



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

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### HIGHLIGHTS

- ▶ Gas phase removal of ammonia from synthesis gas is evaluated.
- ▶ Selective oxidation of ammonia in synthesis gas is possible with addition of NO<sub>x</sub>.
- ▶ V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> and H-mordenite SCR catalyst perform well in reducing environments.
- ▶ On-site generation of the necessary NO<sub>x</sub> is possible by nitric acid decomposition.

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### 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<sub>x</sub>) 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<sub>x</sub> 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<sub>x</sub> over a catalyst. The experiments were carried out in a model synthesis gas consisting of CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub>/NO<sub>x</sub>. The performance of two catalysts, V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> and H-mordenite, were evaluated. On-site generation of NO<sub>x</sub> 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<sub>x</sub>.

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### 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<sub>2</sub>), hydrogen (H<sub>2</sub>), water (H<sub>2</sub>O), methane (CH<sub>4</sub>), lower hydrocarbons (C<sub>2–3</sub>) and tars. If air is used as the oxidant, the gas will also contain large amounts of nitrogen (N<sub>2</sub>). 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<sub>2</sub>S), ammonia (NH<sub>3</sub>), alkali and chloride such as potassium chlo-

ride (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<sub>x</sub> 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<sub>2</sub> and N<sub>2</sub>, 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].

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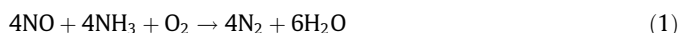
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The removal of ammonia from air or any other oxygen containing gas can be accomplished with selective catalytic oxidation (SCO) over a suitable catalyst. The ammonia is then oxidised to  $N_2$  and  $H_2O$ . Much research has been published in this 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.

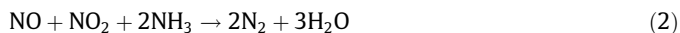
Selective catalytic reduction (SCR) is an industrial process for the removal of nitrogen oxides from combustion flue gases, by injection of nearly equimolar amounts of ammonia into the flue gas [17,18]. The ammonia can be injected into the hot flue gas either as ammonia or as a urea solution [19].

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:



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].



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  $\gamma$ -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  $2.5 \times 10^{-3}$  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.

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