Postprint

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Citation for the original published paper (version of record):

Tuna, P., Brandin, J. (2013)
Selective catalytic oxidation of ammonia by nitrogen oxides in a model synthesis gas.
Fuel, 105: 331-337
http://dx.doi.org/10.1016/j.fuel.2012.08.025

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:
http://urn.kb.se/resolve?urn=urn:nbn:se:lnu:diva-23370
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\textsubscript{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\textsubscript{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\textsubscript{X} over a catalyst. The experiments were carried out in a model synthesis gas consisting of CO, CO\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2} and NH\textsubscript{3}/NO\textsubscript{X}. The performance of two catalysts, V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2} and H-mordenite, were evaluated. On-site generation of NO\textsubscript{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\textsubscript{X}.

Keywords: SCR; Synthesis Gas; V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2}, H-mordenite; Ammonia Removal; Selective Oxidation

1. Introduction

Synthesis gas, generated by natural gas reforming, or by gasification of heavy oils or other coal-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\textsubscript{2}), hydrogen (H\textsubscript{2}), water (H\textsubscript{2}O), methane (CH\textsubscript{4}), lower hydrocarbons (C\textsubscript{2-3}) and tars. If air is used as the oxidant, the gas will also contain large amounts of nitrogen (N\textsubscript{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 (H₂S), ammonia (NH₃), 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 CHPs, or for the production of synthesis gas, the ammonia levels in the producer gas typically range from 0.04 to 1.8 mol-% [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 NOₓ 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 H₂ and N₂, over a reforming catalyst (usually Ni-based) at high temperature (~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 is can be accomplished with selective catalytic oxidation (SCO) over a suitable catalyst. The ammonia is then oxidised to N₂ and H₂O. 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 H₂ is very low, compared to a real synthesis gas produced in a gasifier. In others [11-15], it is not clear if the process studied really is SCO or ammonia cracking driven by the temperature increase, caused by CO and H₂ 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 the injection of nearly equimolar amounts of ammonia into
the flue gas [16, 17]. The ammonia can be injected into the hot flue gas either as ammonia or as a urea solution [18].

Since the NO\textsubscript{X} in normal combustion flue gases consists of 90-95 % nitrogen monoxide (NO), and the rest being nitrogen dioxide (NO\textsubscript{2}), it is normally considered that the reaction over a solid catalyst, for instance V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2} [19] or an acidic zeolite [20], proceeds according to reaction 1.

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \tag{1}
\]

Oxygen (O\textsubscript{2}) participates in reaction 1, and in combustion flue gases the oxygen level is normally 2-10 mol-%. Without oxygen, the rate of reaction, or conversion, falls to relatively low values [21].

Reactions 2 and 3, given below, do not require any oxygen. Reaction 2 has a much higher reaction rate than reaction 1 and is thus called the fast SCR reaction[21].

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \tag{2}
\]

\[
6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \tag{3}
\]

As mentioned above, the proportion of NO\textsubscript{2} in the NO\textsubscript{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 oxidized to NO\textsubscript{2} [21] to improve low-temperature SCR performance and improve the oxidation of soot in the particulate filter [18].

If the opposite reaction is considered, i.e. the removal, \textit{inverse SCR} or selective catalytic oxidation (SCO), of ammonia in a gas stream by injection of NO\textsubscript{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\textsubscript{2} into hot synthesis gas [22]. 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 mol-% before the catalyst bed. In their patent, VTT
claims that the process can be used to reduce NOX 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 NO2 is injected into the producer gas, the ammonia can be selectively oxidized according to reaction 3. However, NO2 is not stable in this environment. It is well known that NOX is reduced by CO and H2, for instance CO is oxidised to CO2 and NOX is reduced to N2 by 3-way catalysts in automotive applications [23]. Before the introduction of NH3-SCR, hydrogen was used industrially to reduce NOX over precious-metal catalysts at low temperature. This has recently received increasing attention [24, 25]. 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. Material and Methods

Figure 1 shows a schematic illustration of the experimental set-up. The gases are supplied from gas bottles using mass-flow controllers. The CO, CO2, H2, and a mixture of 0.5 mol-% ammonia in N2, are mixed and injected in the top of the reactor. The NO2 is injected separately inside the reactor, approximately 50 mm above the catalyst. The NO2 is either supplied from a gas bottle with a mixture of 1.0 mol-% NO2 in N2 by a mass-flow controller or the NOX generator described below.

Figure 1. Experimental set-up used for selective ammonia oxidation. In experiments employing only NOX, the N2/NH3 is replaced by pure N2.
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 Figure 2.

![Figure 2. Enlargement of the reactor inlet and catalytic bed.](image)

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 Figure 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 mol-%. 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-minute 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 Figure 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: \( \text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2 \) 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 \( \text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2 \) 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 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 \( \text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2 \) 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 [26], 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 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 [27]. The desorption isotherm was used for the analysis and the results are presented in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Results of the BET analysis for the catalysts used.</th>
</tr>
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<tbody>
<tr>
<td></td>
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<tr>
<td>----------------</td>
</tr>
<tr>
<td>BET surface area (m(^2) g(^{-1}))</td>
</tr>
<tr>
<td>Langmuir surface area (m(^2) g(^{-1}))</td>
</tr>
<tr>
<td>Desorption surface area of pores (m(^2) g(^{-1}))</td>
</tr>
<tr>
<td>Micropore area (m(^2) g(^{-1}))</td>
</tr>
<tr>
<td>Desorption volume of pores (cm(^3) g(^{-1}))</td>
</tr>
<tr>
<td>Micropore volume (cm(^3) g(^{-1}))</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
</tr>
</tbody>
</table>
2.2 NO\textsubscript{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 AGM ammonia gas monitor, water was excluded. Since the gas is explosive when mixed with air, a normal chemiluminescence NO\textsubscript{X} meter could not be used, and the nitrogen oxide level was measured as a total NO\textsubscript{X} level using two different Dräger short-term tubes (2-100·10\textsuperscript{-4} and 0.01-0.5 mol-% NO\textsubscript{X}) [28]. These tubes are for total NO\textsubscript{X} and do not indicate the ratio of NO\textsubscript{2}/NO\textsubscript{X}.

Table 2. Gas composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (vol-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2} or (N\textsubscript{2}/NH\textsubscript{3})</td>
<td>65</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>11</td>
</tr>
<tr>
<td>CO</td>
<td>13</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>11</td>
</tr>
<tr>
<td>NO\textsubscript{X}</td>
<td>0.02</td>
</tr>
</tbody>
</table>

NO\textsubscript{X} was measured at the reactor outlet when the reactor was empty, and when it was filled with each of the catalysts, V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2} or H-mordenite. At lower concentrations the accuracy for the 0.01-0.5 mol-% NO\textsubscript{X} Dräger tubes was insufficient. The gas was sampled and diluted 20:1 and the lower range 2-100·10\textsuperscript{-4} mol-% Dräger tubes was used to give a more accurate reading. No NH\textsubscript{3} was present in the NO\textsubscript{X}-only experiments and pure N\textsubscript{2} was used instead of the N\textsubscript{2}/NH\textsubscript{3} mix.

2.3 Ammonia Oxidation in Reducing Environments

The effect of water in ordinary SCR is limited [18], but the lack of water in the gas will affect the equilibrium in some reactions such as the Boudouard reaction (4) since the formed carbon will not be consumed by steam according to reaction 5.

\[
2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad (4)
\]

\[
\text{H}_2\text{O} + \text{C} \leftrightarrow \text{CO} + \text{H}_2 \quad (5)
\]
At the higher temperatures lower amounts of ammonia was measured which could indicate dissociation of ammonia according to reaction 6.

\[ 2\text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2 \]  \hspace{1cm} (6)

The NO\textsubscript{2} is injected as a mixture of NO\textsubscript{2} in N\textsubscript{2} containing 1 mol-% NO\textsubscript{2}. The gas flow was 1.6 Ndm\textsuperscript{3}/min for the model synthesis gas and N\textsubscript{2}/NO\textsubscript{2} contributed an additional 0.4-0.5 Ndm\textsuperscript{3}/min depending on stoichiometry between NH\textsubscript{3} and NO\textsubscript{2}. The gas hourly space velocity for the V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2} catalysts was 210 000 h\textsuperscript{-1} and for the H-mordenite 75 000 h\textsuperscript{-1}.

2.4 NO\textsubscript{2} Generation

In a full-scale plant, the NO\textsubscript{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 reaction 7.

\[ 4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (7)

Nitric acid can also be reacted with copper or iron to form nitrogen oxides according to reactions 8 and 9 [29].

\[ \text{Fe} + 4\text{H}^+ + \text{NO}_3^- \rightarrow \text{Fe}^{3+} + \text{NO} + 2\text{H}_2\text{O} \]  \hspace{1cm} (8)

\[ \text{Fe} + 6\text{H}^+ + 3\text{NO}_3^- \rightarrow \text{Fe}^{3+} + 3\text{NO}_2 + 3\text{H}_2\text{O} \]  \hspace{1cm} (9)

It is commonly known that concentrated nitric acid yields high NO\textsubscript{3}/NO\textsubscript{X} ratios and that the reactions occur fast when heated. A small NO\textsubscript{X} generator was built in the lab to test the feasibility of ammonia oxidation using NO\textsubscript{X} generated on-site. The generator is illustrated in Figure 3.

The NO\textsubscript{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\textsuperscript{3}/min which corresponds roughly to a stoichiometry of 1:2 for NH\textsubscript{3}:NO\textsubscript{2}, assuming 100 % conversion from HNO\textsubscript{3} to NO\textsubscript{2}.
The NO\textsubscript{X} generated by the NO\textsubscript{X} generator was strongly coloured yellow to brown, indicating the presence of NO\textsubscript{2}.

### 3. Results

#### 3.1 NO\textsubscript{X} Reduction in the Model Synthesis Gas

The results of NO\textsubscript{X} reduction in synthesis gas without ammonia present are shown in Figure 4. The reading error of the Dräger tubes was estimated to ±10% of the value. The error bars are given in Figure 4.

![Figure 4. NO\textsubscript{X} levels with the empty reactor (●) and the two catalysts V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2} (■) and H-mordenite (▲) with an inlet NO\textsubscript{2} level of 0.2 vol-%.](image)

As can be seen in Figure 4, the homogenous gas phase reduction (empty reactor) of NO\textsubscript{2} to N\textsubscript{2} is slower than with a catalyst. The measurements show the total NO\textsubscript{X}, the NO\textsubscript{2}/NO\textsubscript{X} ratio is not known. H-mordenite is more effective at reducing NO\textsubscript{X} at temperatures above 573 K than the V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{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\textsubscript{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 NO₂

Figure 5 shows the result from a typical experiment using NO₂ from a gas bottle. The N₂/NO₂ was added to the stream when the ammonia concentration was just below 0.2 mol-%.

![Graph showing ammonia concentration at the outlet using the V₂O₅/WO₃/TiO₂ catalyst and bottled gas at 598 K.]

When the injection of NO₂ starts, the ammonia concentration falls to a value of about 0.034 mol-%. The NH₃:NO₂ stoichiometry was increased to 1:1.125 and the outlet concentration falls to 0.015 mol-%. The final stoichiometry of 1:1.25 gives a gas with only 0.005-0.006 mol-% ammonia at the reactor outlet. The N₂/NO₂ 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 [30], for each point. The maximum margin of error in the inlet molar ratio was 12 10⁻⁴ mol-% (2000 10⁻⁴ mol-% inlet) and 4 10⁻⁴ mol-% (96110⁻⁴ mol-% 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:

\[ \text{Conv} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \]  

(11)
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 [31].

\[ E_f = \left| \frac{df(x,y)}{dx} \right| E_x + \left| \frac{df(x,y)}{dy} \right| E_y \]  

(12)

In our case, \( E_f \) is the error of margin of the conversion, \( \frac{df(x,y)}{dx} \) 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 \( \text{NH}_3 \) and \( \text{NO}_x \).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Conversion (%)</th>
<th>Margin of error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>76.2</td>
<td>0.1</td>
</tr>
<tr>
<td>598</td>
<td>83.6</td>
<td>0.2</td>
</tr>
<tr>
<td>623</td>
<td>83.1</td>
<td>0.1</td>
</tr>
<tr>
<td>648</td>
<td>77.5</td>
<td>0.1</td>
</tr>
<tr>
<td>673</td>
<td>54.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The maximum margin of error in the conversation at \( \text{NH}_3:\text{NO}_x \) 1:1 is less than 0.5%. (with 54.3 % conversion at 673K). 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.

Figure 6 shows the conversion of \( \text{NH}_3 \) for the \( \text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2 \) catalyst using bottled gas at different temperatures. As can be seen in Figure 6, conversion over the \( \text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2 \) catalyst is high up to 623 K after which it starts to decline. The total amount of \( \text{NO}_x \) at the reactor outlet was measured at 623 K, and found to be to roughly 0.005 mol-% at a stoichiometry of 1:1, 0.005-0.01 mol-% at 1:1.125 and slightly above 0.01 mol-% at 1:1.25.
Figure 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$_2$O$_5$/WO$_3$/TiO$_2$ catalyst.

Figure 7 shows the NH$_3$ conversion for the H-mordenite catalyst at different temperatures using bottled gas.

Figure 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.
It can be seen by comparing Figures 6 and 7 that the activity for H-mordenite is lower than the V$_2$O$_5$/WO$_3$/TiO$_2$ catalyst. The operating temperature of the H-mordenite catalyst is higher than for the V$_2$O$_5$/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 mol-% at a stoichiometry of 1:1, 0.002 mol-% at 1:1.125 and 0.009 mol-% 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 Figure 8. The experiment was run at 598 K using the V$_2$O$_5$/WO$_3$/TiO$_2$ catalyst.

![Figure 8. Ammonia oxidation using NO$_X$ generated from nitric acid.](image)

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 Figures 8 and 5. This is probably because the generated NO$_X$ contains both NO$_2$ and NO. 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. This is especially interesting for IGCC plants and plants using catalysts that are sensitive to ammonia such as those employed...
in methanol synthesis [32], FeCr water gas shift catalysts [33] and other catalysts, such as for FT synthesis, 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 [34]. The conversion of ammonia was high with both the SCR catalysts although they differ both chemically and structurally.

The fast SCR reaction must be much faster than the reduction of NO\textsubscript{X} by hydrogen and CO, in the gas phase and on the catalyst surface. A sufficient amount of the injected NO\textsubscript{X} should survive in the gas long enough to react with the ammonia on the catalyst surface, without being converted into N\textsubscript{2}. The NO/NO\textsubscript{X}-ratio in the surviving portion should not exceed 50 mol-% to ensure that the reaction follows the fast SCR path.

Injecting an excess amount of NO\textsubscript{X} into the gas to compensate for possible homogeneous or heterogeneous NO\textsubscript{X} side-reduction by H\textsubscript{2} or CO prior the fast SCR step will not be a problem. An excess of NO\textsubscript{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\textsubscript{X} in the hot gas is sufficiently long, it will be reduced to N\textsubscript{2}.

However, it was not proven categorically in this work that the ammonia was converted directly into nitrogen, as we were only able to measure total NO\textsubscript{X}. The only alternative product would be nitrous oxide (N\textsubscript{2}O). 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\textsubscript{2}O with ammonia [35].

The reduction efficiency was lower using the NO\textsubscript{X} generator than when using NO\textsubscript{2} from a gas bottle. The flow of NO\textsubscript{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\textsubscript{X} reaches the catalyst, the NO\textsubscript{2}/NO\textsubscript{X} ratio may be less favourable than in the case of pure NO\textsubscript{2}. Another difference is that the NO\textsubscript{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$_2$S. The
SCR reaction is not very dependent on the amount of water in the gas, and the activity and
selectivity change only slightly [36]. 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 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 than the fresh (3.5%).

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 mol-% 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\textsubscript{2} must be addressed before large-scale oxidation of ammonia in synthesis gas can be undertaken. The experimental results show that NO\textsubscript{X} generated in the lab was able to oxidize a considerable portion of the ammonia in the gas. The generated NO\textsubscript{X} could contain some NO, as indicated by the higher amount of NO\textsubscript{X} in the outgoing gas compared with the case using bottled N\textsubscript{2}/NO\textsubscript{2}.

It is well known that some SCR catalysts in oxidising environment, particularly catalysts using TiO\textsubscript{2} as support, are resistant towards or even promoted by, sulphur dioxide, SO\textsubscript{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 synthesis gas produced from biomass, coal or other hydrocarbon-containing feedstocks.

**Acknowledgements**

The authors gratefully thank financial support from the European Commission in the framework of the FP7 Integrated Project “GreenSyngas” (Project NO. 213628). The authors also thank the Swedish Energy Agency (STEM), E.ON Sweden, Statoil Gas AS and Swedish Gas Center (SGC) for their financial support.
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