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Selective catalytic reduction of N_2O and NO_x in a single reactor in the nitric acid industry

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Abstract

The nitric acid industry is a source of both NO_x and N_2O. The simultaneous selective catalytic reduction of both compounds using propane as a reductant has been investigated. A stacked catalyst bed with first a Co-ZSM-5 catalyst and second a Pd/Fe-ZSM-5 catalyst gives >80% conversion of N_2O and NO_x above 300 °C at atmospheric pressure. At 4 bar absolute pressure (bara) the Co-ZSM-5 DeNO_x catalyst shows higher NO_x and propane conversion. This leaves not enough propane for the Pd/Fe-ZSM-5 DeN_2O catalyst, which causes a 'dip' in N_2O conversion. Reducing the space velocity (SV) of the first catalyst bed secures high NO_x and N_2O conversions from 300 °C and up at 4 bara. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The nitric acid industry is one of the major sources of the greenhouse gas nitrous oxide (N_2O). Nitrous oxide is formed as a by-product in the oxidation of ammonia on a Pt/Rh gauze catalyst. The off gas concentration of N_2O is typically between 1000 and 2000 ppmv. Next to N_2O, nitric acid plants also emit NO and NO_2 (NO_x). NO_x are the main product of the Pt/Rh gauze catalyst and are subsequently absorbed in water to form nitric acid. The absorption step not being 100% efficient gives rise to the NO_x emission (typically 100–500 ppm).

In part of the existing nitric acid plants a conventional NH_3-based DeNO_x system is in use. Several options are currently in development for N_2O abatement [1]. This paper focuses on N_2O abatement downstream the NO_x-absorption section of a nitric acid plant. This has the advantage that the N_2O abatement system has no influence on the HNO_3 production. A disadvantage is that direct decomposition of N_2O—the easiest method for N_2O abatement—is not possible in many nitric acid plants, because the off gas temperature is too low.

ECN[1] has developed a catalyst for the hydrocarbon-assisted selective catalytic reduction of N_2O [2]. The catalyst is an ion-exchanged ZSM-5 zeolite promoted with Pd to prevent CO emission and hydrocarbon slip. In a previous study the catalyst was tested in a representative gas composition of a nitric acid plant [3]. Fe-ZSM-5 catalyses the direct decomposition of N_2O, but under conditions representative for the off gases of a nitric acid plant a temperature of higher than 400 °C is necessary. At lower temperatures (>250 °C) the same catalyst is active in SCR of N_2O with propane

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as a reductant. The rate of both direct decomposition and SCR of N_2O increases with pressure. Fe-ZSM-5 is also used for hydrocarbon-SCR of NO_x [4], but maximum conversions of N_2O and NO_x occur in different temperature ranges [5].

This paper describes our research on developing and testing catalysts for combined SCR of N_2O and NO_x in a single reactor under conditions that prevail in the tail gases of a nitric acid plant. This means in the presence of water and oxygen, and under pressure since almost all nitric acid plants are operated at elevated pressure (4–12 bar absolute pressure (bara)).

2. Experimental

Fe-ZSM-5 is prepared by wet ion exchange with $(NH_4)_2Fe(SO_4)_2$ (Merck) onto NH_4-ZSM-5 (AlSi Penta SM27) at 80 °C for 24 h (for details, see [3]). A Pd amount of 0.15 wt.% was added to this catalyst by dry impregnation with $Pd(NO_3)_2$. Co-ZSM-5 was prepared by wet ion exchange of Na-ZSM-5 (AlSi Penta SN27) with $Co(NO_3)_2$ (Aldrich) at 80 °C for 24 h. Both catalysts were calcined at 550 °C.

The bulk composition of the catalyst was examined by ICP. Temperature-programmed reduction (TPR) was used to get information on the location of the iron and cobalt on the zeolite. Table 1 summarises the results.

The Fe-ZSM-5 catalyst has only 50% of the Fe actually on the charge compensation sites, which means that the actual Fe/Al ratio is 0.2. The rest of the iron is present in the form of Fe_2O_3 on the outside of the zeolite particle, as was observed by TPR and by SEM [3]. In the TPR spectrum of Co-ZSM-5 only a single reduction peak at around 700 °C was observed, which was assigned to Co in the ion exchange positions [6].

Table 1
Composition of the catalysts

Catalyst	Si/Al	Fe or Co (wt.%)	(Fe or Co)/Al	Percentage in exchange sites[a]
Pd/Fe-ZSM-5	11.4	2.3	0.4	50
Co-ZSM-5	12.4	2.6	0.4	100

[a] By integrating the TPR peaks, the H_2/Fe or H_2/Co ratio can be found, which gives information on the fraction of Fe or Co that is actually located in the ion exchange sites.

The performance of the catalysts was tested in a flow setup (see [3]). The standard gas composition was 1500 ppmv N_2O, 500 ppmv NO, 1500 ppmv C_3H_8, 2.5 vol.% O_2, 0.5 vol.% H_2O, and balance N_2. When a different concentration of one of the components was used, the concentration is given in the caption of the graphs.

The reactor is a 2.5 mm diameter stainless steel tube. Prior to entering the catalyst zone, the gases pass a preheating section with α-Al_2O_3 particles. The catalysts were applied in a sieve fraction of 0.7–1.4 mm and are placed on a quartz frit. When a stacked two-catalyst bed was used, the catalysts are separated with a quartz frit. To allow higher space velocities (SVs, 60,000 and 120,000 h^{-1}), the Co-ZSM-5 catalyst was diluted with inert α-Al_2O_3 particles.

In the outlet of the reactor a back-pressure regulator has been installed to allow experiments at pressures up to 5 bara. The quantitative analysis of the gas-phase components was performed using a Fourier transform infrared (FT-IR) spectrometer.

At the start of each experiment, the reactor temperature was increased to 175 °C at 3 °C/min under N_2 flow and flushed for 2 h. Subsequently, a background IR scan was made and the reaction gas mixture is then applied and fed to the catalyst for 2 h at 175 °C. Following equilibration, the gas composition was analysed by FT-IR analysis by averaging 120 IR scans (resolution 1 cm^{-1}). The reactor temperature was increased with steps of 25 °C at 5 °C/min to 500 °C. After an equilibration time of 20 min, FT-IR analysis was performed twice at each temperature. The conversions were calculated by relating the FT-IR data at a certain temperature to bypass values. The temperature was measured at the inlet and the outlet of the catalyst bed. In the graphs the catalyst inlet temperature is given. It must be noted that the temperature rise due to reaction of 1500 ppm of propane with NO, N_2O and O_2 is about 100 °C. So when the propane conversion is complete at for example 350 °C, the outlet temperature of the second catalyst bed is 450 °C.

3. Results and discussion

The catalytic system used was a combination of two catalysts in one reactor: the iron-containing zeolite

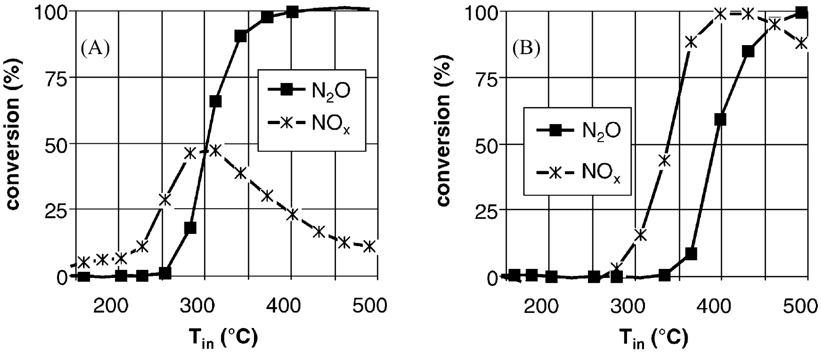

Fig. 1. NO_x and N_2O conversion vs. catalyst inlet temperature on (A) Pd/Fe-ZSM-5 and (B) Co-ZSM-5. Conditions: $p = 1$ bar; SV = 30,000 h^{-1}; 1500 ppmv N_2O; 500 ppmv NO; 2.5 vol.% O_2; 0.5 vol.% H_2O; 1500 ppmv C_3H_8; balance N_2.

catalyst that was described in our previous publication [3] and a cobalt-containing zeolite catalyst. The performance of both individual catalysts is reported in Fig. 1. In both cases the SV is 30,000 h^{-1} and propane is used as a reductant (1500 ppmv C_3H_8 on 1500 ppmv N_2O + 500 ppmv NO).

The Fe-ZSM-5 catalyst previously used for N_2O destruction is also active in NO_x removal [5]. However, at the temperature where N_2O reduction is high (reactor inlet temperatures higher than 300 °C), the conversion of NO_x starts to decrease. The NO_x conversion with the iron-containing catalyst reaches a maximum value of 50% at 300 °C under these conditions. The decrease of NO_x conversion is caused by the consumption of the reductant propane in two other reactions, i.e. the reaction of propane with N_2O and the combustion of propane. The SCR of N_2O with propane also competes with propane combustion. However, at higher temperatures, where propane is consumed by the combustion reaction, direct decomposition of N_2O takes place, so N_2O conversion remains high.

On the Co-ZSM-5 catalyst (Fig. 1B), NO_x destruction starts at a reactor inlet temperature of 300 °C, and reaches almost 100% NO_x conversion at around 400 °C. N_2O destruction takes place at a much higher temperature than on the iron-containing zeolite: 90% N_2O conversion is reached only above 450 °C. In fact, the N_2O conversion is the same as when no propane is added. So SCR of N_2O does not take place on the Co-ZSM-5 catalyst, only direct decomposition.

The use of the two catalysts in one reactor combines the high NO_x conversion of the cobalt-containing catalyst with the high N_2O destruction of the iron-containing system. Both beds have an SV of 30,000 h^{-1}, which gives a combined SV of 15,000 h^{-1}. The gases first pass the Co-ZSM-5 catalyst and than the Pd/Fe-ZSM-5 catalyst. At atmospheric pressure, conversion of N_2O is higher than 70% at a reactor inlet temperature of 300 °C (see Fig. 2). NO_x destruction reaches 70% at about 340 °C. NO_x conversion goes through a maximum at around 425 °C, but does not become lower than 80% below 500 °C.

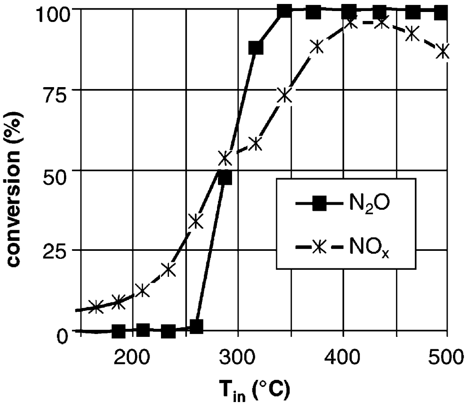

Fig. 2. NO_x and N_2O conversion vs. catalyst inlet temperature on a stacked bed of Co-ZSM-5 and Pd/Fe-ZSM-5 catalysts in one reactor. Conditions: $p = 1$ bara; SV = 15,000 h^{-1} (30,000 h^{-1} + 30,000 h^{-1}); 1500 ppmv N_2O; 500 ppmv NO; 2.5 vol.% O_2; 0.5 vol.% H_2O; 1500 ppmv C_3H_8; balance N_2.

3.1. Effect of pressure and SV

When the volume of both catalyst beds is halved, i.e. the SV is increased from 30,000 to 60,000 h^{-1} for each bed, the overall SV becomes 30,000 h^{-1}. As expected, destruction of both NO_x and N_2O take place at somewhat higher temperatures. NO_x conversion is higher than 70% from a reactor inlet temperature of about 380 °C and N_2O destruction from about 320 °C. The maximum NO_x conversion is lower at an SV of 30,000 h^{-1}: ~85% versus >95% at an SV of 15,000 h^{-1}.

Increasing the pressure has a positive effect on the performance of the catalytic system. Especially the conversion of NO_x improves strongly with pressure. At an overall SV of 30,000 h^{-1} (60,000 h^{-1} for each catalyst bed), both N_2O and NO_x conversion are higher than 70% above a catalyst inlet temperature of 300 °C (Fig. 3). The conversion of N_2O initially reaches full conversion at about 325 °C, but at higher temperatures the conversion of N_2O decreases to 85%. Above 400 °C the N_2O conversion is complete again.

This 'dip' in N_2O conversion is caused by the propane being consumed in the reaction with NO and the combustion reaction with O_2 on the Co-ZSM-5 catalyst. Not enough propane reaches the second catalyst to carry out the reduction of N_2O. Above 400 °C the conversion of N_2O increases again because the direct decomposition reaction takes over from the propane-assisted N_2O reduction. To get an insight in the behaviour of the system at higher pressures than 4 bara, an experiment with twice as much Co-ZSM-5 catalyst than Pd/Fe-ZSM-5 was performed (combined SV of 20,000 h^{-1}). Fig. 4 shows that in this case the 'dip' in the N_2O conversion is more prominent. The figure shows also that N_2O conversion follows the conversion curve for SCR with propane at lower temperature, and direct decomposition of N_2O at higher temperature.

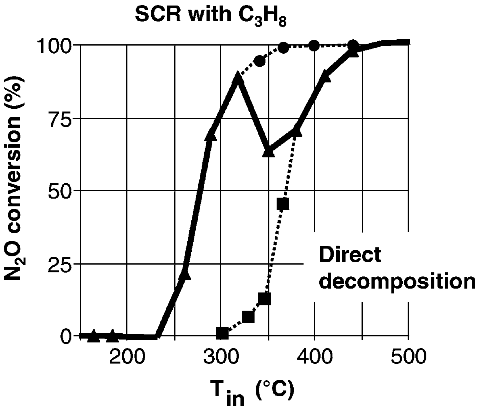

Fig. 4. N_2O conversion vs. catalyst inlet temperature on a stacked bed of Co-ZSM-5 and Pd/Fe-ZSM-5 catalysts in one reactor. Conditions: $p = 4$ bara; SV $= 20{,}000\,h^{-1}$ ($30{,}000\,h^{-1} + 60{,}000\,h^{-1}$); 1500 ppmv N_2O; 500 ppmv NO; 2.5 vol.% O_2; 0.5 vol.% H_2O; 1500 ppmv C_3H_8; balance N_2. C_3H_8 SCR: Pd/Fe-ZSM-5 catalyst only (SV $= 30{,}000\,h^{-1}$), same conditions; direct decomposition: Pd/Fe-ZSM-5 catalyst only (SV $= 30{,}000\,h^{-1}$), same condition without C_3H_8.

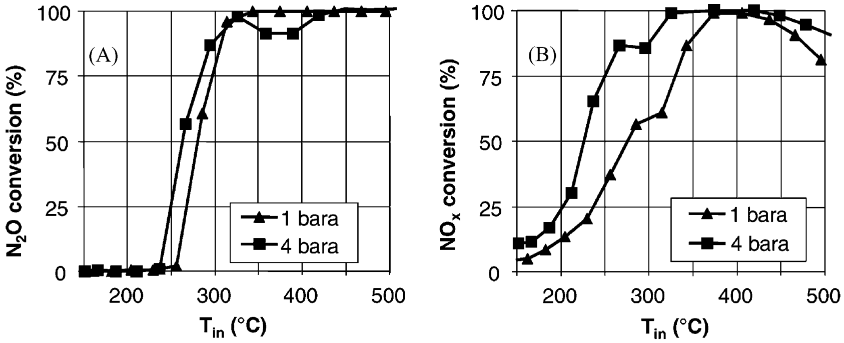

Fig. 3. N_2O (A) and NO_x (B) conversion vs. catalyst inlet temperature on a stacked bed of Co-ZSM-5 and Pd/Fe-ZSM-5 catalysts in one reactor. Conditions: $p = 1$ and 4 bara; SV $= 30{,}000\,h^{-1}$ ($60{,}000\,h^{-1} + 60{,}000\,h^{-1}$); 1500 ppmv N_2O; 500 ppmv NO; 2.5 vol.% O_2; 0.5 vol.% H_2O; 1500 ppmv C_3H_8; balance N_2.

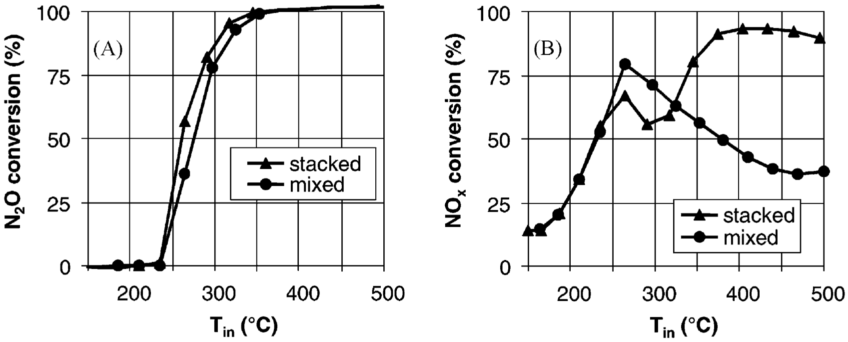

Fig. 5. N_2O (A) and NO_x (B) conversion vs. catalyst inlet temperature on Co-ZSM-5 and Pd/Fe-ZSM-5 in a stacked and a mixed configuration. Conditions: $p = 4$ bara; SV = 24,000 h^{-1} (120,000 h^{-1} + 30,000 h^{-1}); 1500 ppmv N_2O; 500 ppmv NO; 2.5 vol.% O_2; 0.5 vol.% H_2O; 1500 ppmv C_3H_8; balance N_2.

The lack of propane in the second catalyst bed can be solved by introducing extra propane between the first and second catalyst beds [7]. However, this would make the system more complicated and hence more expensive. Two alternative solutions to avoid the 'dip' in N_2O conversion were investigated: firstly, a catalyst configuration with a high SV through the first Co-ZSM-5 bed and a higher volume of the Pd/Fe-ZSM-5 catalyst. In a second experiment these two catalysts were mixed, so that the Pd/Fe-ZSM-5 DeN_2O catalyst is also present at the inlet of the catalyst bed, where the propane concentration in the gas is still high.

Fig. 5 shows that for both the mixed and the stacked catalyst configuration the 'dip' in the N_2O conversion curve is absent. The two configurations give about the same N_2O conversions at a given catalyst inlet temperature. However, the NO_x conversion on the mixed catalyst reaches high levels at around 250 °C, but decreases strongly at higher temperatures. High NO_x and N_2O conversion do not occur at the same temperatures on the mixed catalyst. On the stacked catalyst NO_x conversion is higher than 80% between 350 and 500 °C and at these temperatures also N_2O conversion is high.

In the stacked catalyst the gases first pass the Co-ZSM-5 catalyst, where NO_x and a part of the propane reacts. Because of the high SV of this catalyst (120,000 h^{-1}), not all propane reacts and enough propane is left for the SCR of N_2O on the second catalyst bed. In the mixed configuration at the inlet of the catalyst the propane is consumed in the reaction with NO_x on Co-ZSM-5 and the reaction with N_2O (and O_2) on Pd/Fe-ZSM-5. At high temperatures all propane is consumed in the first part of the catalyst bed, so the Co-ZSM-5 particles further upstream the catalyst bed have no propane available for the reduction of NO_x. N_2O conversion remains high, because at these temperatures direct decomposition of N_2O takes place.

4. Conclusions

The Pd/Fe-ZSM-5 catalyst can be used for the SCR of NO_x and N_2O, but the temperature windows for both reactions do not overlap. Co-ZSM-5 shows high NO_x conversions above 300 °C, but N_2O conversion takes place only above 400 °C. With a stack of a Co-ZSM-5 catalyst and a Pd/Fe-ZSM-5 catalyst it is possible to remove NO_x and N_2O in a single reactor by SCR with propane. At a pressure of 4 bara especially the NO_x reduction activity of the Co-ZSM-5 catalyst increases, which causes that not enough propane reaches the second catalyst bed to carry out the SCR of N_2O. Reducing the SV of the first bed solves this problem.

Acknowledgements

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