High temperature and high concentration SCR of NO with NH$_3$: Application in a CCS process for removal of carbon dioxide

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Abstract

In this study we investigated a number of commercial SCR catalysts (A to E) for the application in a high temperature (about 525 °C) and high concentration (5000 ppm NO) system in combination with a CO$_2$ capture project. A very important property of the catalyst in this system is its thermal stability. This was tested under dry conditions and modeled with the general power law model using second order decay of the BET surface area with time. Most of the materials did not have a very high thermal stability. It is likely that the zeolite based materials could be used but they too need improved stability. The SCR activity and the possible formation of the byproduct N$_2$O was determined by measurement in a fixed bed reactor between 300 and 525 °C. All materials showed activity high enough for a design of 96 % conversion in the first of the twin SCR reactor system proposed. The amount of catalyst needed vary a lot and are much higher for the zeolithic materials. The formation of N$_2$O was increased with temperature for almost all materials but the zeolithic ones. The selectivities for N$_2$ production at 525 ^{o}C was 98.6 % for the best material and 95.7 % for the worst at 1000 ppm NO in the inlet. At 500 ppm NO the values were much better i.e. 98.3 and 99.9 % respectively. The stoichiometry was determined at 400 °C for catalyst A and followed the standard SCR reaction.

Keywords:

High Temperature SCR

High concentration SCR

Thermal stability

Commercial catalysts

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1. Introduction

The reduction of NO_x from flue gases via catalytic reduction using e.g. ammonia as a reagent is today considered an established technology, selective catalytic reduction of NO_x (SCR). The catalysts used for this reaction under normal operating conditions, such as for cleaning up combustion gases in association with electricity production, are normally vanadia based [1-4] albeit noble metals (amongst the first ones used) [5-9] and zeolite types [10-14] have been suggested. The catalysts used have different properties with respect to performance as a function of temperature, with the noble metal catalysts more active in the lower temperature region, the vanadia-based catalysts in the medium temperature region and the zeolite-type catalysts in the higher region [2].

The use of SCR is traditionally associated with large scale combustion of oil, gas, coal and to some extent biomass with levels ranging from 100-700 ppm in the flue gas [3]. However, there has been an increased interest in the on-board SCR reaction, using hydrocarbons or urea as the reducing agent, with the advent of more stringent emission regulations in the EU and US [15]. There are most often three positions in a large scale combustion process where SCR is placed; either directly after the combustion chamber (high-dust position), after a flue gas filtration step (low-dust position) or after flue-gas treatment with respect to sulphur and water (tail-end position) [3]. There is an inherent energy saving in performing the SCR reaction in either the high of low dust positions, but with one drawback: the monoliths used will have to have a lower channel-per-square-inch number to allow for dust to pass through the system without building up pressure drop. This means that more catalysts will have to be used to achieve the desired reduction of NO_x compared to the dust-free situation. A tail-end process will operate in a no-dust environment, but there is a substantial energy loss involved in increasing the temperature of the now cold gas to the desired reaction temperature.

However with the advent of new methods of power production such as Oxyfuel combustion, as well as in niche applications, there is a need for treating effluent streams with higher concentrations of NO_x.

Out of the niche applications, nitric acid plants, cement calcination and FCC catalyst regeneration may result in NO_x levels in the 1 000 - 2 000 ppm range [3].

2. Analysis of the SCR requirements in the Oxyfuel process

In the use of Oxyfuel combustion, where nitrogen is removed prior to combustion and flue gases recirculated, high levels of NO_x can be achieved. This is particularly true after compressing the resulting CO_2 where in the compressor vent-gas stream levels are estimated to surpass 10 000 ppm.
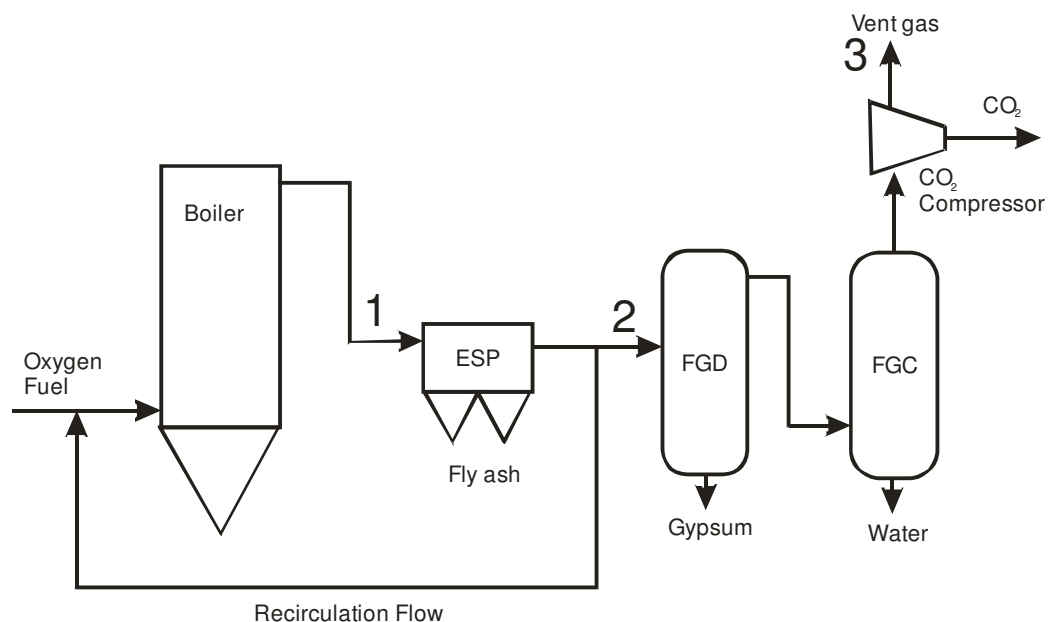
Figure 1. Schematics of an Oxyfuel process

In figure 1 a schematic representation of an Oxyfuel process is given. There are four locations possible to fit a SCR unit for removing the NO_x from the flue gas:

1) The high dust position after the boiler but before the ElectroStatic Precipitation filter (ESP).

2) The low dust position after the flue gas split but before the Flue Gas desulphurization unit (FGD).

3) In the vent-gas stream after the compressor.

The layout and data used in this study was provided by a planned industrial plant in Europe. In this case, none of the gas streams 1-3 has sufficiently high temperatures to perform a SCR operation with ammonia. To obtain sufficient temperature, the flue gas has to be heated. In Table 1 the power required to heat the streams to 300°C, without heat recuperation have been calculated.

Table 1. The required power to heat each stream to SCR operating conditions.

Stream #	Mass flow (kg/s)	Inlet temp (°C)	Outlet temp (°C)	Required power (MW)
1	924	182	300	126
2	311	100	300	70
3	16	148	300	2.3

Disregarding the lack of temperature to facilitate the SCR reaction, the catalytic reactor size requirements can be analysed. If an appropriate NO_x conversion is assumed (approximately 90 % of the NO_x content in the flue gas), the actual catalyst volume of the fictive SCR reactor can be calculated using the appropriate space velocity (depending on the process configuration). The Gas Hourly Space Velocity (GHSV) required is assumed to be 3 000 h^{-1} for high dust, 6 000 h^{-1} for low dust and 8 000 h^{-1} for tail end. These assumptions, together with a gas density of 1.5 kg/Nm^3, give the results in Table 2.

Table 2. Estimated catalyst volume.

Stream #	configuration	GHSV (h^{-1})	Catalyst volume (m^3)	Equivalent cube side (m)
1	High dust	3 000	739	9.0
2	Low dust	6 000	124	5.0
3	Tail end	8 000	4.4	1.6

The vent gas stream, position 3, will need heating though, but as will be shown below; the heat released during the SCR reaction with high concentration of NO_x makes the process autothermal.

To eliminate the high concentration of NO_x present in the vent gas stream, a twin bed SCR unit with adiabatic operation is proposed. This paper investigates the theoretical possibilities for positioning such a purification step using process simulations. After selecting the proper type of plant setup, a number of commercial catalysts have been screened for their performance under high temperature, and high concentration conditions. The catalysts have been tested for activity and side formation of N_2O. They have also been characterised using BET to elucidate the impact of long term high temperature (525 °C) exposure. The impact of elevated levels of CO_2 in the reaction gas mixture has also been studied.

3. Process Simulations

The twin bed process has been simulated using the Aspen plus® software and there is a few features that stand out; the gas composition and other parameters used in the simulations can be viewed in Table 3.

Table 3. Gas composition and other parameters used for simulations.

Gas Components	Concentration (% by volume)
NO_2	0.1
NO	1.8
N_2	41.9
O_2	14.3
Ar	4.4
CO_2	37.6
Parameters	
Inlet temperature	150 °C
Operating pressure	2 bar(g)
Flow rate	15.5 kg/hr

$$4\ NO + 4\ NH_3 + O_2 => 4\ N_2 + 6\ H_2O \qquad \Delta H = \text{-408 kJ/mol NO} \qquad \text{reaction 1}$$
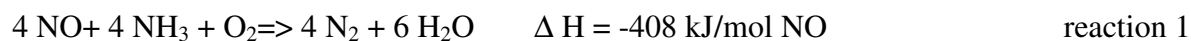
The most important feature is the amount of heat that is released by reaction1. In normal flue gases from combustion plants, the NO_x levels are in the range of 100-1000 ppm by volume. These levels give adiabatic temperature increases of 1 to 10 °C by the heat of reaction. However, in the case with NO_x concentrations of 1.9 vol. %, there will be an adiabatic temperature increase of 180 °C at the desired degree of conversion (96%). The gas is also dry; after the compressor the water content is very low. However, after the injection of the ammonia water solution, the process gas will contain approximate 5 vol. % water.

By utilizing this temperature increase, the process should be able to be operated autothermally. A simplified process flow diagram with the simulation results is depicted in Figure 2.
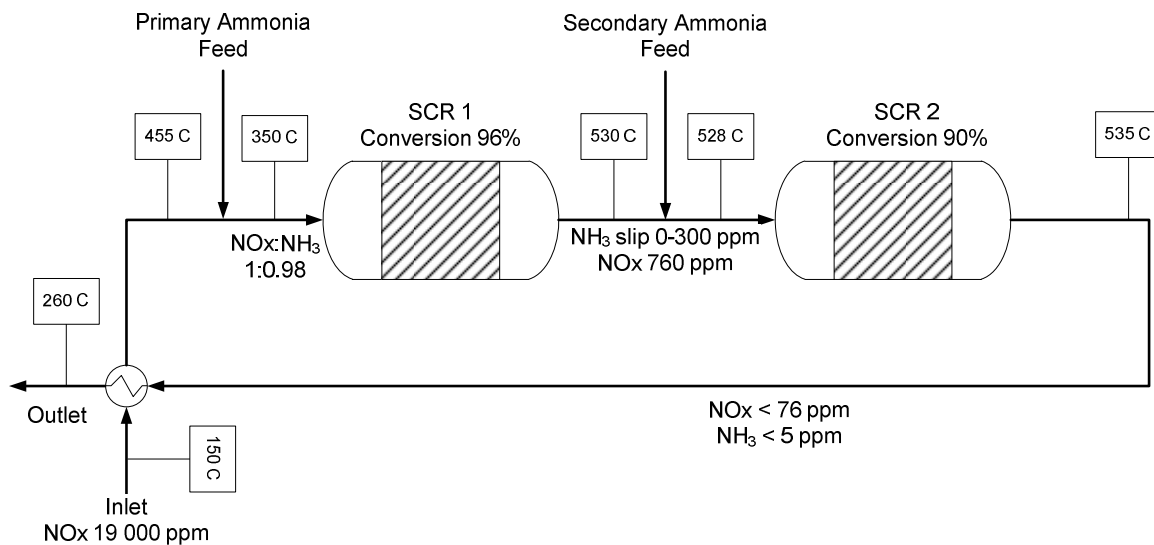
Figure 2. Process flow diagram with temperatures and simulated conversions.

As can be viewed in the figure, the process is envisioned as a two-step process with heat recuperation. The inlet feed enters at about 150 °C and passes through a heat exchanger. This heat exchanger increases the temperature of the stream to 455 °C, using the heat in the stream exiting the two stage SCR system. In the first stage primary ammonia is dosed in an ammonia-to-NO_x ratio of 0.98. Before entering the first reactor, the dosed ammonia (25 % solution in water) is vaporized and the temperature of the stream drops to 350 °C. The NO_x is then converted by 96 % in the first reactor, leaving a slip of NO_x of about 800 ppm and some ammonia depending on the selectivity. However the most marked feature is that the exit temperature is 530 °C.

A second reactor has been added to the system as a polishing step, reducing the reminder of NO_x by a secondary ammonia feed, converting NO_x to 90 %. This yields an exit temperature of 535 °C which is used to heat the incoming stream before the gas is released to ambient. This secondary polishing reactor operates under more traditional conditions, albeit the temperature is much higher than traditionally. The fact that the system operates auto-thermally, at least according to the process simulations, makes the reactor system suitable as a

tail-end application. The system will however require catalysts especially suited for the relatively high operating temperature since normal, vanadia-based, catalysts lose their selectivity via ammonia oxidation at about 425 °C [16].

4. Experimental Procedure

4.1 Equipment

For the investigation of the various catalysts, an experimental setup has been constructed, which can be viewed in Figure 3.
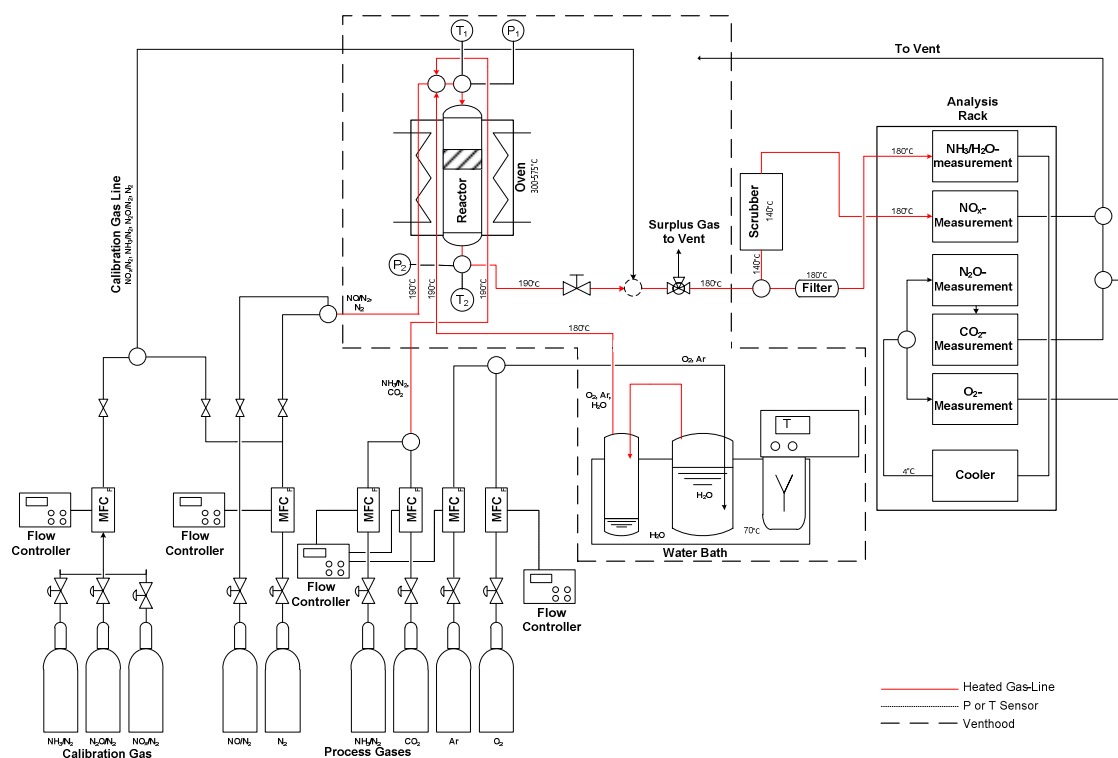

Figure 3. The setup used in the experimental part of the work.

The gases (Strandmöllen A/S) are fed from gas bottles to the reactor using a series of Bronkhorst High-Tech B.V. mass-flow controllers. Ammonia and NO are supplied in bottles with concentrations of 30 % in nitrogen. The moisture to the system is added by passing Ar and O_2 through a tempered water bath to achieve the correct moisture level of the inlet gas.

The moist Ar/O_2-mixture, the mixture of NH_3/CO_2 and the mixture of NO/N_2 are conveyed to the reactor in individual gas lines, preheated inside the reactor oven and mixed in a heated mixer close to the reactor inlet. All inlet gas lines are heat traced to 180 °C to avoid condensation and gas phase reactions. The SCR reaction is performed in a stainless steel reactor with an inner diameter of 8 mm. The outlet gas is analyzed with respect to NH_3, H_2O, NO, N_2O, CO_2 and O_2. The reactor is positioned within an oven that heats the reactor to the desired temperature. The NH_3 and H_2O analysis was performed using laser photometry with a SICK GME 700 and the O_2 was measured using a paramagnetic instrument named PMA 30 from M&C. The N_2O and CO_2 measurements were both performed using NDIR detection, albeit with two different instruments, one SICK/SIDOR IR and one Fuji Electric Systems Co. ZRE Gas Analyzer, whilst NO was measured using a ECO PHYSICS CLD 700 RE ht chemiluminescense instrument.

The reactor is in itself 465 mm long and the catalyst bed is positioned 135 mm from the inlet, which is at the top of the reactor. A thermocouple is placed just before the catalyst bed which is supported on quartz wool and is normally 30 mm or sometimes 10 mm high. Another thermocouple is positioned just after and in contact with the bed measuring the outlet temperature. To avoid condensation of potential products such as ammonium nitrate/nitrite, all sampling lines are insulated and heated to 190 °C. The gas is scrubbed with phosphoric acid before entering the NO_x analysis instrument. The use of stainless steel as a reactor material is not preferred in the case of SCR catalyst testing due to its ability to oxidize ammonia at higher temperatures. However, the use of a quarts reactor is impractical which is why the inside of the used reactor was plated with gold prior to use lowering the ammonia oxidation to acceptable levels (about 1.5 % at 405 °C) in an empty reactor.

4.2 Catalysts used

In all, 8 different catalysts were obtained from commercial suppliers and a development company. A preliminary test for thermal stability by heating in air in Pt crucibles at 525 °C for 15 h showed one of the materials to be unsuitable because of heavy sintering to 14 % of the initial surface area. The catalysts chosen for the investigation are denoted A-E. The full monoliths and the pellets were crushed and sieved to get a useful fraction (0.71-0.80 mm) for testing. Such large particles were used in order not to obtain a disturbing pressure drop. 1.5 ml of catalyst was used in most experiments for the testing. Catalyst A was also tested with 0.5 ml catalyst.

4.3 Activity and selectivity measurements

At the start of the project the concentration of NO_x in the vent gas stream was assumed to be about 2 %. Later the range in which NO_x could be expected was changed to 0.5 - 2 %. Therefore, and also because of experimental difficulties in measuring higher values, the lower value was chosen as the high concentration alternative in the experiments. Most of the catalysts have been subjected to a low (1 000 ppm NO) and a high (5 000 ppm NO) concentration test at a stoichiometry of 1.1 or a 10 % surplus of ammonia. The space velocity (SV) was 120 000 h^{-1} unless otherwise noted. NO_x was represented as NO only to make the comparison of catalyst materials the worst case scenario since the standard SCR reaction is slower than the fast SCR one (equal amounts of NO and NO_2) [17]. The composition of the gas used for the experiment with CO_2 was as follows: CO_2 34.33, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 43.34 mol. %. In addition, the gas contained NO and NH_3 reported separately below. In the experiments without CO_2, the composition was similar to the one used above (H_2O 5.03, Ar 4.02, O_2 13.06), however the N_2 was 76.83 mol. %. The total gas flow was 3

l_{NTP}/min in all instances and the pressure at the reactor outlet was 1.2 bar. The catalysts were tested in the SCR reaction between 325 and 525 °C at intervals of 25 °C. The activity was measured at steady state.

In some of the comparisons given below a rate constant for the reduction of NO by the standard SCR reaction is calculated from the following mass balance for an isothermal catalytic bed reactor:

$$dV/(Q_{in}*CNO_{in}) = dx/(-k*CNO_{in}*(1-x))$$

Where V is the volume of catalyst, Q_{in} is the volumetric total flow, CNO_{in} is the concentration of NO in the inlet to the reactor, x is the conversion of NO, and k is the rate constant. The rate constant is given in arbitrary units on the recommendation of the catalyst suppliers.

4.4 Thermal treatment

The thermal treatment of the catalysts was performed in order to test their stability at the expected operating conditions (525 °C, see above). It was performed with about 0.5 g of catalyst in Pt crucibles placed in an oven. The atmosphere was air. Samples were sintered for various lengths of time ranging from 15 to 777 h. At the 777 h treatment porcelain ships were used instead since they produced much lower scatter in data than the Pt crucibles. The time dependency of the surface area of sintered materials can be represented by the general power law equation (GPLE) [18].

$$dS/dt = - k*(S-S_{eq})^2$$

S is the surface area at time t, k is the sintering rate constant, and S_{eq} is the equilibrium surface area reached at infinitive time. A high value of S_{eq} and a low value of k are warranted for the materials which should be used in our process. The values of the parameters k and S_{eq} were determined from areas versus time data from the sintering experiments using the program Scientist 3.0.

4.5 Catalyst characterization

4.5.1 Catalyst surface area by N_2 physisorption

All materials were analyzed for changes in their BET surface area measured by adsorption of nitrogen at liquid nitrogen temperature using a Micromeritics ASAP 2400 instrument after degassing for 16 h at 350 °C. Pore volume analysis was performed using the BJH method [19]. The Halsey formula [20] was used for calculation of the thickness of the adsorbed layer (t value). The desorption isotherm was use for the analysis.

5. Results

5.1 Effect of CO_2

In the application of the SCR process in the vent-gas steam of the compressor in the CCS (Carbon Capture and Sequestration) process, the gas composition is far from what is normal in flue gases. The concentration of NO_x may be in the 0.5 to 2 % range and the content of CO_2 is over 30 %. Thus a study of the effect of CO_2 on the SCR reaction is warranted. Our experiments were performed at low concentration (1 000 ppm NO, 1 100 ppm NH_3) simulating the conditions in the second reactor of the proposed system. Temperatures reported are always given as measured directly after the catalyst bed.
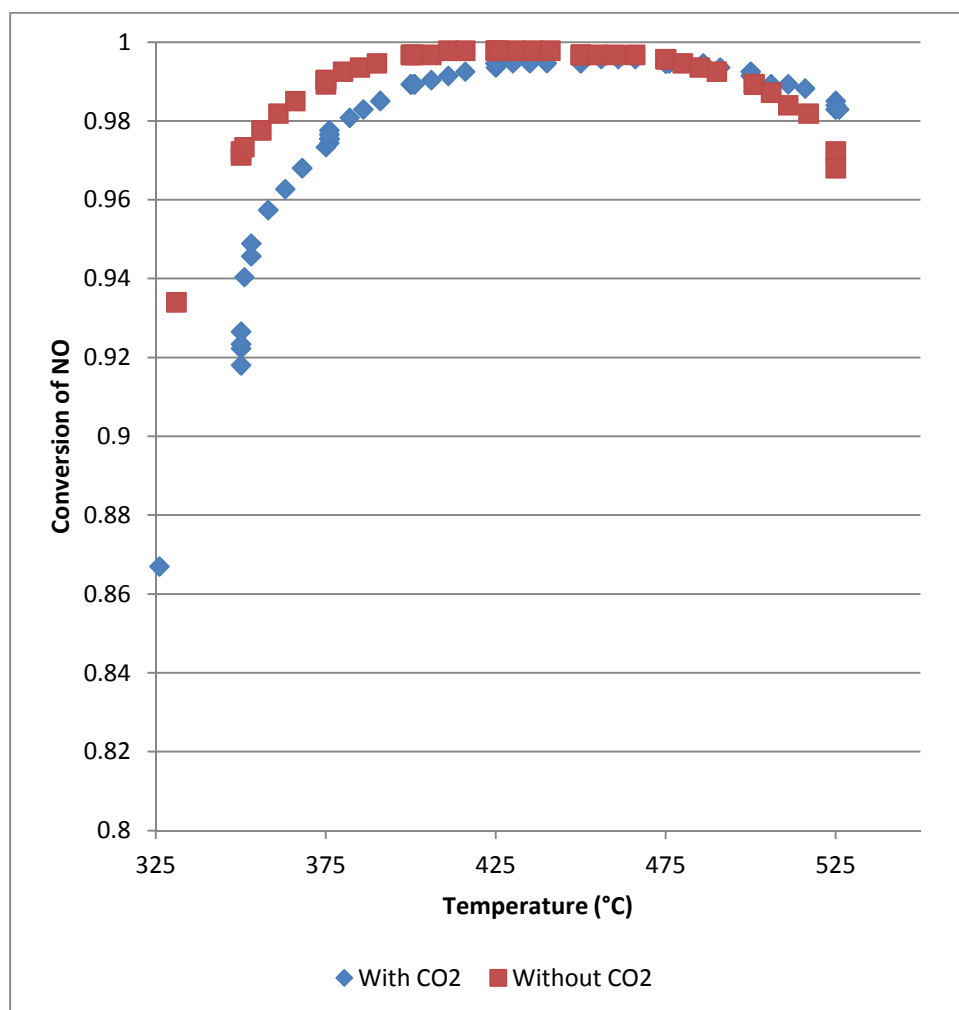
Fig. 4. The effect of CO_2 on the conversion of 1 000 ppm NO by 1 100 ppm NH_3 at various temperatures for 1.5 ml of catalyst A, SV 120 000 h^{-1}, 1.2 bar, CO_2 34.33 or 0, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 43.34 or 77.67 mol. %, 3 l$_{NTP}$/min.

The effect of CO_2 was investigated for the most active catalyst (A). Figure 4 shows seemingly small differences in the conversion especially above 98 % conversion and perhaps some shifting of the conversion upwards in temperature, but the changes are seemingly rather small. Later experiments were performed without CO_2 present because of its supposed little influence on the conversion of NO, but mainly because of problems regulating its inlet flow.
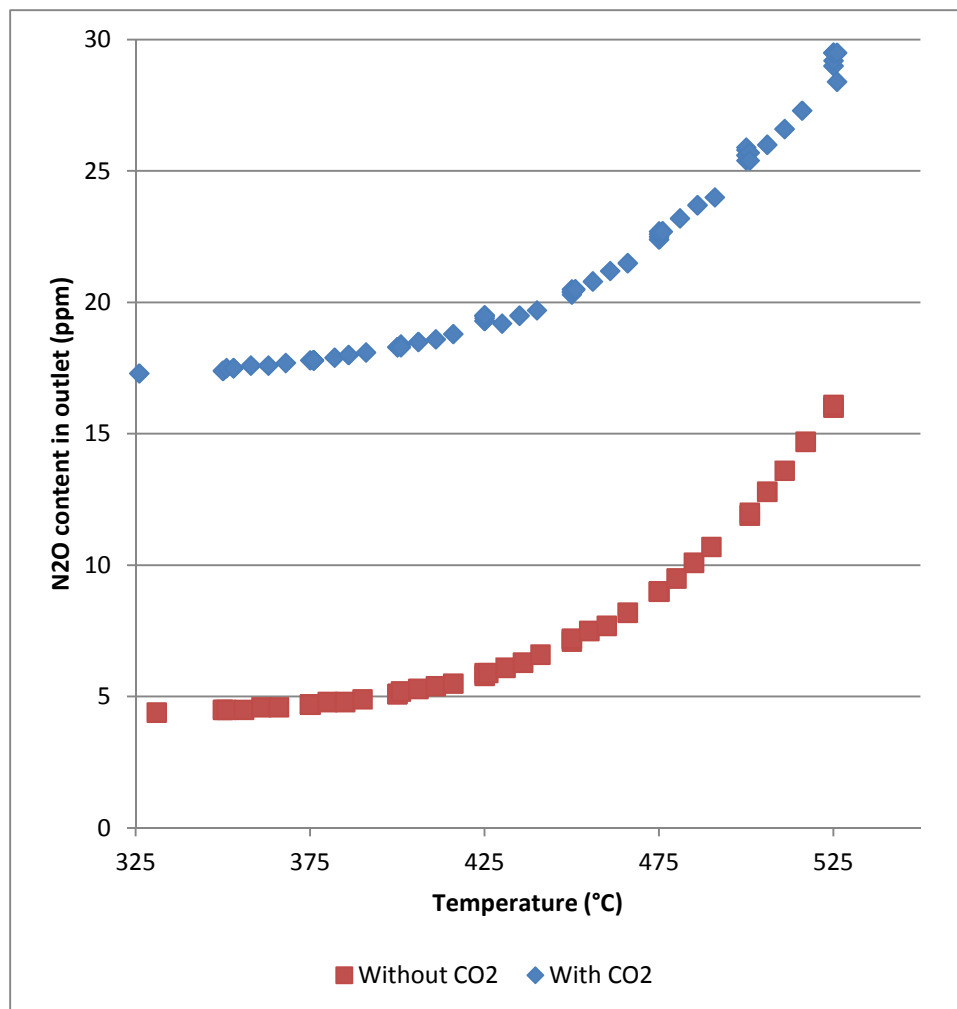
Fig. 5. The effect of CO_2 on the content of N_2O in the outlet from the reactor at various temperatures for 1.5 ml of catalyst A, 1 000 ppm NO, 1 100 ppm NH_3, SV 120 000 h^{-1}, 1.2 bar, , CO_2 34.33 or 0, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 43.34 or 77.67 mol. %, 3 l_{NTP}/min.

The effect of CO_2 on the measurements of N_2O is on the other hand clear (Fig. 5). A large contribution of CO_2 (34.33 % CO_2 in the gas used) is seen in the values of N_2O measured. Thus there seems to be a cross sensitivity of the SIDOR instrument to CO_2. This is also a reason to remove CO_2 from later experiments.

Another effect of CO_2 seems to be the inhibition of the formation of N_2O at high temperatures as it rises faster above 425 °C without CO_2 present. Therefore the measurement of N_2O without CO_2 present is a conservative measurement.

5.2 Effect of the stoichiometry of NH₃/NO at 400 °C

To investigate the influence of the stoichiometry between ammonia and NO (NH_3:NO) has

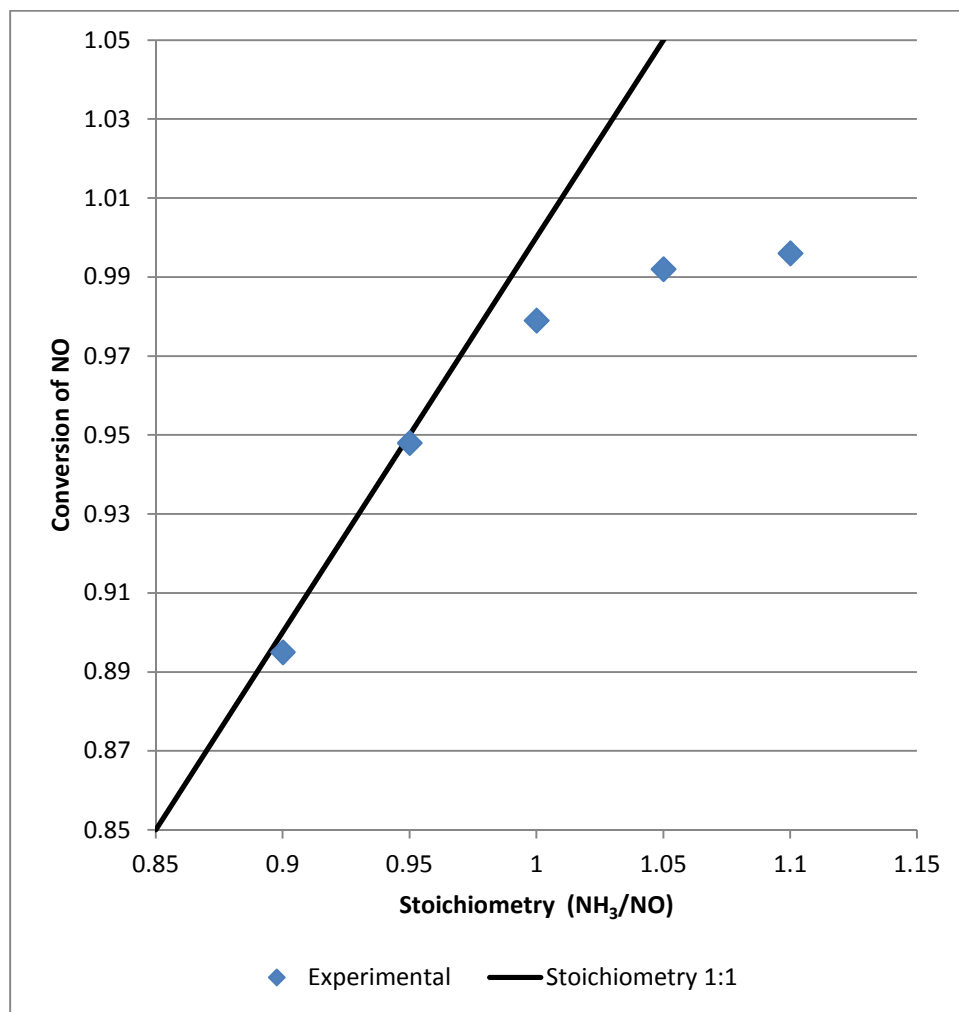been varied from 0.9 to 1.1 and the results are depicted in Figure 6.

Fig. 6. The effect of the stoichiometry at 400 °C on the conversion of NO for 1.5 ml of

catalyst A, 1 000 ppm NO, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 77.67 mol. %, 3 l_{NTP}/min, SV

120 000 h^{-1}, 1.2 bar

At low values of the stoichiometry the overall reaction follows the value (1:1) expected for

the standard SCR reaction. At higher amounts of NH_3 (>0.95 NH_3/NO) the conversion is

leveling off. The highest conversion obtained in these experiments was 99.6 % at a stoichiometry of 1.1. This was the value of the stoichiometry used for further experiments, since very high total conversions are warranted in the system (see process description above). The cause for this leveling off in the conversion of NO is side reactions of ammonia oxidation. Some examples of such oxidations are given below:

$$4 \text{ NH}_3 + 3 \text{ O}_2 => 2 \text{ N}_2 + 6 \text{ H}_2\text{O} \qquad\qquad \text{reaction 2}$$

$$4 \text{ NH}_3 + 4 \text{ O}_2 => 2 \text{ N}_2\text{O} + 6 \text{ H}_2\text{O} \qquad\qquad \text{reaction 3}$$

$$4 \text{ NH}_3 + 5 \text{ O}_2 => 4 \text{ NO} + 6 \text{ H}_2\text{O} \qquad\qquad \text{reaction 4}$$

The formation of N_2O was constant at 5 ppm at 400 °C at all values of the stoichiometry from 0.90 to 1.10 and can thus be said to be independent of the ratio, at least at this temperature and in the region investigated.

5.3 Comparison of catalyst activities and selectivities

The catalysts have all been subject to catalyst testing under both low (1 000 ppm NO) and high (5 000 ppm NO) concentration conditions. The results from the conversion experiments at the low NO concentration level is depicted in Figure 7.
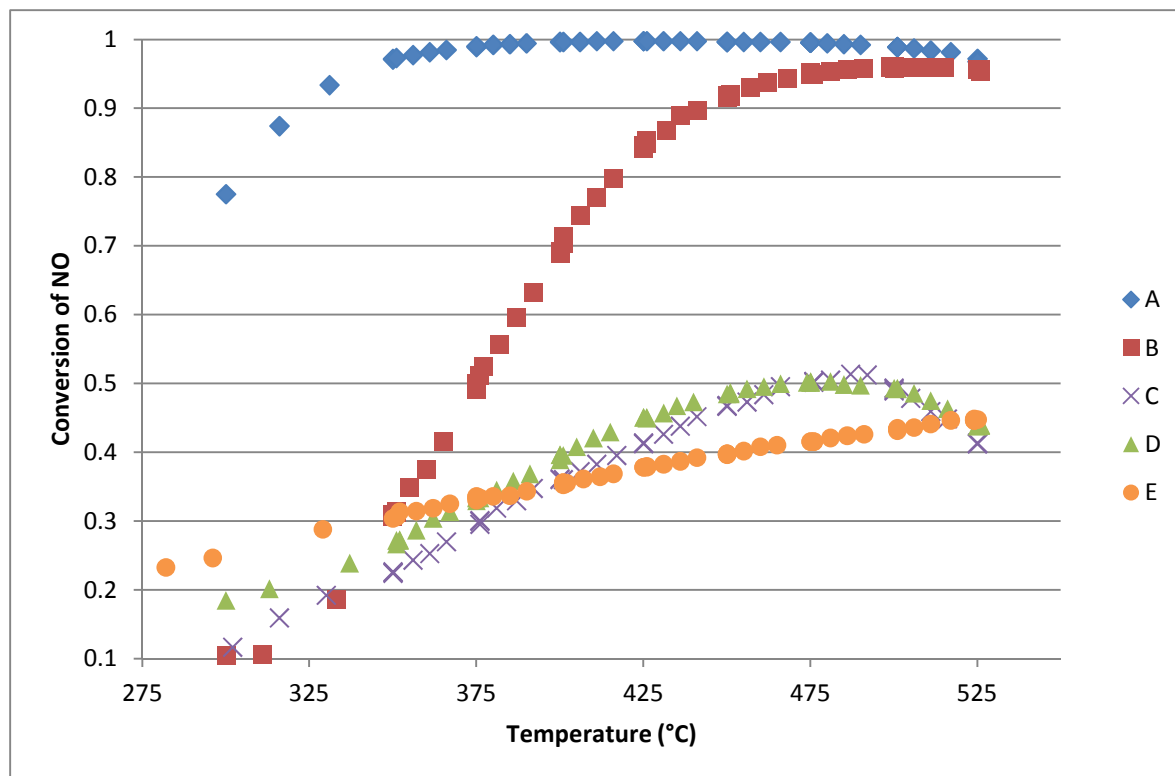
Fig 7. The effect of the temperature on the conversion of 1 000 ppm NO by 1 100 ppm NH_3 for 1.5 ml of all catalyst A-E, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 77.67 mol. %, 3 l_{NTP}/min, SV 120 000 h^{-1}, 1.2 bar.

There is a very large difference in activity of the catalysts tested. Catalyst A fulfills the conversion criteria for the process (> 96 % in first reactor), at the very high space velocity of 120 000 h^{-1} even at temperatures slightly below 350 °C. Catalysts A and B are thought to be of the vanadia-based type, but given the manufacturers restraints, this cannot be investigated. The supposed content of vanadia in sample B is much smaller than in A, based on previous experience. This is the cause for the much lower activity for sample B compared to A. Sample B would need a SV of around 14 000 h^{-1} to reach 96 % conversion at 350 °C, assuming a first order reaction in NO. The corresponding calculated values for all of the catalysts are found in Table 4. The temperature 375 °C is needed in the high concentration experiments in order to

give a 96 % conversion for catalyst A. Therefore all materials are compared at this temperature.

Catalysts C and E are probably of a zeolithic type. Catalyst C and D have the same conversion against temperature behavior leading to the conclusion that this material could also be zeolithic. Sample C would need about 10 000 in SV, D about 12 000, and E about 14 000 to obtain the required conversion of 96 %. Thus all materials could be used if the SV is chosen correctly. Of course this means that the amount of catalyst needed will be about 10 times higher for samples B-E compared to catalyst A.

Table 4. Required SV for 96 % conversion assuming a first order reaction in NO for both high and low inlet concentrations of NO.

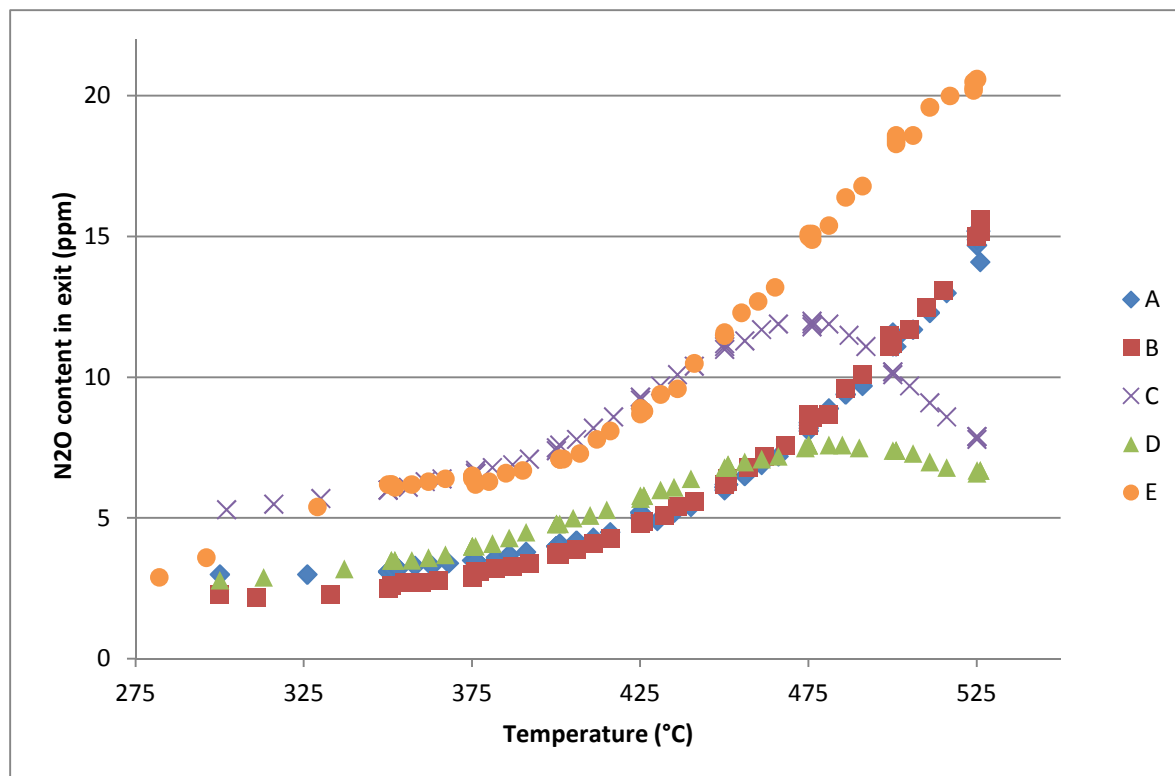| Catalyst	Required SV (h^{-1}) for 96 % conversion at 1000 ppm NO (350°C)	Required SV (h^{-1}) for 96 % conversion at 5000 ppm NO (375°C)
A	120 000	120 000
B	14 000	24 000
C	10 000	22 000
D	12 000	19 000
E	14 000	N/A[a]

[a]N/A = not applicable

Fig 8. The effect of the temperature on the formation of N_2O, 1 000 ppm NO, 1 100 ppm NH_3 for 1.5 ml of all catalyst A-E, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 77.67 mol. %, 3 l_{NTP}/min, SV 120 000 h^{-1}, 1.2 bar.

Reaction 5 is common when N_2O is formed in the SCR process.

$$4 \text{ NO} + 4 \text{ NH}_4 + 3 \text{ O}_2 \Rightarrow 4 \text{ N}_2\text{O} + 6 \text{ H}_2\text{O} \qquad \text{reaction 5}$$
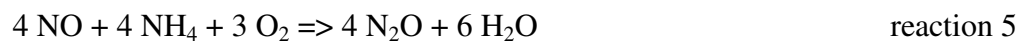
The selectivity towards N_2 is important and is defined below.

Selectivity to N_2 = 1-(ppm N_2O in exit/ppm NO converted)

Catalysts A and B have almost the same formation of N_2O at all temperatures. Catalysts C and D show clear maxima in the amount of N_2O formed. This could be explained by reaction 6 below.

$2 N_2O => 2 N_2 + O_2$ N_2O decomposition reaction 6
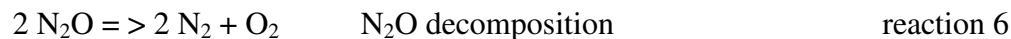
The same catalysts, with the exception of E, were investigated also at high concentrations. The conditions were the same as above, but with 5 000 ppm of NO and 5500 ppm NH_3 in the inlet gas, Figure 9.
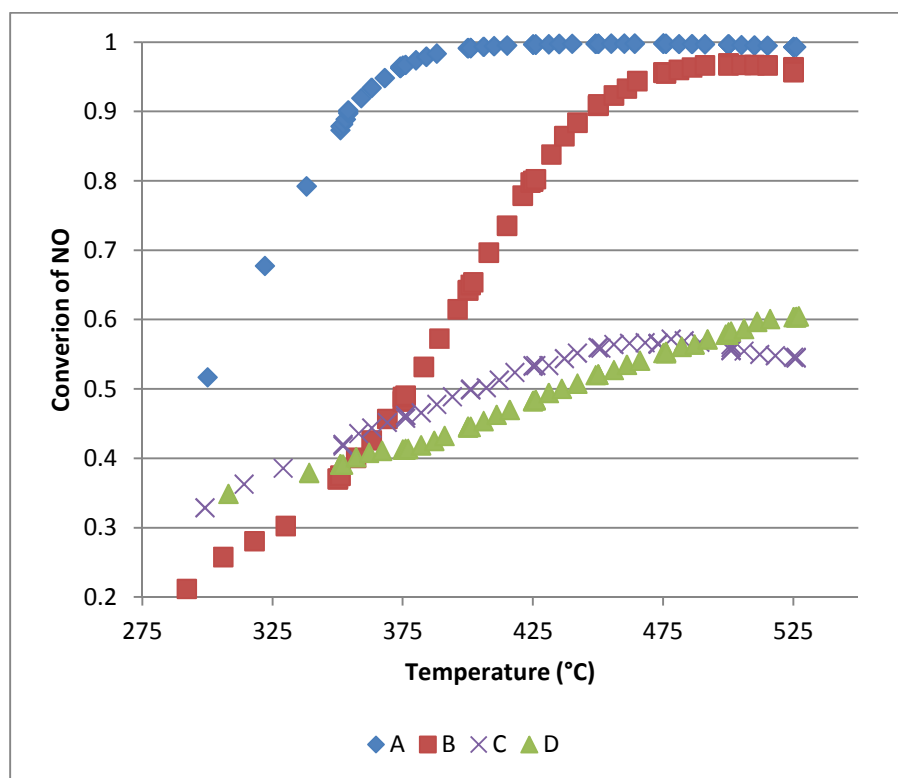

Fig 9. The effect of the temperature on the conversion of 5 000 ppm NO by 5 500 ppm NH_3 for 1.5 ml of all catalyst A-D, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 76.83 mol. %, 3 l_{NTP}/min, SV 120 000 h^{-1}, 1.2 bar.

Also at high concentration of NO there is a very large difference in activity of the catalysts tested. All materials have a maximum in the conversion curve albeit at different temperatures. Catalyst A again fulfills the conversion criteria for the process (> 96 % in first reactor) above 374 °C even at the very high space velocity of 120 000 h^{-1}. Catalysts A and B have principally the same conversion against temperature curves albeit catalyst B is moved to the higher temperature regime. Catalyst B shows conversion above 96 % only at temperatures above 480 °C but needs a SV of around 24 000 at 375 °C. Catalysts C and D have similar activities with maximum conversions of about 57 and 60 %. Samples C and D need SV of 22 000 and 19 000 at the same conditions as above.
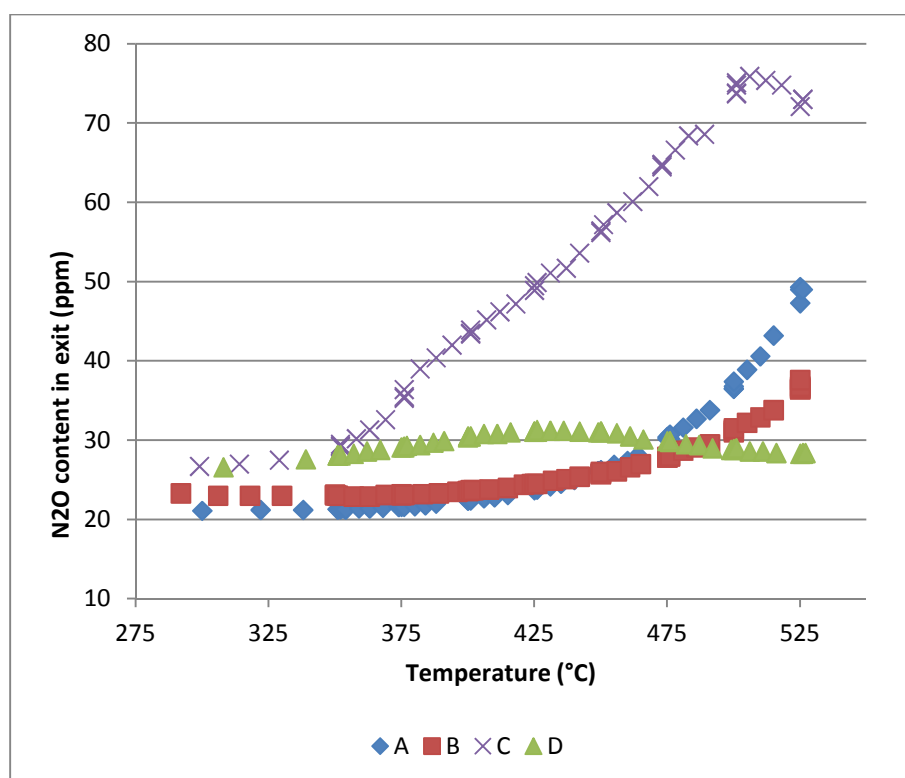

Fig 10. The effect of the temperature on the formation of N$_2$O, 5 000 ppm NO, 5 500 ppm NH$_3$ for 1.5 ml of all catalyst A-E, H$_2$O 5.03, Ar 4.02, O$_2$ 13.06 and N$_2$ 76.83 mol. %, 3 l$_{NTP}$/min, SV 120 000 h^{-1}, 1.2 bar.

Catalysts A and B have almost the same formation of N_2O at temperatures below 450 °C.

Catalysts C and D shows a clear maximum in the amount of N_2O formed. The highest amount

of N_2O was formed on sample D with about 2.5 times that of catalyst D. In fact catalyst D is

the best material for temperatures above 490 °C when it comes to low content of N_2O in the

outlet gas. Comparison of selectivities as above shows that samples A, B and D has values

below 1 % i.e. half the selectivity observed at low NO concentrations. Sample C gives 2.6 %

N_2O. It should be observed that these values are not corrected for any errors in the analysis of

N_2O which seems to give a base emission of 22 to 27 ppm N_2O at low temperatures and high

NO concentrations. The N_2 selectivities at 525 °C are in this case much higher and are 97.3 %

for catalyst C and 99.1 % for catalyst D (worst and best cases).

5.4 Effect of space velocity

It is also of interest to investigate the effect of the space velocity. Therefore the first catalyst,

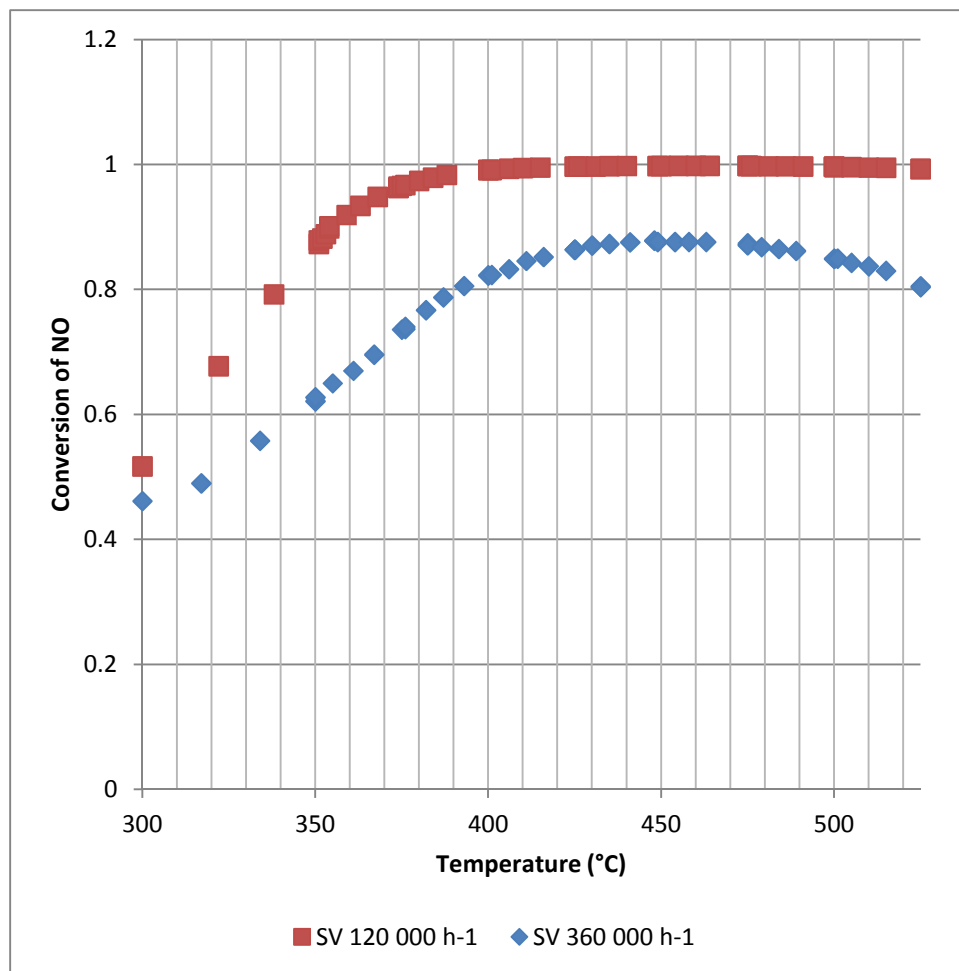catalyst A, has been subject to further testing at higher SV, Figure 11.

Fig. 11. Conversion of NO as a function of temperature at two space velocities for 1.5 ml and 0.5 ml of catalyst A, 5 000 ppm NO, 5 500 ppm NH_3, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 76.83 mol. %, 3 l_{NTP}/min, SV 120 000 and 36000 h^{-1}, 1.2 bar.

In the kinetic regime, which is unlikely to prevail in our experiments, if the reaction was of first order in NO, the conversion should be independent on the concentration of NO (see above). For a conversion of NO of 63 % for SV 120 000 h^{-1} the corresponding conversion should be 39 % for 360 000. Experiments show higher than expected values for the lower SV indicating either another rate-dependency on NO concentration or the influence of diffusion. The increase in rate with temperature is slower for higher SV meaning lower activation energy (Fig. 11). This is not understood; the higher rates of sample A at low SV should give higher influence of diffusion and thus lower activation energies. Preliminary simulations

show temperature increases in the catalyst bed in the range of 30 – 40 °C when the outlet

temperature is around 525 °C. Further investigations of these effects are under way and will
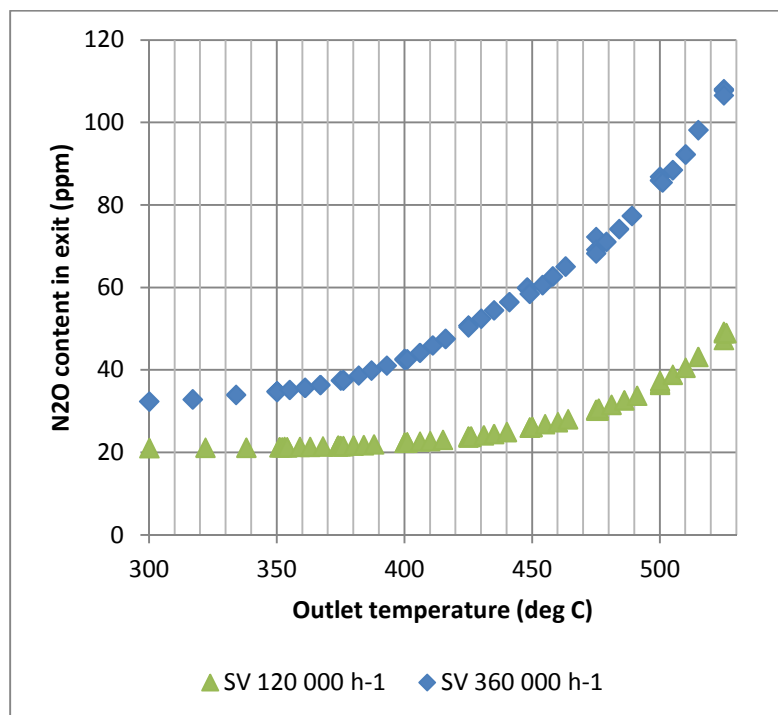
be published separately.

Fig. 12. N_2O content as a function of temperature at two space velocities for 1.5 ml and 0.5 ml

of catalyst A, 5 000 ppm NO, 5 500 ppm NH_3, H_2O 5.03, Ar 4.02, O_2 13.06 and N_2 76.83

mol. %, 3 l_{NTP}/min, SV 120 000 and 36000 h^{-1}, 1.2 bar.

The formation of N_2O seems to be influenced by the space velocity; high values giving more

N_2O. Also at high SV the increase with temperature is more pronounced than at low SV.

5.5 Thermal stability of the catalysts

The thermal stability of the materials was investigated by measuring their BET surface areas.

Catalysts A and B have areas in the fresh state of 64 to 69 m^2/g (Table 5). Catalysts C and E

have BET areas of about 400 m^2/g, micropore areas and micropore volumes which are quite

large leading to the conclusion that they are zeolithic materials. Catalyst D has a surface area

of 129 m^2/g and its origin is more unclear and could be a combination of a zeolite with

something else.

Table 5. Surface areas and pore structure of the catalysts in the fresh state

Catalyst	BET surface area (m^2/g)	S_{micro} (m^2/g)	V_{por} (cm^3/g)	V_{micro} (cm^3/g)
A	64.4	2.6	0.2748	0.0007
B	69.0	7.3	0.2512	0.0028
C	360	266	0.2884	0.1233
D	129	68	0.2201	0.0312
E	410	316	0.3182	0.1473

Table 6. Surface areas and pore structure of the catalysts after 777 h at 525 °C in air

Catalyst	BET surface area (m^2/g)	S_{micro} (m^2/g)	V_{por} (cm^3/g)	V_{micro} (cm^3/g)
A	51.3	3.6	0.2816	0.0012
B	53.2	7.7	0.2492	0.0030
C	364	270	0.3094	0.1258
D	117	58	0.2149	0.0263
E	402	307	0.3254	0.1430

The area after 777 h of treatment at 525 °C in air relative to the area of the fresh samples are:

for the materials A 79.7 % , B 77.1 %, C 101 %, 90.7 % and E 98.0 %. The materials C and E,

based on zeolites, have god thermal stabilities in air as shown in Table 6. Material D loses 10 % of its area after 777 h. The materials A and B loose about 22 to 25 % of their area after 777 h. The changes in pore volume are hardly measurable, compare Tables 5 and 6.
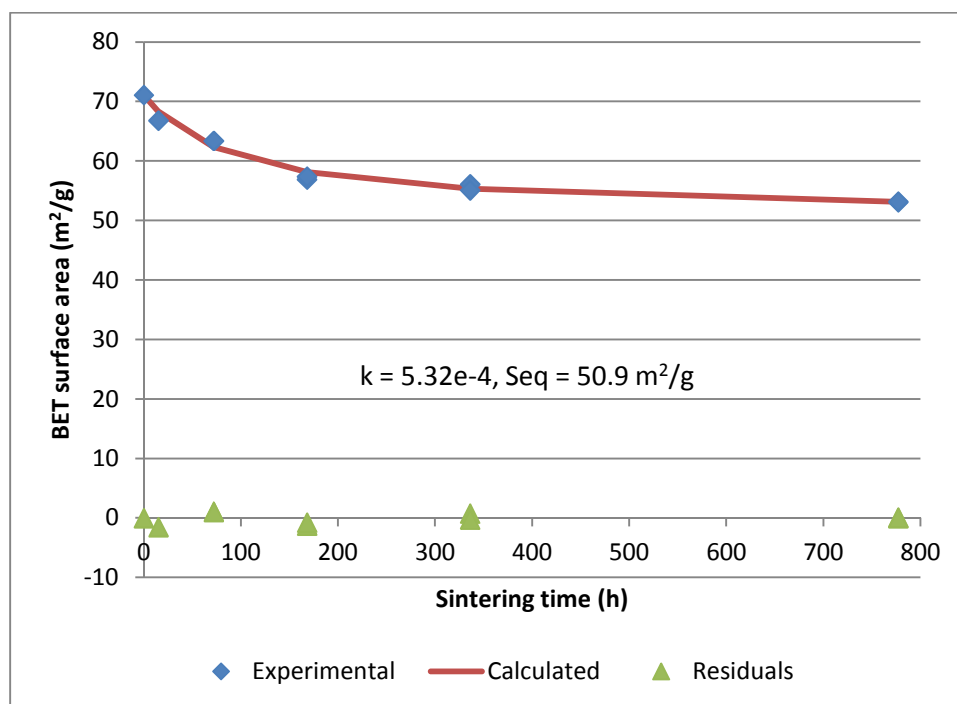

Fig 13. Effect of sintering time on the BET surface area of catalyst B in air at 525 °C and fit of data to the second order GPLE model.

An example of the fit of sintering data to the GPLE model is shown in Figure 13 for catalyst B. Similar plots are obtained for the other materials and the results from the statistic evaluation are given in Table 7.

Table 7. Statistic data for the fit of experimental sintering data to the GPLE model

Catalyst	k	sdev	Seq	sdev	Seq/S0
	$(g/m^2,h)$		(m^2/g)		
A	3.25e-4	4.17e-4	43.8	7.0	0.68
B	5.32e-4	1.04e-4	50.9	0.9	0.74
C	9.40e-5	7.63e-5	354.9	10.1	0.99
D	3.28e-4	118	112.6	4.1e6	0.87
E	6.30e-4	1.81e-3	396.0	11.6	0.97

The surface area at infinite time is thus more precisely described by the model than the rate of its decrease with time. Catalyst D has a special combination of materials making it hard to get a representative sample from it. This is clearly shown in the results where unreasonably high standard deviations are obtained.

5.6 Discussion

With high NO_x concentrations in a gas stream, such as from the Oxyfuel process descried in this paper, alternative NO_x reduction measures may be applicable. In this case, the use of a two bed system would allow for a total NO_x reduction surpassing 99.5 %. This system could, according to the process simulations performed, also be designed to be autothermal in a tail-end set-up. Interestingly enough, the autothermicity of the SCR unit also includes the vaporization of the ammonia-containing water solution.

However, the temperature increase over the catalyst bed will require a non-traditional catalyst. Out of the catalysts investigated within the scope of this study, there are several alternative catalysts that are more or less suitable for the applications. In general the side-product formation of N_2O was acceptable, ranging from below 2 % to 4 % selectivity. The example

simulated above corresponds to a 1 GW power plant. The emissions of greenhouse gases, calculated as CO_2 equivalents, are estimated to be reduced by over 99.9 % by post compression and storage. The N_2O contributes to about 2 % of the emissions if 4 % selectivity is assumed and if this is compared to not performing the storage the N_2O contribution would be less than 1ppm.

The effect of CO_2 on the reduction of 1000 ppm NO has been analyzed using 1st order kinetics for catalyst A. By this analysis we have shown that the rate constant is about 3 times larger for conditions without CO_2 in the gas. Thus a quite large decrease in activity is seen in the presence of 34 % CO_2. The activation energies were 49.6 and 42.7 kJ/mol without and with CO_2 present. These data are in contrast to the information given by M. Magnusson et al. [21], for a commercial vanadium based catalyst, where they state that there is no influence of CO_2 at least at the level of 6 %. No influence of CO_2 is also reported for a Fe-HBEA catalyst [22]. On a Fe-cerium-tungsten mixed oxide catalyst [23] there is a somewhat lower conversion in the presence of 5 % CO_2 at temperatures below 225 °C. At 450 °C there is a larger effect. When 5 % CO_2 is added the conversion drops to 85.0 %. This result is similar to ours even if the catalyst is not the same.

One explanation could be that the rate of diffusion decreases with the gas molecular weight. We calculated binary gas diffusion coefficients according to the Chapman-Enskog theory. The calculated values for the diffusion coefficient for NO respective NH_3 in pure CO_2 are about 70% compared with the values in pure N_2. The gas mixtures in the experiments are not pure N_2 or CO_2, however, a substantial addition of CO_2 to a predominant N_2 atmosphere should decrease the diffusion coefficient of NO and NH_3. The SCR reaction is fast and usually enters the pore diffusion limiting region and a decreased diffusion coefficient further limits the mass transport.

When we compare activities, our results show that the rate constants for A and B are 4.71 and 0.69 respectively at 375 °C and 4.60 and 3.18 at 500 °C. Recalculation, taking into account the lower space velocity of 100 000 h^{-1}, of the data of Heo et al. [24], gives values of 2.45 for a 2.2 % vanadia on titania catalyst at 375 °C and 2.37 at 500°C. Our catalyst A has about 2 times higher activity. The low activity of catalyst B is assumed to be caused by its lower content of vanadia (data not supplied because of commercial reasons). The activation energies determined in the low temperature region were 49.6 and 89.9 kJ/mol for A and B respectively. The value for A is probably decreased by internal diffusion limitations.

M. L. M. Oliviera et al. [25] studied a commercial V_2O_5-WO_3/TiO_2 catalyst in a fixed bed reactor with particles of the size of 0.25 to 0.40 mm. At 350 °C the conversion of 1000 ppm NO at GHSV = 48 000 h^{-1} was 91.8 % in 10 % water. Our results show a conversion for A of 97.4 % at GHSV = 120 000 h^{-1} and 5 % water with a particle size of 0.71 to 0.80 mm. Thus again our catalyst A has a very high apparent activity even if the activity is decreased by pore diffusion compared to some other materials. At 500 °C the results of Oliviera et al. [25] show that the conversion was 90 % while ours for A was 99 %. Also at high temperatures, our material shows superior performance. The conclusion is based on the assumption that the effect of water is not much larger with 10 compared to 5 % water.

For the catalysts, which are based on zeolites, C and E but probably also D, the rate constants were 0.35, 0.41 and 0.41 at 375 °C. At 500 °C the values were 0.67, 0.57 and 0.68. Thus very similar activities, on a catalyst volume basis, were obtained on all materials despite the large difference in surface areas (see Table 5). Activation energies were 38.6, 13.2 and 33.4 kJ/mol out of which at least the value for catalyst E is in the diffusion regime. Calculation of data given by Heo et al. [24] gives rate constants in the region of 1.94 for 375 °C and 2.93 at 500 °C for a Fe-ZSM-5 catalyst. Thus our materials C, D and E have a 4 to 5 times lower activity than Heo's.

M. L. M. Oliveira et al. [25] show a 99.6 % conversion (k=2.21) at GHSV of 48 000 h^{-1} at 350 °C for Cu-mordenite and 73.8 % (k=0.54) for Cu-ZSM-5 in the presence of 10 % water. The activity of the Cu-mordenite falls rapidly above 400 °C to about 20 % at 550 °C. Thus this material is not suited for high temperature applications probably because of copper migration in wet conditions. The activity of the ZSM-5 material, in the same report, remains almost constant at temperatures up to 550 °C. There is a slow deactivation of both zeolithic materials though.

Already in 1994, R. M. Heck et al. [26] presented a zeolite based material for high temperature SCR developed by Engelhard. The conversion of NO$_x$ was 98 % at 500 to 593 °C. It has been used alone or in combination with a vanadia based material in natural gas fired gas turbines, natural gas fired industrial boilers, chemical plants and coal boilers since 1985. No information is given on the long time stability though but since they were used commercially it should be acceptable.

A. M. Frey et al. [27] used a Fe-BEA zeolite catalyst and showed it to be superior to 3 % catalyst of V$_2$O$_5$/TiO$_2$, Fe-ZSM-5 and ZSM-12 yielding 99.1 % conversion of 1000 ppm NO at 525 °C. This is about 30 % better performance than our material A and about 8 times better than our zeolithic materials. It should be noted that our investigation was performed with a particle size of 0.71-0.80 mm while theirs was only 0.18-0.355 mm. Their result will show the intrinsic behavior while ours are lowered by diffusion limitations. In a study by H. Y. Huang et al. [28] the activation energy for a Fe-ZSM-5 catalyst was 54 kJ/mol between 240 and 300 °C. The effectiveness factor was between 0.99 and 0.95. Thus it can be concluded that our results are all limited by diffusion processes. This is especially true at temperatures above 350 °C.

Our results, from measurement at 5000 ppm NO, show that the vanadia based materials A and B have rate constants of 3.39 and 0.658 at 375 and 5.68 and 3.39 at 500 °C. These values are

just a little lower at 375 °C than the values obtained at 1000 ppm NO. At 500 °C on the contrary the values are somewhat larger. Thus the use of a first order in NO rate expression in the comparison is justified. We have only found very little information in literature on experiments at high NO concentrations. There is information from commercial use in Italy in cleaning from nitric acid manufacture by Rhone Poulenc [29] showing a 93.3 % conversion of 3000 ppm NOx at 240 °C and a gas flow of 39 500 m^3/h. In the same paper the authors present data on their DN 110 catalyst between 140 and 410 °C. The conversion of 800 ppm NO and 200 ppm NO_2 at a SV of 8 000 h^{-1} is almost 100 % between 265 and 330 °C. At higher temperature the conversion drops to 84 % at 410 °C. In 1995 J. A. Sullivan et al. [30] presented results from a study at both high concentrations (0.6 % NO) and temperatures up to 500 °C. A 8% WO_3, 4 % V_2O_5 on titania catalyst gave a rate constant of 0.93 at 500 °C which is much lower than our catalyst A. A Cu-ZSM-% catalyst gave a value of 2.1 which is about 3 times larger than the values obtained by us for the zeolite materials. Another study [31] was using 2 000 ppm NO at SV 250 000 h^{-1} and a Cu-faujasite catalyst. The conversion approached 100 % at temperatures between 360 and 450 °C. It is not stated that water is added in this reaction study.

The formation of N_2O as a side product in the SCR reaction is known since a long time for vanadia based materials. The presence of water usually lowers the amount of N_2O formed on catalyst with high amounts (10 - 30 %) of V_2O_5 [32]. We now report values increasing with temperature for some materials up to 20 ppm at 1000 ppm in the inlet in the presence of 5 % water. For some materials there is a maximum in the amount of N_2O formed. M. L. M. Oliveira et al. [25] reported 65 ppm for a vanadia catalyst, none for a Cu-mordenite catalyst and 41 ppm for a Cu-ZSM-5 catalyst at 10 % water and GHSV 48 000 h^{-1}.

At 2000 ppm NO, Delahay et al. [31] using a Cu-faujasite catalyst obtained 320 ppm N_2O at 450 °C. The selectivity to N_2O increased with oxygen content to 6 % at 4 % O_2. The

formation of N_2O was also much accelerated by the amount of Cu in the catalyst. This much too high amount of N_2O makes this catalyst unsuitable for our application.

For 5 000 ppm NO in the reactor inlet the amount of N_2O formed was larger in our experiments, up to 76 ppm in the worst case (catalyst C) and 50 ppm for catalyst A (Figure 10) than at 1 000 ppm NO. In all cases the amount formed is larger at higher concentrations of NO (compare values in Figures 8 and 10). There seems to be a blank formation of 22 to 27 ppm of N_2O which is seen at low temperatures (Figure 10) and which is proportional to the amount of NO present. A plausible explanation for this amount could be that some amount of ammonium nitrate is formed and decomposed in the system according to [33]:

$$NH_4NO_3 => N_2O + 2\ H_2O \hspace{3cm} \text{reaction 6}$$

This reaction is normally proceeded by:

$$2\ NH_3 + 2\ NO_2 => N_2 + NH_4NO_3 + H_2O \hspace{2cm} \text{reaction 7}$$

We do not have any NO_2 in the reactor inlet so the origin of the blank N_2O is not understood unless NO_2 is formed by oxidation of NO on the catalyst. By experiments in an empty reactor with 5 000 ppm NO and 5 500 ppm NH_3 in the presence of CO_2 we have shown that NO alone does not produce any N_2O on the reactor walls up to 430 °C but gives a blank signal of about 15 ppm even when corrected for the effect of CO_2 on the N_2O measurements. There is 4 ppm formed from NH_3 alone by oxidation and the blank signal is 0 in this case (reaction 3). When all components are present there is also a formation of N_2O from the reaction 5 with a blank signal of 15 ppm. The blank signal could be interference in the IR instrument.

The catalyst that produces the least amount of N_2O is D and especially so at high temperatures. Unfortunately there is no information on the formation of N_2O in the 0.6 % NO study [31] so a comparison of our data is impossible.

In Figures 8 and 10 it can be seen that the N_2O formation reaches a maximum at a certain temperature for the presumed zeolithic materials. This could of course be caused by a change in the reaction forming N_2O. However, it is known that zeolites at high temperatures are capable to decompose N_2O in the presence of NO_x (reaction 5). This NO_x promoted decomposition of N_2O does not consume any NO_x itself. This means that the NO_x present acts as a co-catalyst and the gas leaves the reactor at conditions close to the thermodynamic equilibrium between NO, NO_2 and O_2 since acidic zeolites are good catalysts for this reaction [34-36]. The highest amount of N_2O was formed on sample E, where a small tendency of lowering of the amount can be seen at very high temperatures. Catalyst E was excluded from experiments at high NO conditions because of its tendency to form high N_2O levels at high temperatures. Its selectivity to N_2 is only 95.7 % at 525 ^{o}C compared to 98.6 % for catalyst D. This decomposition of N_2O to N_2 and O_2 has been observed by R.W. van den Brink et al. [37, 38] and I. Melián-Carbrera et al. [37] on zeolithic catalysts. The first authors used a Fe-ZSM-5 catalyst and showed the conversion of N_2O to be shifted upwards in temperature when water (1 %) was added. At 3 bar and SV 20 000 h^{-1} 1 500 ppm N_2O was converted by 75 % already at 420 °C. Our maximum in the N_2O formation is at the same temperature for catalyst D. Catalyst C has a maximum at around 510 °C. We have only seen the maxima on the presumed zeolithic materials. I. Melián-Carbrera et al. studied Fe zeolites of the types ferrite, BEA, MFI and ZSM-5. The best material was Fe-ferrite converting 4500 ppm N_2O at 3 bar to 98.2 % at 462 °C and W/F = 8.95e^2 kgsmol-1 [37].

The effect of space velocity for catalyst A is shown in Figure 11 for 5000 ppm NO in the inlet. At higher space velocities the conversion gets lower as expected. At maximum conversion at about 455 °C the rate constant is 6.2 and 2.1 for SV 120 000 and 360 000 h^{-1}. Thus the factor is about 3 as expected from the 3 times smaller amount of catalyst used. This

ratio is as low as 1.8 at 335 °C and increases with temperature to the maximum. The activation energies are 65.0 and 39.2 kJ/mol for low and high space velocities.

Similar behavior of activity at with SV is reported for a vanadia catalyst by M. L. M. Oliviera [25] and a WO_3-V_2O_5/TiO_2 catalyst by J. A. Sullivan et al. [30]. A lower space velocity (larger catalyst volume in our case) also gives lower amounts of N_2O on catalyst A (Figure 12). Is this an indication that N_2O is an intermediary product? This question remains unsolved.

There is a thorough study on the sintering of 10, 20 and 30 % V_2O_5 on silica-titania [18]. The changes in BET surface area were evaluated by for instance the GPLE method. For a second order GPLE equation values o f k and S_{eq} for a 10 % catalyst in dry air were 0.0041 and 89.7 m^2/g at 600 °C which is closest to our temperature of 525 °C. Their value for S_{eq} is 42.7 % of the unsintered value. Our values were 0.00033 and 43.9 m^2/g respectively for catalyst A meaning that S_{eq} is 66.8 % of the unsintered value. Thus catalyst A is more stable at 525 °C than the 10 % from ref [18] is at 600 °C in dry air. This could be caused by the presumably lower content of vanadia in catalyst A but also the lower temperature and the absence of water vapor.

There is an excellent review of the use of zeolithic catalyst in the ammonia SCR by Brandenberger et al. [39]. They especially refer to SAPO materials with a high acidity and with a much higher thermal stability than other zeolites. Cu-SAPO-34 has been used for the SCR with C_3H_6 [40]. After treatment at 800 °C in 3 % water for 2 h the activities decreased from 28.7 % conversion of 5 000 ppm NO by 1 000 ppm C_3H_6 at 500 °C to 24.4 % at 700 °C. The effect of time up to 66 h is to reduce the conversion of 1 000 ppm NO with 1 000 ppm C_3H_6 from 41.0 to 29.9 %. Thus the thermostability is not that good (reduction in activity 27 %).

Another material with quite good thermal properties; coprecipitated WO_3-TiO_2 with a surface area of around 70 m^2/g, was aged in 10% water in air [X]. A 20 % WO_3 catalyst maintained its fresh activity when reducing 100 ppm NO at a SV of 11 000 h-1 for about 8425 h at 550 ^{o}C. At the same time the BET surface area decreased from 80 to 48 m^2/g, i.e. by 60 %. These are values in the same range as ours. That no deactivation was obtained could be explained by the surplus of catalyst used. We have a SV of 120 000 h^{-1} compared to 11 000 h^{-1} in their experiments. Still this material could be of interest because of the relatively good thermal stability shown.

There is however a recent patent application [41] wherein a Cu-Y type catalyst, designated C, with Na content below 0.4 % is used for NH_3 SCR. It is heat treated for 50 h at 800 °C in 10 % steam prior to activity measurements; at 450 °C the conversion of NO drops from 96.3 to 93.6 % after aging. The rate constant thus drops by 16.6 %. Even this material does not seem to be stable enough. A series of Ce exchanged zeolites were studied by W. E. J. van Kooten et al. [42]. The conversion of 900 ppm NO was highest for Ce-ZSM-5 at 500 °C. This catalyst and Ce-mordenite show fast deactivation. Ce-ZSM-5 lost 80 % of its active sites during 50 h steaming at 600 °C. The most stable materials were Ce-beta and Ce-Y of which Ce-beta is the most active one. A new publication on a Cu-beta catalyst is presented by N. Wilken [43]. After aging at 500, 600, 700 and 800 °C for 2 h in 5 % water activities were measured with 400 ppm NO and NH_3. At 500 °C treatment temperature the conversion of NO is about 90 %. There is a small decrease in conversion with treatment temperature up to 800 °C but at 900 °C the conversion drops to 67.9 %. Thus this material might be considered stable enough for our application. Further long time studies are necessary to verify the material's stability though.

6. Conclusions

The major problem with using the investigated catalyst materials, in the process proposed, is that some of them do not show very good thermal stability at the outlet temperature of the catalyst reactor. In this respect the zeolithic materials are more stable than the vanadia-based ones.

When comparing catalysts activities, catalyst A needs only on fifth of the amount of catalyst needed for catalyst B at high concentration conditions. Activity is no problem for any of the materials but the amounts of catalyst needed will be higher compared to A.

The formation of N_2O is mostly small. In this respect the materials A, B and D are superior especially at high temperatures and high concentrations of NO.

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