Selective catalytic oxidation of ammonia by nitrogen oxides in a model synthesis gas

Per Tunå [a],*, Jan Brandin [b]

[a] Department of Chemical Engineering Lund University, Getingevägen 60, SE-22100 Lund, Sweden
[b] Departament of Bioenergy Technology, Linnaeus University, 351 95 Växjö, Sweden

HIGHLIGHTS

▶ Gas phase removal of ammonia from synthesis gas is evaluated.
▶ Selective oxidation of ammonia in synthesis gas is possible with addition of NO_X.
▶ $V_2O_5/WO_3/TiO_2$ and H-morenite SCR catalyst perform well in reducing environments.
▶ On-site generation of the necessary NO_X is possible by nitric acid decomposition.

ARTICLE INFO

ABSTRACT

Synthesis gas generated by the gasification of nitrogen-containing hydrocarbons will contain ammonia. This is a catalyst poison and elevated levels of nitrogen oxides (NO_X) will be produced if the synthesis gas is combusted. This paper presents a study of the selective oxidation of ammonia in reducing environments. The concept is the same as in traditional selective catalytic reduction, where NO_X are removed from flue gas by reaction with injected ammonia over a catalyst. Here, a new concept for the removal of ammonia is demonstrated by reaction with injected NO_X over a catalyst. The experiments were carried out in a model synthesis gas consisting of CO, CO_2, H_2, N_2 and NH_3/NO_X. The performance of two catalysts, $V_2O_5/WO_3/TiO_2$ and H-mordenite, were evaluated. On-site generation of NO_X by nitric acid decomposition was also investigated and tested. The results show good conversion of ammonia under the conditions studied for both catalysts, and with on-site generated NO_X.

1. Introduction

Synthesis gas, generated by natural gas reforming, or by gasification of heavy oils or other carbon-containing feedstocks, is one of the most important intermediates in the chemical industry, and has been used for a long time for the production of essential bulk chemicals such as ammonia and methanol, as well as fuels. In the gasification process, the hydrocarbons in the feedstock (natural gas, coal, organic waste, woody biomass, etc.) are converted into a mixture of gases, consisting mainly of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), water (H_2O), methane (CH_4), lower hydrocarbons (C_{2-3}) and tars. If air is used as the oxidant, the gas will also contain large amounts of nitrogen (N_2). Depending on the origin and composition of the feedstock, and the process conditions, the gas produced will contain varying amounts of contaminants, such as sulphur, predominantly as hydrogen sulphide (H_2S), ammonia (NH_3), alkali and chloride such as potassium chloride (KCl), and hydrogen cyanide (HCN). If the feedstock used, for instance coal or biomass, contains high amounts of nitrogen, the gas produced will contain high levels of ammonia [1–4]. In the case of biomass gasification for the production of energy gas, for instance, for use in Combined Heat and Power Plants (CHP), or for the production of synthesis gas, the ammonia levels in the producer gas typically range from 0.04 to 1.8 vol.% [2,4,5].

This ammonia must be removed from the produced synthesis gas before usage, since it could poison the catalysts in the subsequent synthesis steps or form NO_X when combusted. Ammonia is very water soluble and can easily be removed with a water scrubber or a flue gas condenser. This has two drawbacks, the gas must be cooled down, which can increase operating costs and the ammonia is not eliminated as it ends up in the process water and must be handled by other processes.

Ammonia in the synthesis gas could be decomposed, to H_2 and N_2, over a reforming catalyst (usually Ni-based) at high temperature ($\sim$1073 K), a process called ammonia cracking. However, the conversion of ammonia is, as is hydrocarbon reforming, restrained because of sulphur poisoning [6].

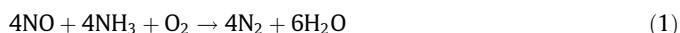The removal of ammonia from air or any other oxygen containing gas can be accomplished with selective catalytic oxidation (SCO) over a suitable catalyst. The ammonia is then oxidised to N_2 and H_2O. Much research have been published in this area, for instance [7,8]. But due to the low oxygen content in synthesis gas, this has little to no relevance as a comparison.

A few publications on SCO have been performed under reducing conditions by injection of oxygen. In some of them [9,10] the concentration of CO and H_2 is very low, compared to a real synthesis gas produced in a gasifier. In others [11–16], it is not clear if the process studied really is SCO or ammonia cracking driven by the temperature increase, caused by CO and H_2 combustion in the catalytic bed due to the oxygen injection.
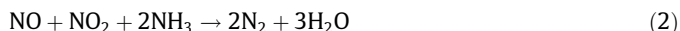
Selective catalytic reduction (SCR) is an industrial process for the removal of nitrogen oxides from combustion flue gases, by injection of nearly equimolar amounts of ammonia into the flue gas [17,18]. The ammonia can be injected into the hot flue gas either as ammonia or as a urea solution [19].

Since the NO_X in normal combustion flue gases consists of 90–95% nitrogen monoxide (NO), and the rest being nitrogen dioxide (NO_2), it is normally considered that the reaction over a solid catalyst, for instance $V_2O_5/WO_3/TiO_2$ [20] or an acidic zeolite [21], proceeds according to the following reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

Oxygen (O_2) participates in reaction (1), and in combustion flue gases the oxygen level is normally 2–10 vol.%. Without oxygen, the rate of reaction, or conversion, falls to relatively low values [22].

Reactions (2) and (3), do not require any oxygen. Reaction (2) has a much higher reaction rate than reaction (1) and is thus called the fast SCR reaction [22].

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad (2)$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad (3)$$

As mentioned above, the proportion of NO_2 in the NO_X content in flue gas is normally low and the effects of the fast SCR reaction are usually undetectable. In some diesel automotive SCR applications a part of the NO content in the flue gas is catalytically oxidised to NO_2 [22] to improve low-temperature SCR performance and improve the oxidation of soot in the particulate filter [19].

If the opposite reaction is considered, i.e. the removal, inverse SCR or selective catalytic oxidation (SCO), of ammonia in a gas stream by injection of NO_X over a suitable catalyst. It should be straightforward as long as the gas contains oxygen.

Attempts to remove ammonia from producer gas have previously been made on an industrial scale by applying the inversed SCR technique. Valtion Teknillinen Tutkimuskeskus (VTT) was granted a patent in 1996 for the removal of ammonia in a gasification process by co-injection of NO and O_2 into hot synthesis gas [23]. This ammonia removal is also SCO or ammonia cracking as it was performed at 673–973 K over a γ-alumina catalyst and the oxygen level in the gas was increased to 2 vol.% before the catalyst bed. In their patent, VTT claims that the process can be used to reduce NO_X emissions to the environment after combusting the producer gas, for instance in a gas turbine for power production.

This paper describes the application of the fast SCR reaction (3) in a model producer gas without the addition of oxygen. If NO_2 is injected into the producer gas, the ammonia can be selectively oxidised according to reaction (3). However, NO_2 is not stable in this environment. It is well known that NO_X is reduced by CO and H_2, for instance CO is oxidised to CO_2 and NO_X is reduced to N_2 by three-way catalysts in automotive applications [24]. Before the introduction of NH_3–SCR, hydrogen was used industrially to reduce NO_X over precious-metal catalysts at low temperature.

This has recently received increasing attention [25,26]. Without a catalyst, the rate of these reactions is comparatively slow, at least at temperatures up to 600–700 K in the SCR temperature range.

2. Materials and methods

Fig. 1 shows a schematic illustration of the experimental set-up. The gases are supplied from gas bottles using mass-flow controllers. The CO, CO_2, H_2, and a mixture of 0.5 vol.% ammonia in N_2, are mixed and injected in the top of the reactor. The NO_2 is injected separately inside the reactor, approximately 50 mm above the catalyst. The NO_2 is either supplied from a gas bottle as a mixture of 1.0 vol.% NO_2 in N_2 by a mass-flow controller or from the NO_X generator described below.

The reactor consists of a glass tube, 6.35 mm in diameter with a bulb in the middle containing the catalytic bed. A thermocouple (1 mm in diameter) and a steel tube (1.6 mm) for NO_2 injection were inserted into the reactor inlet as shown in Fig. 2.

The glass reactor is placed in an oven and heated to the desired reaction temperature. The temperature in the different experiments was measured just above the bed, using the thermocouple in Fig. 2.

Ammonia was measured using a Bacharach AGMSZ ammonia gas monitor. The AGMSZ uses infrared light to measure the ammonia content in a gas in the range 2.5×10^{-3} to 1 vol.%. This instrument operates at room temperature and to avoid the condensation of water, which would interfere with the measurements, it was necessary to keep the moisture content in the gas below saturation pressure at room temperature during the experiment. The ammonia analyser uses a purging mechanism to reset the base value. A solenoid valve used to switch the inlet to fresh air rather than the measurement inlet. Purging is controlled by the analyser and typically occurs in 5–10-min intervals, depending on the ammonia concentration. The switching of the valve causes a temporary pressure build-up in the reactor. The effect of the purging can be seen in Fig. 8 as a small "bumps" in the ammonia signal. The disturbance in the signal is easily identified in the signal.

2.1. The catalysts

The experiments were performed on two different catalysts: $V_2O_5/WO_3/TiO_2$ and H-mordenite. The H-mordenite used was manufactured by Zeolysts with a Si/Al ratio of 21. The vanadium based catalyst was a commercial catalyst that contains $V_2O_5/WO_3/TiO_2$ but the exact composition is not known and permission to analyse the catalyst was not granted. The catalysts were chosen as example of the two types of SCR catalysts used industrially today, but also because of the differences in chemical composition, structures and difference in operating temperature. Because of this, it is possible they have different resistance to the reducing environment.

For SCR, the $V_2O_5/WO_3/TiO_2$ is usually operated in the temperature range 573–673 K and the H-mordenite above 623 K. Due to the higher activity of the vanadium based catalyst compared to the H-mordenite [27], different space velocities were used for each catalyst. The catalyst particle size was 0.16–0.18 mm.

All materials were analysed to detect any significant changes in their BET and Langmuir surface area before and after use, by measuring the adsorption of nitrogen at liquid nitrogen temperature with a Micromeritics ASAP 2400 instrument after degassing for 16 h at 623 K. Pore volume analysis was performed using the BJH method [28]. The desorption isotherm was used for the analysis and the results are presented in Table 1.
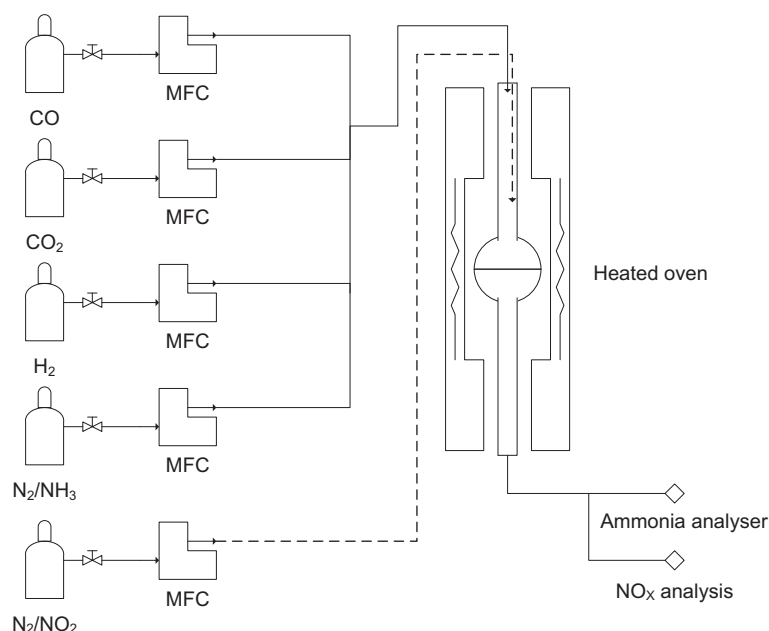
Fig. 1. Experimental set-up used for selective ammonia oxidation. In experiments employing only NO_X, the N_2/NH_3 is replaced by pure N_2.
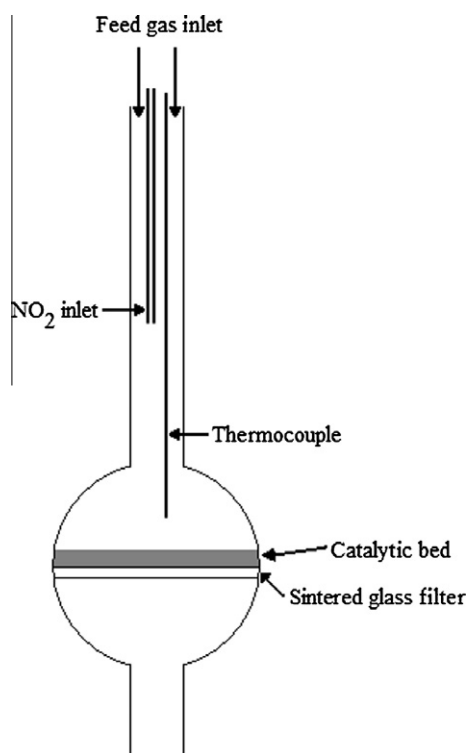

Fig. 2. Enlargement of the reactor inlet and catalytic bed.

2.2. NO_X reduction in model synthesis gas

In order to investigate whether nitrogen oxides were reduced over the catalysts, experiments were run without ammonia in the gas. The gas composition used is presented in Table 2 and is representative of the gas obtained after an air-blown gasifier, with the exception of water. Water/steam is normally a major component in synthesis gas, but due to the limitations the Bacharach

Table 1
Results of the BET analysis for the catalysts used.

	Fresh $V_2O_5/$ WO_3/TiO_2	Used $V_2O_5/$ WO_3/TiO_2	Fresh H-mordenite	Used H-mordenite
BET surface area ($m^2 g^{-1}$)	69	69	410	390
Langmuir surface area ($m^2 g^{-1}$)	95	96	540	530
Desorption surface area of pores ($m^2 g^{-1}$)	82	80	110	120
Micropore area ($m^2 g^{-1}$)	5	7	320	300
Desorption volume of pores ($cm^3 g^{-1}$)	0.26	0.26	0.30	0.30
Micropore volume ($cm^3 g^{-1}$)	0.0016	0.0024	0.15	0.14
Average pore diameter (nm)	13	13	11	10

AGMSZ ammonia gas monitor, water was excluded. Since the gas is explosive when mixed with air, a normal chemiluminescence NO_X meter could not be used, and the nitrogen oxide level was measured as a total NO_X level using two different Dräger short-term tubes ($2–100 \times 10^{-4}$ and $0.01–0.5$ vol.% NO_X) [29]. These tubes are for total NO_X and do not indicate the ratio of NO_2/NO_X.
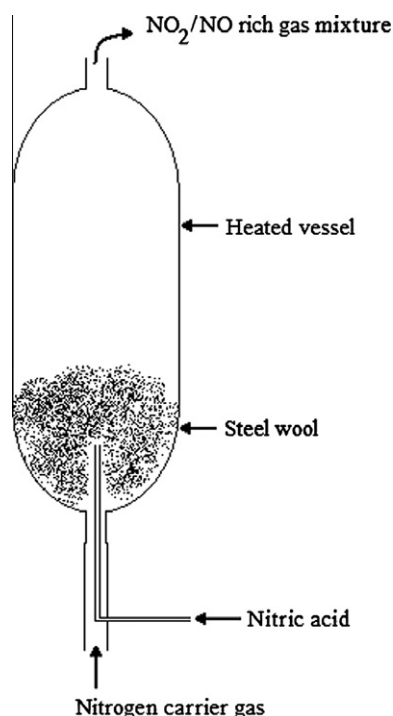
NO_X was measured at the reactor outlet when the reactor was empty, and when it was filled with each of the catalysts, $V_2O_5/$ WO_3/TiO_2 or H-mordenite. At lower concentrations the accuracy for the $0.01–0.5$ vol.% NO_X Dräger tubes was insufficient. The gas was sampled and diluted 20:1 and the lower range $2–100 \times 10^{-4}$ -vol.% Dräger tubes was used to give a more accurate reading. No NH_3 was present in the NO_X-only experiments and pure N_2 was used instead of the N_2/NH_3 mix.

2.3. Ammonia oxidation in reducing environments

The effect of water in ordinary SCR is limited [19], but the lack of water in the gas will affect the equilibrium in some reactions

Table 2
Gas composition.

Component	Composition (vol.%)
N_2 or (N_2/NH_3)	65
CO_2	11
CO	13
H_2	11
NO_X	0.2
NH_3	0.2

Fig. 3. The laboratory NO_X generator used to produce NO_2.

such as the Boudouard reaction (4) since the formed carbon will not be consumed by steam according to reaction (5).

$$2CO \leftrightarrow C + CO_2 \tag{4}$$

$$H_2O + C \leftrightarrow CO + H_2 \tag{5}$$

At the higher temperatures there was a lower ammonia start concentration which could indicate dissociation of ammonia according to the following reaction:
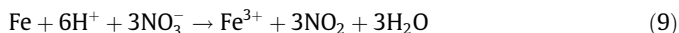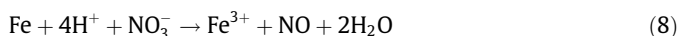
$$2NH_3 \rightarrow N_2 + H_2 \tag{6}$$

The NO_2 is injected as a mixture of NO_2 in N_2 containing 1 vol.% NO_2. The gas flow was 1.6 Ndm^3/min for the model synthesis gas and N_2/NO_2 contributed an additional 0.4–0.5 Ndm^3/min depending on stoichiometry between NH_3 and NO_2. The gas hourly space velocity for the $V_2O_5/WO_3/TiO_2$ catalysts was 210,000 h^{-1} and for the H-mordenite 75,000 h^{-1}.

2.4. NO_2 generation

In a full-scale plant, the NO_2 required for ammonia oxidation should be created on-site. A suggestion of a feasible process for this is the decomposition of nitric acid according to the following reaction:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2 \tag{7}$$

Nitric acid can also be reacted with copper or iron to form nitrogen oxides according to the following reactions [30]:

$$Fe + 4H^+ + NO_3^- \rightarrow Fe^{3+} + NO + 2H_2O \tag{8}$$

$$Fe + 6H^+ + 3NO_3^- \rightarrow Fe^{3+} + 3NO_2 + 3H_2O \tag{9}$$

It is commonly known that concentrated nitric acid yields high NO_2/NO_X ratios and that the reactions occur fast when heated. A small NO_X generator was constructed to test the feasibility of ammonia oxidation using NO_X generated on-site. The generator is illustrated in Fig. 3.

The NO_X generator consists of a stainless steel vessel, which is heated electrically. The temperature of the vessel was 503 K during the experiments. Nitric acid (65 wt.%) was injected into the vessel at a rate of 40 mm^3/min. If the assumption of 100% conversion from HNO_3 to NO_2 where true, it would roughly correspond to a stoichiometry of 1:2 for $NH_3:NO_2$. The NO_X generated by the NO_X generator was strongly coloured yellow to brown, indicating the presence of NO_2.
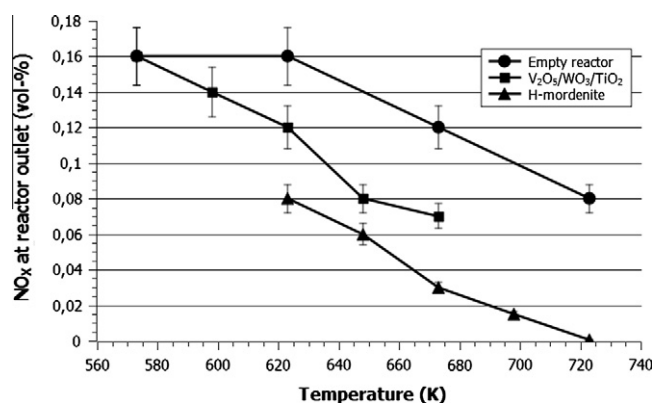
3. Results

3.1. NO_X reduction in the model synthesis gas

The results of NO_X reduction in synthesis gas without ammonia present are shown in Fig. 4. The reading error of the Dräger tubes was estimated to ±10% of the value. The error bars are given in Fig. 4.

As can be seen in Fig. 4, the homogenous gas phase reduction (empty reactor) of NO_2 to N_2 is slower than with a catalyst. The measurements show the total NO_X, the NO_2/NO_X ratio is not known. H-mordenite is more effective at reducing NO_X at temperatures above 573 K than the $V_2O_5/WO_3/TiO_2$ catalyst. At temperatures above 623 K, carbon deposits were formed on the thermocouple and on the catalyst surface. This was only observed when there was no NH_3 in the gas. The Boudouard reaction (4) is an equilibrium reaction that is dependent on temperature. The lack of water in the gas leads to the production of carbon, since the carbon formed is not consumed by the steam normally present in producer gas.

3.2. The SCR reaction in the model synthesis gas with bottled NO_2

Fig. 5 shows the result from a typical experiment using NO_2 from a gas bottle. The N_2/NO_2 was added to the stream when the ammonia concentration was just below 0.2 vol.%.

Fig. 4. NO_X levels with the empty reactor (●) and the two catalysts $V_2O_5/WO_3/TiO_2$ (■) and H-mordenite (▲) with an inlet NO_2 level of 0.2 vol.%.
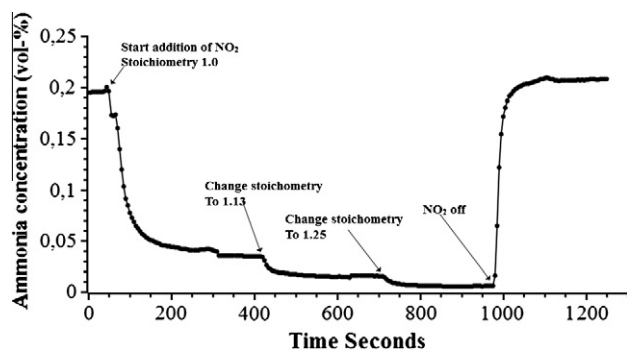
Fig. 5. Ammonia concentration at the outlet using the $V_2O_5/WO_3/TiO_2$ catalyst and bottled gas at 598 K.

Table 3
Calculated conversions of ammonia (molar ratio 1:1) with margins of error.

Temperature (K)	Conversion (%)	Margin of error (%)
573	76.2	0.1
598	83.6	0.2
623	83.1	0.1
648	77.5	0.1
673	54.3	0.4

When the injection of NO_2 starts, the ammonia concentration falls to a value of about 0.034 vol.%. The NH_3:NO_2 stoichiometry was increased to 1:1.125 and the outlet concentration falls to 0.015 vol.%. The final stoichiometry of 1:1.25 gives a gas with only 0.005 vol.% ammonia at the reactor outlet. The N_2/NO_2 injection is then turned off and the ammonia concentration increases to a value similar to the initial concentration.

When the IR-instrument stabilized on a plateau, there was very little variation in the ammonia signal. Approximately 15 measurements were collected for each plateau and the mean value and the margins of error at 95% confidence interval was calculated, with the free software Statcato [31], for each point. The maximum margin of error in the inlet molar ratio was 12×10^{-4} vol.% (2000×10^{-4} vol.% inlet) and 4×10^{-4} vol.% (961×10^{-4} vol.% out) in the outlet molar ratio for all points with the vanadium catalyst.

The conversion (Conv) of ammonia was calculated in the ordinary way as:

$$Conv = (C_{in} - C_{out})/C_{in} \tag{10}$$

However, since the concentrations, or molar ratios, have margins of error, also the conversion will have a margin of error. This was calculated for each point with the error propagation formula [32]:

$$E_f = |df(x,y)/dx| * E_x + |df(x,y)/dy| * E_y \tag{11}$$

Here, E_f is the error of margin of the conversion, $|df(x,y)/dx|$ the partial differential of the conversion with respect to x (inlet molar ratio, if y is outlet molar ratio) and E_x the margin of error in parameter x. In this way the conversion and margin of error was calculated for the conversion, in Table 3 the results are shown for the run with equimolar ratio (1:1) of NH_3 and NO_X.

The maximum margin of error in the conversation at NH_3:NO_X 1:1 is less than 0.5% (54.3% conversion at 673 K). The margins of errors for the molar ratios of 1:1.125 and 1:1.25 for both vanadium and the mordenite catalyst are very similar.

Fig. 6 shows the conversion of NH_3 for the $V_2O_5/WO_3/TiO_2$ catalyst using bottled gas at different temperatures.

As can be seen in Fig. 6, conversion over the $V_2O_5/WO_3/TiO_2$ catalyst is high up to 623 K after which it starts to decline. The total
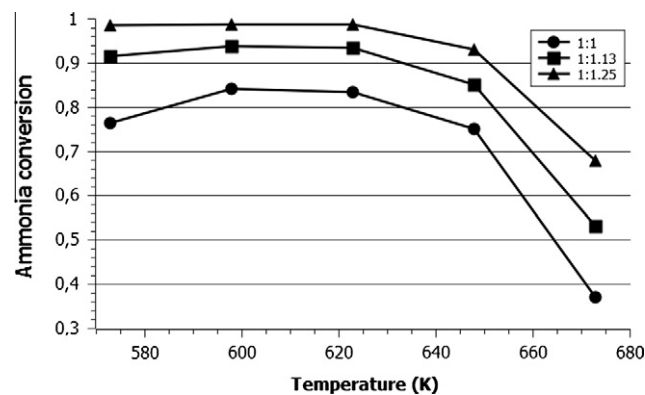

Fig. 6. Conversion of ammonia at different temperatures for three NH_3:NO_2 stoichiometries 1:1 (●), 1:1.125 (■) and 1:1.25 (▲) with the $V_2O_5/WO_3/TiO_2$ catalyst.
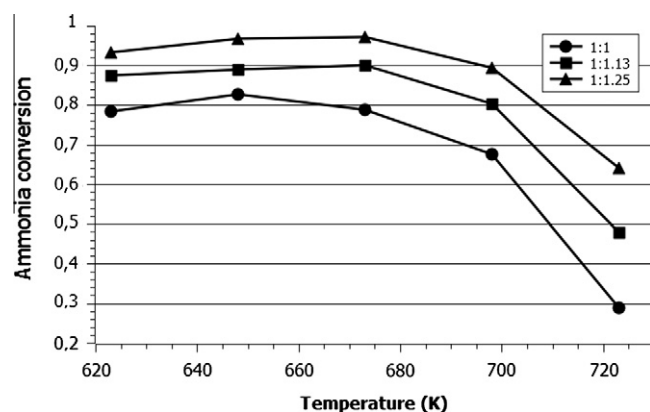

Fig. 7. Conversion of ammonia at different temperatures for three NH_3:NO_2 stoichiometries 1:1 (●), 1:1.125 (■) and 1:1.25 (▲) with the H-mordenite catalyst.
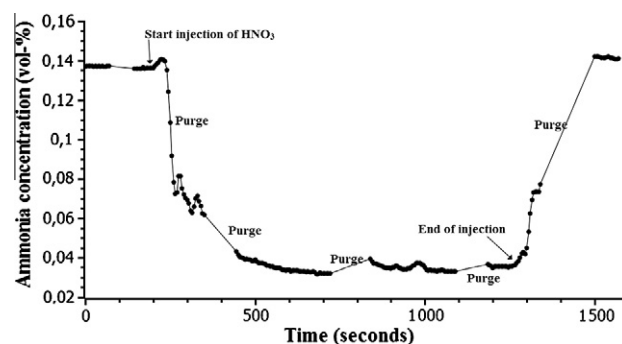

Fig. 8. Ammonia oxidation using NO_X generated from nitric acid.

amount of NO_X at the reactor outlet was measured at 623 K, and found to be to roughly 0.005 vol.% at a stoichiometry of 1:1, 0.005–0.01 vol.% at 1:1.125 and slightly above 0.01 vol.% at 1:1.25.

Fig. 7 shows the NH_3 conversion for the H-mordenite catalyst at different temperatures using bottled gas.

It can be seen by comparing Figs. 6 and 7 that the activity for H-mordenite is lower than the $V_2O_5/WO_3/TiO_2$ catalyst. The operating temperature of the H-mordenite catalyst is higher than for the $V_2O_5/WO_3/TiO_2$ catalyst and shows a peak in conversion at 673 K for the two higher stoichiometries. For the 1:1 stoichiometry the peak is at 648 K. NO_X was measured at the reactor outlet and

found to be approximately 0.001 vol.% at a stoichiometry of 1:1, 0.002 vol.% at 1:1.125 and 0.009 vol.% at a stoichiometry of 1:1.25 at a reactor temperature of 673 K.

3.3. Experiments with generated NO_X

The results of the ammonia oxidation experiment using NO_X generated from nitric acid are presented in Fig. 8. The experiment was run at 598 K using the $V_2O_5/WO_3/TiO_2$ catalyst.

Conversion using NO_X generated from nitric acid is somewhat lower than using the bottled gas at the same temperature as can be seen when comparing Figs. 8 and 5. The analyser purges discussed above are indicated in the figure.

4. Discussion

In this study it has been demonstrated that the concept of using NO_X to remove ammonia from synthesis gas produced from gasification is viable. Previous studies has shown that it is possible to remove ammonia from synthesis gas over a catalyst by injecting O_2, either alone or with NO, thus increasing the oxygen levels to a few vol.%. The increased oxygen level put those systems close to traditional SCR in terms of composition as it enables reaction (1). What has been shown here is a route that does not include O_2 which makes it a more efficient process, as less oxidation of the energy carriers (H_2 and CO) in the syngas occurs.

Hot gas ammonia removal is especially interesting for IGCC plants and plants using catalysts that are sensitive to ammonia such as those employed in methanol synthesis [33], FeCr water gas shift catalysts [34] and others, that may also be affected by ammonia. Apart from preventing catalyst poisoning, this method also has the benefit of not depositing all the ammonia in the scrubber liquid. If a catalytic converter is used for the conversion of tars and lower hydrocarbons, some of the ammonia will also be converted. Like hydrocarbon reforming, ammonia cracking over Ni-based catalysts is, sensitive to sulphur poisoning [35].

The fast SCR reaction must be much faster than the reduction of NO_X by H_2 and CO, in the gas phase and on the catalyst surface. A sufficient amount of the injected NO_X should survive in the gas long enough to react with the ammonia on the catalyst surface, without being converted into N_2. The NO/NO_X-ratio in the surviving portion should not exceed 50 vol.% to ensure that the reaction follows the fast SCR path.

Injecting an excess amount of NO_X into the gas to compensate for possible homogeneous or heterogeneous NO_X side-reduction by H_2 or CO prior the fast SCR step will not be a problem. An excess of NO_X in the gas also ensures a high degree of conversion of the adsorbed ammonia on the catalytic surface. If the residence time of the surplus NO_X in the hot gas is sufficiently long, it will be reduced to N_2.

However, it was not proven explicitly in this work that the ammonia was converted directly into nitrogen, since only total NO_X was measured. The only alternative product would be nitrous oxide (N_2O). Reducing conditions were used, with high concentrations of hydrogen and carbon monoxide, and several catalysts, for instance iron exchanged and natural zeolites, are known to either decompose or reduce N_2O with ammonia [36].

The reduction efficiency was lower using the NO_X generator than when using NO_2 from a gas bottle. The flow of NO_X from the generator was not as stable as that from the bottle, which was controlled by a mass flow controller, and there is thus a greater uncertainty in the amount injected. The gas provided by the generator will also contain some NO, and when the NO_X reaches the catalyst, the NO_2/NO_X ratio may be less favourable than in the case of pure NO_2. Another difference is that the NO_X provided by the generator also contains water. It was ensured that the amount was below the dew point at room temperature to avoid condensation in the sample lines and the ammonia analyser.

The lack, or the small amount, of water in the model gas used in these experiments is the main difference compared with a real synthesis gas, others being contaminants such as H_2S. The SCR reaction is not very dependent on the amount of water in the gas, and the activity and selectivity change only slightly [37]. However, the low water content had other effects, for example the deposition of elemental carbon on the metallic thermocouple and on the catalyst surface by the Boudouard reaction. This was, however, only observed when there was no ammonia in the system, indicating that the metal surface was blocked by ammonia preventing the formation of solid carbon.

The fresh vanadium catalyst was yellow in colour and became grey after use. There was little or no change in the BET surface area between the fresh and used vanadium-based catalyst, as can be seen from Table 1. The used H-mordenite catalyst showed a slightly smaller BET surface area (3.5%) and Langmuir surface area (2.8%) than the fresh. The conversion of ammonia was high for both SCR catalysts although they differ both chemically and structurally.

The model synthesis gas used here had high nitrogen content, resembling that produced by air-blown gasifiers. This also reduces the partial pressure of hydrogen. Higher partial pressures of hydrogen could increase the NO_2 reduction, necessitating higher stoichiometries between NO_X and NH_3.

5. Conclusions

Ammonia removal over traditional SCR catalysts in reducing environments by NO_2 injection has been shown to be a working concept using a model synthesis gas and two different kinds of catalysts and has several benefits compared to the traditional SCO using oxygen as oxidising agent. The lower amount of NO_2 required compared to oxygen is the most significant benefit as it reduces the oxidation of hydrogen that occurs with the addition of oxygen.

As NO_2 is only injected at stoichiometric amounts up to 1:1.25, or 0.05 vol.% above the ammonia level, only small amounts of hydrogen/carbon monoxide will be consumed by the homogeneous reduction of the remaining NO_X.

Injecting NO_2 into the gas will consume some hydrogen as NO_2 is reduced to NO, but the SCR reaction is very selective and the side reactions consume only marginal amounts of hydrogen. The selective oxidation of ammonia in a reducing environment such as a synthesis gas is not trivial, and care must be taken to limit the oxidation of hydrogen and carbon monoxide to preserve as much of the energy in the gas as possible.

The problem of generating the NO_2 must be addressed before large-scale oxidation of ammonia in synthesis gas can be undertaken. The experimental results show that NO_X generated in the lab was able to oxidise a considerable portion of the ammonia in the gas. The generated NO_X could contain some NO, as indicated by the higher amount of NO_X in the outgoing gas compared with the case using bottled N_2/NO_2.

It is well known that some SCR catalysts in oxidising environment, particularly catalysts using TiO_2 as support, are resistant towards or even promoted by, sulphur dioxide, SO_2, in the gas. Nevertheless, the catalysts are not necessarily resistant to hydrogen sulphide in reducing atmospheres.

Future work will include long-term testing of the catalysts in reducing environments to determine their stability and performance. The influence of water will also be investigated as will the effect of hydrogen sulphide.

In conclusion, the SCO system presented in this paper has been shown to be suitable for removing ammonia from a model synthesis gas, representing a gas produced from biomass, coal or other

hydrocarbon-containing feedstocks, except for the impurities found in those systems.

Acknowledgements

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