

Critical Aspects in the Catalytic Emission Control of Exhaust Gases Containing NH₃, NO_x and N₂O

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Abstract

Ammonia (NH₃) is a promising fuel for use in marine applications due to its favorable chemical properties. However, emissions of especially nitrous oxide (N₂O), with a global warming potential (GWP) of 273, pose a significant barrier to the adoption of NH₃ as a climate-friendly carbon-free fuel. Removing N₂O from the potential exhaust gas of NH₃-engines is particularly challenging due to the high temperatures required for its decomposition and the inherently complex nature of the exhaust. In this work, we studied relevant but anonymous samples from industrial partners under conditions of N₂O decomposition and of simultaneous conversion of N₂O/NO_x/NH₃. These catalysts displayed high-temperature N₂O decomposition activity as well as inhibitory effects by oxygen and especially water. In the case of the simultaneous conversion of N₂O and NO_x, initial indications of the reaction pathways suggest the presence of different active sites for N₂O decomposition and NO_x reduction and suggest a plausible promotional role of N₂O on NO_x conversion coupled with a positive effect of the reducing agent NH₃ on N₂O conversion. However, considering a reaction environment with a water content potentially as high as ca. 30 vol%, preliminary hydrothermal aging tests revealed a significant negative impact on both N₂O and NO_x conversions that needs to be addressed in the development of practice-relevant catalyst.

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Introduction

NH₃ is being discussed as a potential fuel for prospective combustion engines in the marine sector because it promises net-zero CO₂ emissions [1-3]. Notably, NH₃ has a high energy density (22.5 MJ/kg) and superior volumetric hydrogen density compared to gasoline, methanol and ethanol [4]. Still, due to the high ignition temperature and low flame propagation speed of NH₃, pilot fuels such as H₂, natural gas and Diesel are required to initiate the combustion of NH₃ [5-8]. These disadvantages can potentially negate the significant benefit of NH₃ with respect to CO₂ emissions and thus hinder development of large engines. A major issue from the perspective of engine exhaust gas is the presence of nitrous oxide (N₂O) [9, 10], which has a 273-fold higher global warming potential (GWP) than CO₂, i.e. only 1 ppm of N₂O equals 273 ppm CO₂ [11]. Consequently, exhaust after-treatment strategies must accompany engine development, and engine development must target the lowest possible N₂O emissions.

The option of installing downstream of an NH₃-engine an after-treatment system similar to that of

automotive Diesel-engines, which includes an oxidation catalyst followed by a catalyst able to reduce NO_x using NH₃ according to the selective catalytic reduction (SCR) reaction [12], may appear appealing as it represents already a complete and successful solution for emission control. However, the exhaust gas composition of the NH₃-engine is more complex, and beside N₂O, it contains a large excess of unburnt NH₃ relative to NO_x. Under these conditions, the oxidation catalyst produces most likely additional NO_x and N₂O from the oxidation of unburnt NH₃ [13], thus increasing the fraction of N₂O in the exhaust and making the after-treatment even more challenging.

Here, we have chosen to investigate catalysts that could take advantage of SCR, because of the availability of both NO_x and NH₃ in the engine exhaust gas. Fe-exchanged zeolites are active towards N₂O decomposition as well as SCR and are key players in emission control in stationary and heavy-duty applications [14]. Indeed, the N₂O decomposition has been widely explored and implemented in industry [15]. In this context, Mauvezin et al. [16] observed a significant influence of the zeolite topology (i.e. variations on the Al-O-

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Si three dimensional network coded according to the IZA database[17]) on the catalytic activity for N₂O decomposition, which changed in the order: Fe-FER > Fe-BEA > Fe-OFF > Fe-MFI > Fe-MAZ > Fe-FAU > Fe-MOR. Similarly, Wang et al. [18] suggested that Fe/CHA holds particular interest due to similar reaction rates compared to Fe-FER and the high hydrothermal stability inherent to the chabazite structure. Moreover, past works reported the combined conversion of N₂O and NO over Fe-exchanged zeolites using NH₃ during SCR. Coq et al. [19, 20] evaluated the potential use of Fe-BEA zeolites for the simultaneous SCR of N₂O and NO (N₂O-NO-SCR) using NH₃ as reducing agent under lean conditions. The results revealed that both NO and N₂O conversion increased when both reactants were present compared with the individual removal of either NO or N₂O. Severe hydrothermal aging affected Fe dispersion on extruded Fe-ZSM-5 and Fe-FER catalysts in opposite directions, i.e. Fe agglomeration on Fe-ZSM-5 and re-dispersion on Fe-FER, with an obvious different impact on N₂O conversion under N₂O-NO-SCR conditions [21].

Rhodium (Rh)-based catalysts are among the most active for N₂O decomposition [22, 23] but similar to other platinum group metal-based oxidation catalysts suffer from poor selectivity in NH₃ oxidation causing additional production of N₂O. Thus, they appear less suitable to remove N₂O from a complex feed gas of realistic composition containing NH₃, NO_x and N₂O [13] unless NH₃ concentration in the engine exhaust is maintained low compared to current projections or is removed completely beforehand.

In this work, we tested primarily several relevant catalysts for conversion of N₂O that were provided by industrial partners of a working group of the Research Association of Combustion Engines (FVV). We measured their behavior and particularly the N₂O removal efficiency in a laboratory test rig with a complex model exhaust gas containing also NO and NH₃, representing a generic NH₃-fueled engine. We also point towards the challenges ahead of NH₃-engine development with respect to gas emissions to provide recommendations at early stages of development. Therefore, we also include a study of a commercial oxidation catalyst to demonstrate its incompatibility with the exhaust gas of NH₃-engines. It emerges that the simultaneous conversion of N₂O, NO and NH₃ is a promising approach to control the emissions from such type of engines.

Materials and Methods

Seven catalysts samples of relevant but unknown composition were received in powder form or wash-

coated on cordierite monoliths (200-230 cpsi) from four industrial partners of the FVV working group. In the case of the powder samples, the catalyst mass (m_{cat}) after wash-coating varied between 2.7 and 3.2 g. Samples are labelled A to G. Simply by visual inspection (pink/red color) it was inferred that some of these catalysts included Fe-zeolites. A commercial catalyst for N₂O removal based on an Fe-exchanged zeolite (Fe-BEA; Clariant) was kindly provided in powder form and was wash-coated on cordierite monoliths (230 cpsi) using a standard procedure. A commercial automotive Diesel oxidation catalyst (DOC) was also tested in monolith form (cordierite, 90 g/ft³ Pt, 400 cpsi) for simultaneous SCR of N₂O and NO.

The catalytic tests were conducted under identical reaction conditions to offer a comprehensive overview of the behavior of different sample types. Activity measurements were carried out in a lab scale rig using a model exhaust gas (150 ppm N₂O, 3000 ppm NH₃, 1500 ppm NO, 10 vol% H₂O, 2 vol% O₂) obtained by blending N₂O, NO, NH₃, O₂ and N₂ using electronic mass flow controllers (Brooks). The total gas flow was varied depending on the size of the sample to achieve a gas hourly space velocity (GHSV) of 15,000 h⁻¹. Water was generated through the oxidation of hydrogen on a Pt/Al₂O₃ catalyst. The catalyst samples (rectangular parallelepipeds of slightly different dimensions) were firmly placed in a quartz reactor (inner diameter, 47 mm) comprising multiple heating zones to ensure precise temperature uniformity through the reactor cross section. The outlet gas concentration was sampled using a heated membrane gas pump (KNF) and analyzed using a Fourier transform infrared spectrometer (Thermo-Nicolet Nexus FTIR) equipped with a heated 2-m pathlength cell and a liquid N₂ cooled HgCdTe detector. For the activity measurements, the outlet gas concentration of the distinct gases was obtained at the point where the last 10 FTIR scans showed no significant variation (ca. 20 min), indicating steady state conditions. These values were used in order to calculate the conversions (χ_i) according to:

$$\chi_i = \frac{C_{i,in} - C_{i,out}}{C_{i,in}} \cdot 100 \quad (1)$$

where $C_{i,in}$ and $C_{i,out}$ are the concentrations (ppm) of the gas component i in the inlet and outlet gas, respectively. While the concentration of NH₃ in a real exhaust gas of a NH₃ engine can reach up to 1 vol% (10000 ppm), this analytic does not allow to measure such high gas concentrations of NH₃ and to obtain NH₃ conversion values. Thus, we opted for a symbolic high value of 3000 ppm NH₃ in the gas feed to the catalysts.

The commercial sample was studied in more detail with respect to the influence of N₂O concentration on NO conversion in the feed gas mixture. For this purpose, isothermal experiments were conducted by feeding the base reaction feed but with increasing N₂O concentration from 0 to 500 ppm. Similar experiments were carried out also with increasing concentrations of NH₃ and O₂. In these experiments, higher concentrations of NH₃ were used, because interest was on conversion of N₂O and NO. Finally, the influence of water concentration in the feed was also studied between 0 and 14 vol%.

Preliminary aging experiments were performed on the commercial sample and consisted in the exposure to 29 vol% H₂O at 450°C for 48 h in a reactor exploiting a water feeding system composed of a series of three hydrogen oxidation reactors of the type mentioned above. After aging, the sample was exposed in the same reactor to the feed gas mixture to monitor N₂O and NO conversion using the above-mentioned conditions.

Results and discussion

Figure 1 shows the concentrations of N₂O, NO, NO₂ and NH₃ measured at the reactor outlet as a function of temperature when the commercial Diesel oxidation catalyst (DOC) was exposed to a model gas feed closely resembling NH₃-engine out-like conditions. N₂O concentration was never below the value of 150 ppm fed to the catalyst; clearly N₂O production occurred in the whole temperature range and its concentration reached up to a twelve-fold value at 250°C. The concentration of NO also increased with increasing temperature and surpassed the inlet value above 350°C. The oxidation of NH₃ to N₂O ($2\text{NH}_3 + 2\text{O}_2 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$) and to NO ($4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$) is the origin of this behavior [24]. The NO₂ concentration passed through a maximum value at 350°C as a result of NO oxidation ($\text{NO} + 0.5\text{O}_2 \rightarrow \text{NO}_2$). This is one of the major functions of the DOC in automotive applications besides oxidizing CO and unburnt hydrocarbons to CO₂ [25]. Based on these results, it is irrelevant whether the expected oxidation of NH₃ to N₂ also occurred ($4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$). Although the oxidation of NH₃ to both N₂O and NO removes NH₃ effectively from the feed gas, the N₂O and NO formed in even higher concentrations are even more difficult to abate requiring typically higher temperature than the one at which they were produced. Figure 1 demonstrates that the first catalyst after the NH₃-engine must not contain noble metals, as their presence only aggravates the issue of N₂O emissions.

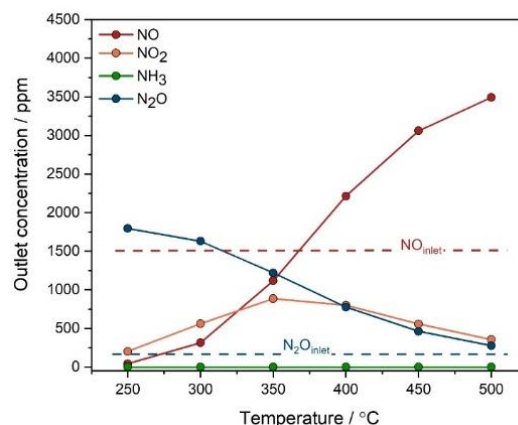


Fig. 1. Outlet N₂O, NO, NO₂, NH₃ concentrations of a commercial DOC under N₂O/NO/NH₃/O₂/H₂O feed. The inlet concentration values of N₂O and NO are indicated by the horizontal dashed lines.

Conditions: 150 ppm N₂O, 10 vol% H₂O, 2 vol% O₂, 1500 ppm NO, 3000 ppm NH₃ and N₂ balance; GHSV = 15000 h⁻¹.

Catalyst Screening

The primary focus of this work was to obtain data on available exhaust after-treatment technologies for N₂O abatement. This involved a series of experiments on nitrogen oxide removal (DeNO_x) and nitrous oxide removal (DeN₂O) using catalysts from different suppliers. To this end, we screened the samples under a range of conditions to identify the potential challenges associated with the low-temperature abatement of N₂O in the presence of NO, NH₃, water and oxygen.

Figure 2 presents the results of N₂O/NO_x conversion on the catalysts in monolith form using various model gas feeds. Under N₂O decomposition conditions (N₂O/O₂, Figure 2a), we observed varying degrees of catalytic activity for N₂O conversion. Notably, catalysts A and C exhibited the highest catalytic activity, achieving a T₅₀ (the temperature at which 50% conversion is achieved) of ca. 325°C and reaching maximum N₂O conversion at 400°C. It is important to note that the presence of water had a significant inhibitory effect on N₂O conversion (Fig. 2b), with most catalysts completely losing their capability to convert N₂O. Similarly, the T₅₀ of sample B increased to 450°C in the presence of water, and complete conversion was barely achieved at 500°C. These findings underscore the critical impact of water on catalytic performance, which becomes relevant especially in NH₃-engine applications where its content can vary considerably, possibly reaching up to 30 vol% H₂O under stoichiometric conditions.

The N₂O and NO_x conversions over selected catalysts obtained in the complex feed containing

NH_3 , NO , and N_2O along with oxygen and water are shown in Fig. 2c and Fig. 2d, respectively. Irrespective of catalyst, N_2O conversion set in above 350°C and was complete at 500°C or higher. The N_2O conversion curves did not differ significantly among the catalysts. Moreover, the activity was partially restored compared to the wet N_2O decomposition case, likely due to the promoting effect of NH_3/NO on the N_2O decomposition. Under the same reaction conditions, NO_x conversion

between 250 and 500°C varied significantly among the catalysts, ranging from 70% NO_x conversion at 350°C to 80% NO_x conversion at 500°C depending on catalyst. Entries B and D are not reported in Figs. 2c,d because under these conditions N_2O and NO were actually produced at higher temperature, likely due to the NH_3 oxidation side reaction, suggesting the different nature and applicability field of these two catalyst samples.

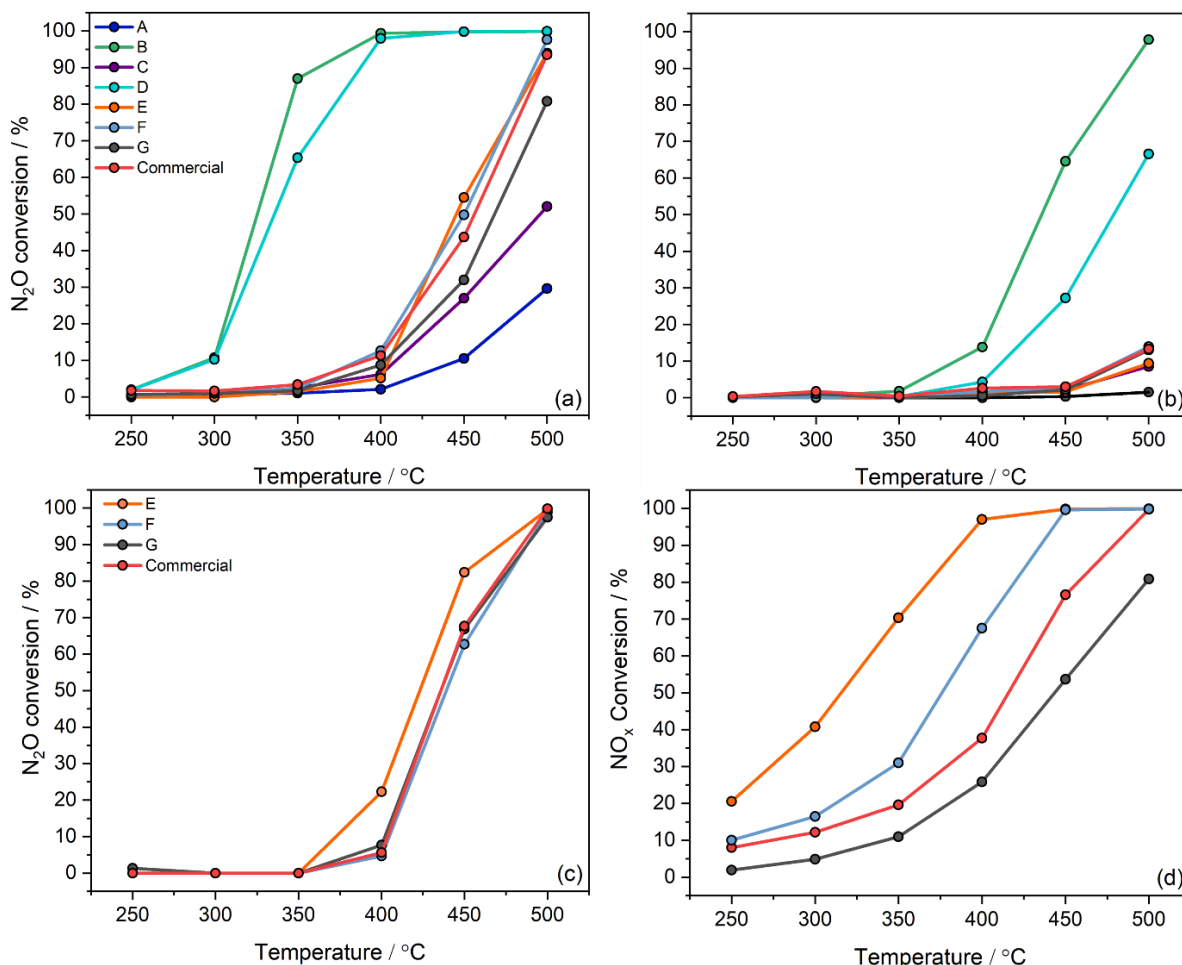


Fig. 2. N_2O decomposition under (a) dry and (b) wet conditions. (c) N_2O and (d) NO_x conversion in $\text{N}_2\text{O}/\text{NO}/\text{NH}_3/\text{O}_2/\text{H}_2\text{O}$ feed. Conditions: 150 ppm N_2O , 0 or 10 vol% H_2O , 2 vol% O_2 , 0 or 1500 ppm NO , 0 or 3000 ppm NH_3 and N_2 balance; $\text{GHSV} = 15000$ h^{-1} .

The different order of activity in DeN_2O ($\text{E} > \text{commercial} + \text{G} > \text{F}$) and DeNO_x ($\text{E} > \text{commercial} > \text{G}$) suggests the presence of different active sites that could be responsible for the activity of these catalysts in both reactions. Specifically, catalysts designed for N_2O decomposition such as the commercial one displayed only limited conversion of NO_x compared, for example, to sample E under these experimental conditions.

Because the commercial catalyst is specifically developed for N_2O decomposition, we explored its behavior under a number of other conditions (Fig. 3a). In the absence of water ($\text{N}_2\text{O}/\text{O}_2$), the catalyst showed a T_{50} of 325°C for N_2O decomposition and achieved maximum N_2O conversion at 450°C . The inhibition effect by water was evident, leading to a 90% loss of N_2O conversion at 500°C . The presence of reducing agents (CO , NO) had a promoting effect on N_2O decomposition and the activity in presence of water was also recovered compared to the case

without the reducing agents. These findings align with prior studies. In this context, Kapteijn et al. [26] first reported the promoting effect of NO on N₂O decomposition over Fe-ZSM-5. Similarly, Guzmán-Vargas et al. [19] confirmed the positive role of the reducing agents using different iron zeolite structures. Delahay et al. [27] considered the effect of the nature of the reductant on the catalytic N₂O decomposition over Fe-BEA using CO, NH₃, H₂, C₁₀H₂₂, and C₃H₆. The overall promoting role of these reducing agents is associated with the enhancement of the oxygen evolution from the catalyst surface that is considered the rate determining step in N₂O decomposition.

Figure 3b displays the N₂O and NO_x conversion under N₂O-NO-SCR conditions at two NH₃:NO ratios (α). Similar to Fig. 2, complete N₂O conversion was achieved at temperatures above 450°C, with T₅₀ of ca. 425°C. N₂O conversion decreased in the presence of excess NH₃ relative to

NO_x. At 450°C, N₂O conversion changed from 95% at $\alpha = 1$ (1500 ppm NH₃) to 65% at $\alpha = 2$ (3000 ppm NH₃). This behavior is attributed to the NH₃ inhibition effect, which will be described in detail further.

The results of Figs. 2-3 reveal that despite the availability of commercial technologies, removal of N₂O emissions from NH₃-fueled engines is challenging. In particular, the conversion of N₂O at lower temperature than 400°C was insufficient over all samples and points out the necessity to discover more suitable catalytic materials. In this context, Fe-zeolites are promising but challenging materials due to the heterogeneous nature of Fe speciation in Fe-zeolites. Different types of Fe species are possible ranging from single sites to nanoparticles or bulk oxides [28]. Furthermore, despite the confirmation of the existence of several sites on Fe-zeolite materials, their role on the reduction of N₂O remains debated.

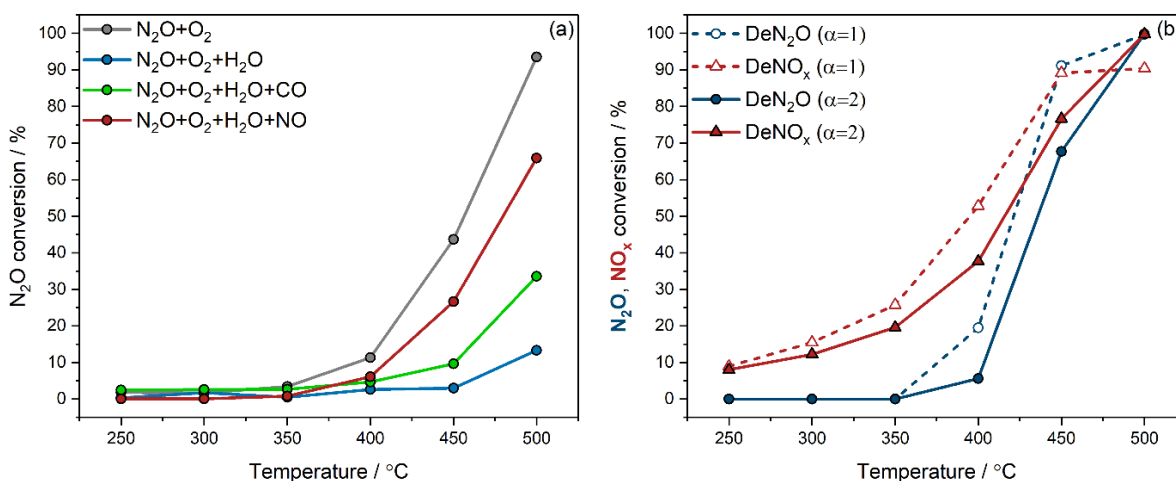


Fig. 3. (a) N₂O decomposition over the commercial catalyst in the presence of H₂O, CO, NH₃ and O₂. (b) N₂O (blue) and NO_x (red) conversion under SCR conditions at two NH₃/NO_x ratios (α). Conditions: 150 ppm N₂O, 0 or 10 vol% H₂O, 2 vol% O₂, 0 or 1500 ppm NO, 0, 1500 or 3000 ppm NH₃ and N₂ balance; GHSV = 15000 h⁻¹; m_{cat} = 3.2 g.

Model gas composition

The commercial catalyst was subjected to systematic variations of the gas composition to explore the activity regime and study the influence of each component (NO, NH₃, N₂O, O₂, H₂O) on NO_x and N₂O conversion. Figure 4 presents the NO_x conversion obtained upon changing the N₂O concentration in the feed at different temperatures, while keeping all other parameters constant. Even at 400°C, a notable 8% increase in NO_x conversion occurred upon increasing the N₂O concentration up to 500 ppm. The most substantial enhancement in NO_x conversion (30%) was achieved at 500 ppm N₂O.

These initial findings confirm the promoting role of N₂O on DeNO_x coupled with the positive effect of reducing agents on DeN₂O, as mentioned above. Further analysis and experimentation are required to gain a comprehensive understanding of the underlying mechanisms driving this enhancement in NO_x conversion and to optimize the operating conditions in N₂O-NO-SCR applications.

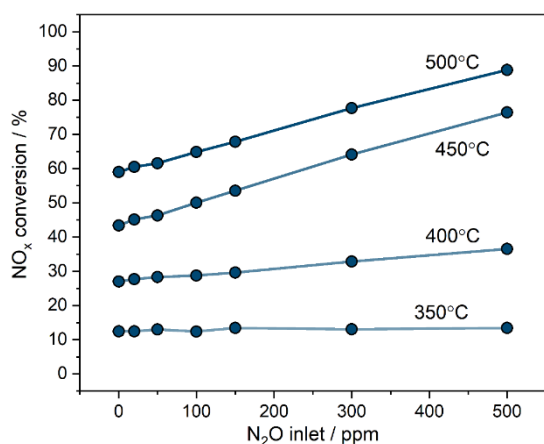


Fig. 4. Influence of N₂O concentration on NO_x conversion under SCR conditions over the commercial catalyst. Conditions: 0-500 ppm N₂O, 10 vol% H₂O, 2 vol% O₂, 1500 ppm NO, 1500 ppm NH₃ and N₂ balance; GHSV=15000 h⁻¹; m_{cat}=2.7 g.

Similar experiments were performed by varying the O₂ concentration. This parameter holds critical importance as it mirrors the potential variations of the O₂ content in the exhaust gas. These variations can be attributed to the various engine technologies that can be adopted for a prospective NH₃-engine, or to factors such as combustion efficiency, air-to-fuel ratios, or specific operational conditions of the engine. While O₂ did not affect significantly N₂O

conversion over a wide range of concentrations (Fig. 5a), a consistent and progressive increase in the NO_x conversion, especially when increasing the O₂ concentration up to 2 vol% was observed (Fig. 5b). This behavior is expected considering that O₂ is one of the essential reactants in the SCR reaction.

Alongside the influence of O₂, the impact of water is of importance in comprehending the catalytic behavior under realistic operating conditions. In dedicated experiments, we observed a notable decrease in catalytic activity in the presence of water, affecting both N₂O (Fig. 6a) and NO_x conversion (Fig. 6b). At 400°C, a significant reduction in N₂O conversion was observed, with a quasi-linear drop from 40% in the absence of water to 22% when 14 vol% H₂O was introduced into the feed. Similarly, at a higher temperature of 450°C, a more subtle but still noticeable effect was observed, resulting in an 8% loss in N₂O conversion with the introduction of 14 vol% H₂O into the feed. The loss of NO_x conversion was ca. 15% at 450°C and 35% at 400°C. These findings underscore the need for consideration of the water content in the design and operation of catalytic systems for simultaneous NO_x and N₂O conversion, especially given the potential high-water content in the exhaust of a prospective NH₃-engine. Additionally, the effect of prolonged exposure to high water contents is of importance under reaction conditions.

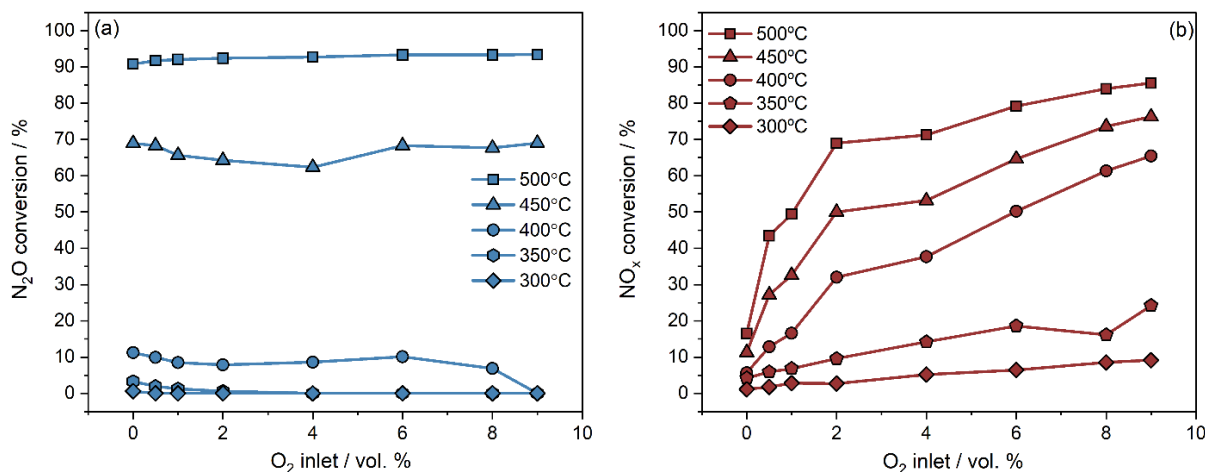


Fig. 5. Influence of O₂ concentration on (a) N₂O conversion and (b) NO_x conversion over the commercial catalyst. Conditions: 150 ppm N₂O, 10 vol% H₂O, 2 vol% O₂, 1500 ppm NO, 1500 ppm NH₃ and N₂ balance; GHSV = 15000 h⁻¹; m_{cat} = 3.2 g.

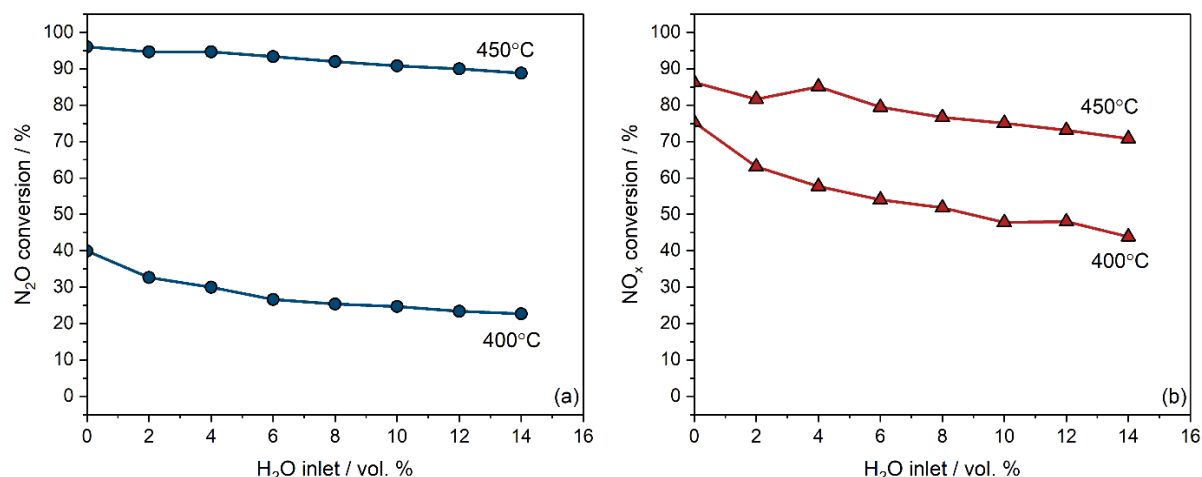


Fig. 6. Influence of H₂O concentration on (a) N₂O conversion and (b) NO_x conversion over the commercial catalyst. Conditions: 150 ppm N₂O, 0-14 vol% H₂O, 2 vol% O₂, 1500 ppm NO, 1500 ppm NH₃ and N₂ balance; GHSV = 15000 h⁻¹; m_{cat} = 3.2 g.

Hydrothermal aging

The long-term deactivation of a catalyst due to exposure to water at elevated temperature (hydrothermal aging, HTA) is a critical factor contributing to changes in DeNO_x and DeN₂O. Here, we opted to study hydrothermal aging at reaction conditions rather than at very high temperature that could be ambiguous with respect to beneficial effects [29, 30] with the knowledge that the average exhaust gas temperature of a NH₃-fueled engine could be between 350 and 500 °C [31].

Figure 7 shows the influence of NH₃ inlet concentration on DeNO_x and DeN₂O at 450°C of the commercial catalysts in its pristine form and after exposure to 29 vol% H₂O at 450°C for 48 h. In both cases, NO_x and N₂O conversion passed through a maximum value. For the pristine catalyst, this corresponded approximately to the optimal NH₃ inlet value ($\alpha = 1$, NH₃ = 1500 ppm). The decrease in NO_x conversion after the maximum with increasing NH₃ concentration in the feed is associated with the NH₃ inhibition effect and with the redox function of the active sites (Fe²⁺/Fe³⁺ pair). The adsorption/interaction of NH₃ with these sites can block the redox function, thus causing a decrease in DeNO_x [32]. Our results reveal that this phenomenon plays a significant role for the catalytic activity towards the N₂O-NO-SCR reaction.

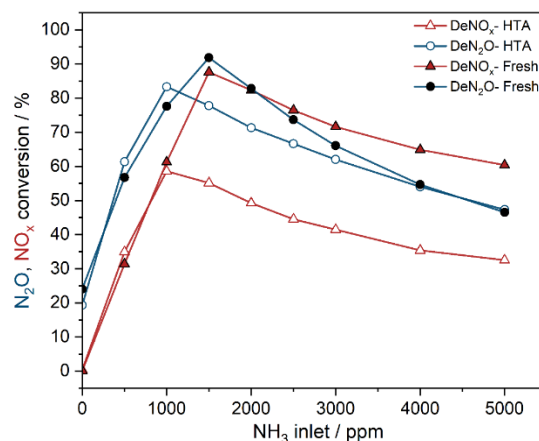


Fig. 7. Influence of NH₃ on NO_x and N₂O conversion over the pristine and aged commercial catalyst. Conditions: 150 ppm N₂O, 10 vol% H₂O, 2 vol% O₂, 1500 ppm NO, 0-5000 ppm NH₃ and N₂ balance; GHSV = 15000 h⁻¹; m_{cat} = 3.2 g.

Aging with 29 vol% H₂O in the feed caused the maximum NO_x conversion to decrease from 90% to 55% and to shift to lower NH₃ inlet values compared to the pristine sample. The maximum N₂O conversion slightly increased but also shifted to lower NH₃ concentrations. The difference between DeNO_x and DeN₂O is more clearly visible for NH₃ concentrations higher than at the maximum conversion. NO_x conversion was constantly lower by ca. 30% in the aged sample, while the difference in N₂O conversion decreased from ca. 15% at 1500 ppm NH₃ ($\alpha = 1$) to ca. 5% at 3000 ppm NH₃ ($\alpha = 2$). This behavior confirms the presence of different active sites responsible for the two reactions under N₂O-NO-SCR conditions. In the case of Fe-exchanged zeolites, the decrease in catalytic activity is caused by dealumination of the zeolite structure in the presence of water, which decreases the acidity of

the zeolite, and the migration of active isolated Fe ions to form clusters that are less active at the same temperature [33].

Conclusions

Our study emphasizes that while commercial technologies are readily available to limit emissions of N₂O and NO_x in the environment, their direct application to emerging NH₃-engines is not straightforward, primarily due to the unique operating conditions of these engines. Achieving low-temperature conversion of N₂O (around 350°C) in the presence of the complete exhaust gas mixture including NO_x, N₂O, NH₃, oxygen and water is challenging. This difficulty is exacerbated by the inhibitory effects of water, oxygen and the required optimal NH₃ feed, which emerge as critical factors. The high levels of water vapor in the exhaust gas of an NH₃-engine introduce additional challenges related to hydrothermal aging of the catalyst, thus its long-term performance. Therefore, further research and the development of tailored exhaust gas treatment solutions for these engines is crucial. This advancement is pivotal to ensure that the systems align with net-zero emission goals, addressing both efficiency and environmental sustainability.

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Conflicts of Interest

The authors declare no conflict of interest.

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