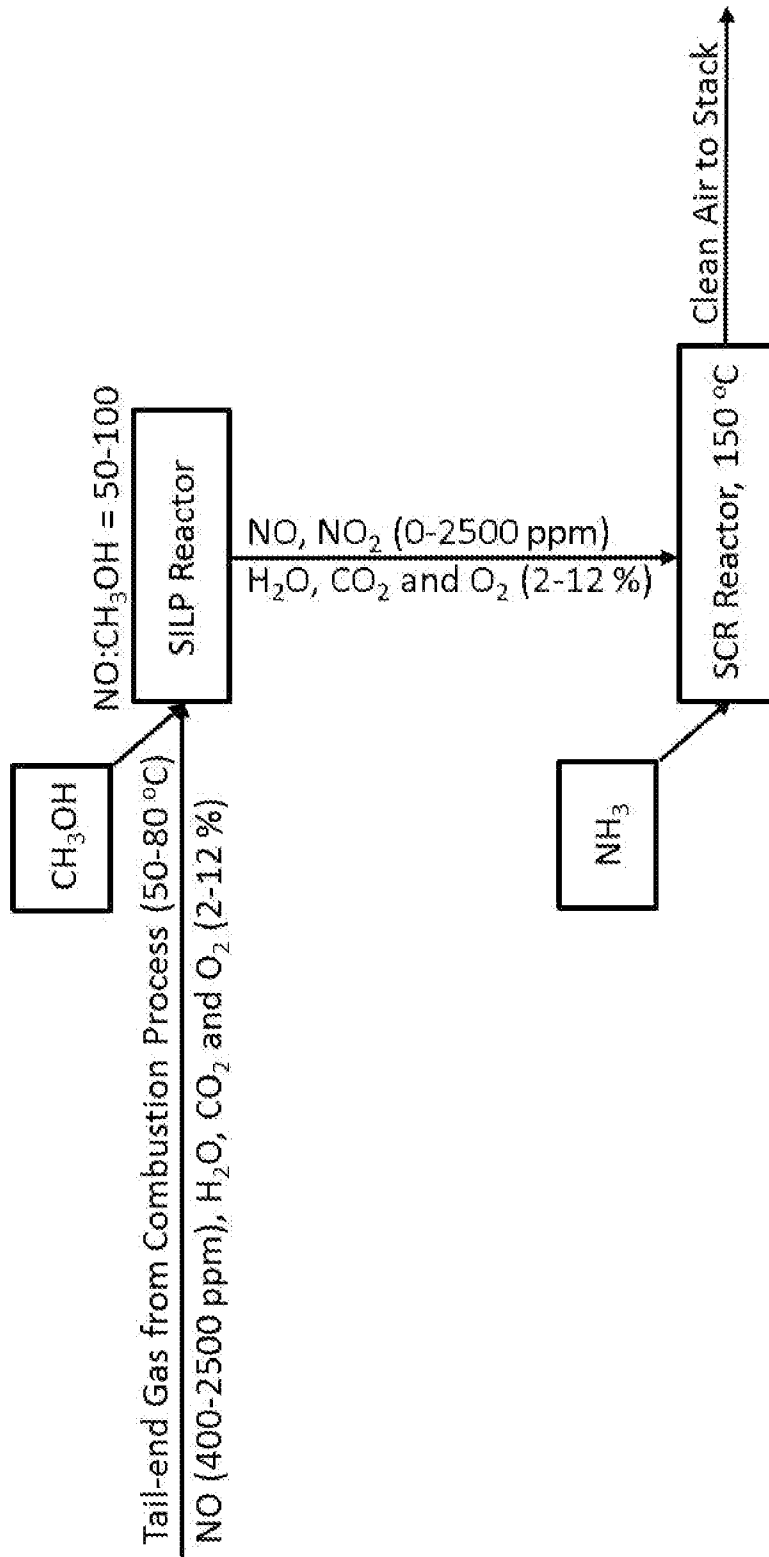


Figure 3



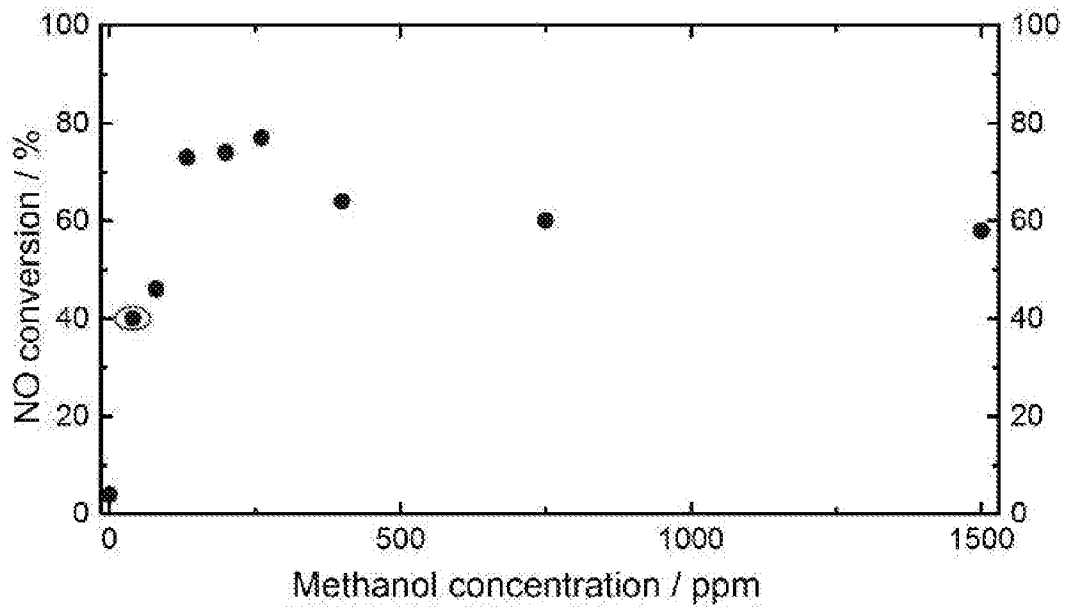


Figure 4

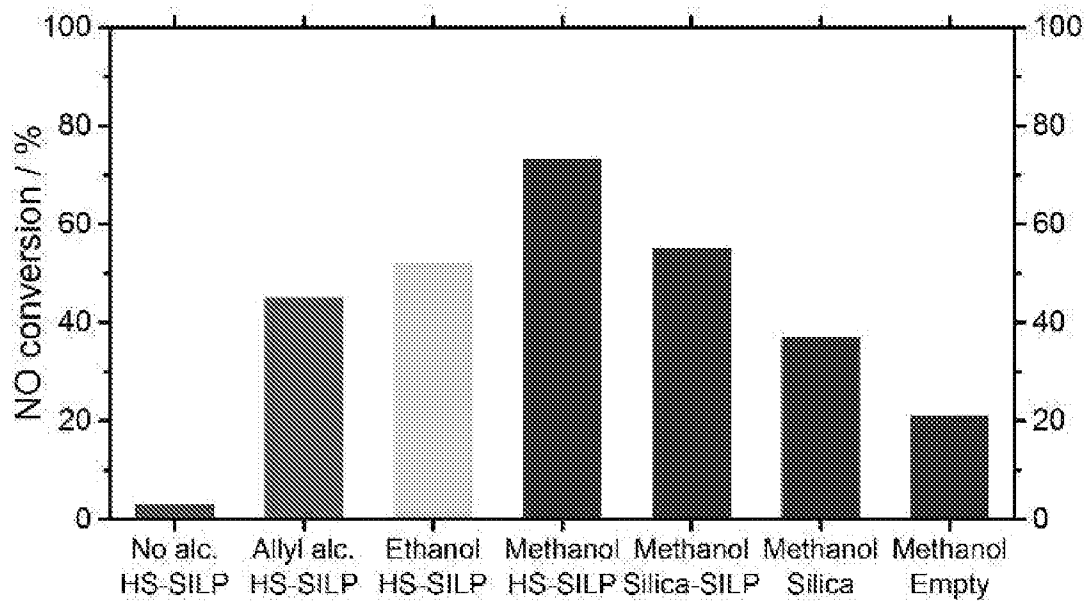
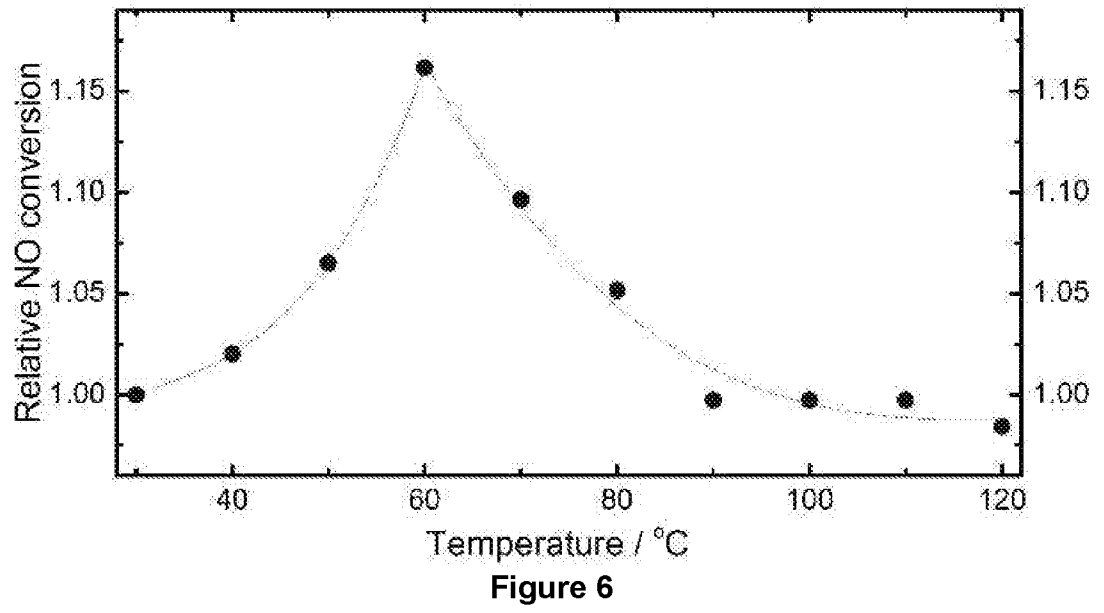


Figure 5





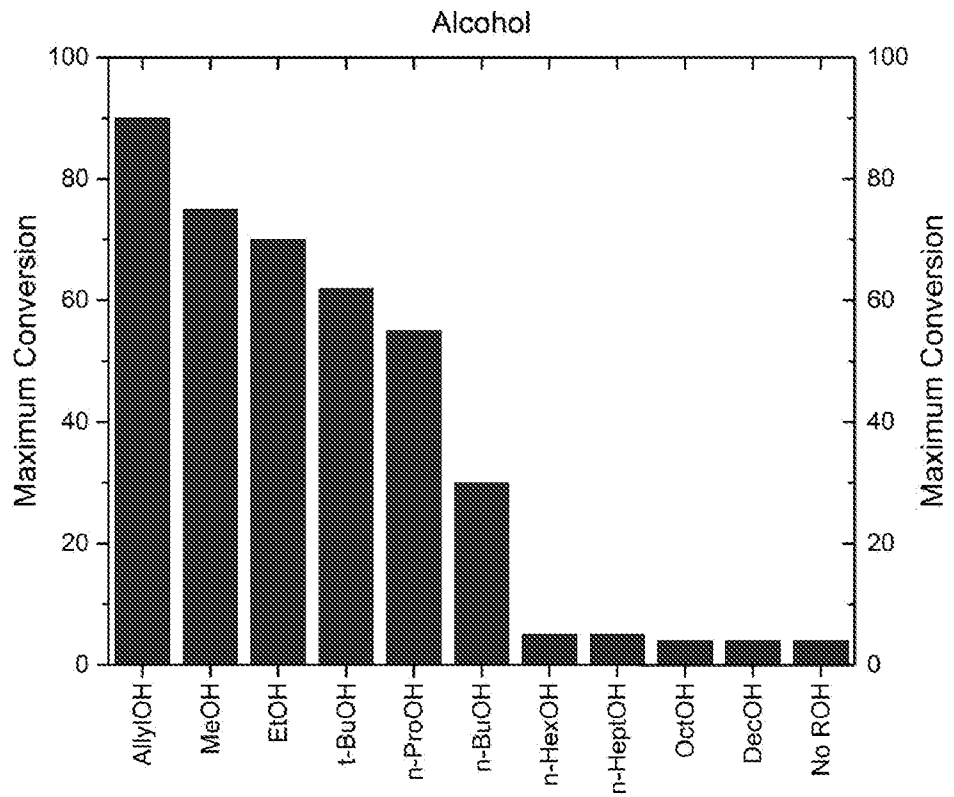
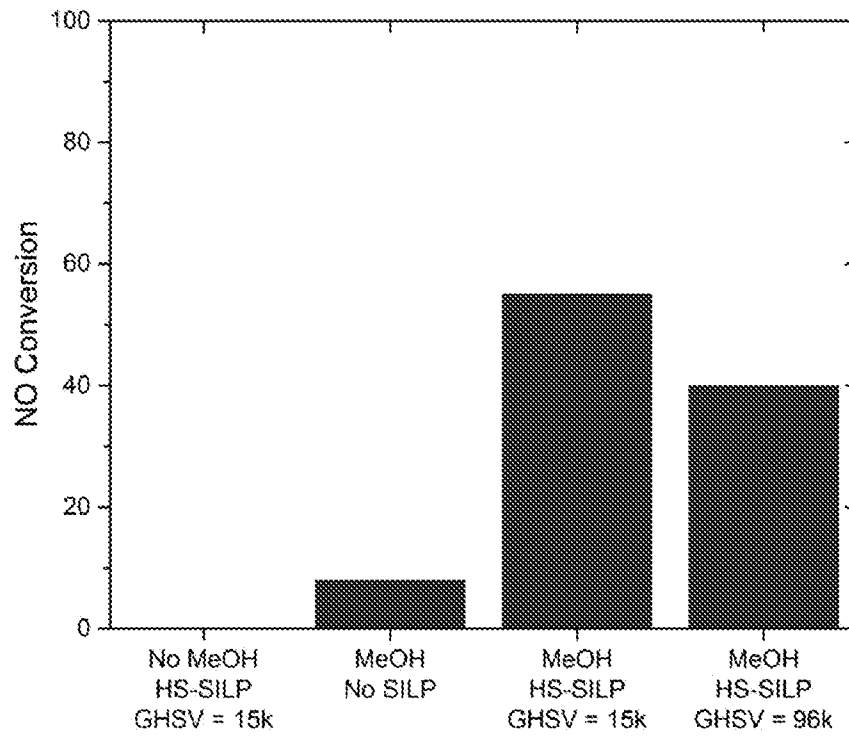


Figure 7

**Figure 8**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK2018/050222

A. CLASSIFICATION OF SUBJECT MATTER B01D 53/56 (2006.01), B01D 53/78 (2006.01), B01D 53/79 (2006.01), B01D 53/90 (2006.01), B01D 53/94 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) CPC/IPC: B01D, B01J, F01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched DK, NO, SE, FI: Classes as above.		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPODOC, WPI, FULL TEXT: ENGLISH, CHEMICAL ABSTRACTS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/158849 A1 (DANMARKS TEKNISKE UNIVERSITET [DK]) 22 October 2015. See entire document, in particular page 6, lines 4 - 22; page 11, lines 1-28; page 14, lines 17 -32; page 22, lines 1 - 35; and claims.	1-10
A	US 4350669 A (3ZUMT et al.) 21 September 1982 See abstract; column 2, lines 6 - 60; and claims.	1-10
A	US 5240689 A (JONES) 31 August 1993 See abstract and claim 1	1-10
A	US 4783325 A (JONES) 08 November 1988 See abstract and claims 1 and 12.	1-10
A	US 5047219 A (EPPERLY et al.) 10 September 1991 See abstract and column 3, lines 1-43.	1-10
A	JPS5637029 A (MITSUBISHI HEAVY LTD) 10 April 1981 See abstract.	1-10
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search	Date of mailing of the international search report	
18/10/2018	26/10/2018	
Name and mailing address of the ISA Nordic Patent Institute Helgeshoj Allé 81 DK - 2630 Taastrup, Denmark. Facsimile No. + 45 43 50 80 08	Authorized officer Hans Christian Schi0tz Rudbeck Telephone No. +45 43 50 81 25	

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK2018/050222

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<u>WO 2013/079597</u> Ai (DANMARKS TEKNISKE UNIVERSITET [DK]) 06 June 2013 See claims.	1-10
A	JOHNSON, W.L. et al. "Mechanistic investigation of ethanol SCR of NO <sub>x</sub> over Ag/A1203", CATALYSIS TODAY, 2012, Vol. 184, No. 1, pages 166-177. See abstract.	1-10

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PCT/DK2018/050222

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WO 2013079597 AI 2013.06.06	CA 2856792 AI 2013.06.06 AU 2012343846 AI 2014.06.12 AU 2012343846B B2 2016.10.13 KR 20140112492 A 2014.09.23 CN 104080524 A 2014.10.01 CN 104080524B B 2017.03.08 EP 2785436 AI 2014.10.08 EP 2785436 BI 2016.01.13 US 2015037232 AI 2015.02.05 US 9289719 B2 2016.03.22

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/DK2018/050222

Patent document cited in search report / Publication date	Patent family member(s) / Publication date
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