Impact of gas phase reactions and catalyst poisons on the NH$_3$-SCR activity of a V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst at pre-turbine position

Deniz Zengel$^a$, Matthias Stehle$^a$, Olaf Deutschmann$^{a,b}$, Maria Casapu$^a$, and Jan-Dierk Grunwaldt$^{a,b,*}$

$^a$ Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstr. 20, 76131 Karlsruhe, Germany

$^b$ Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

* Jan-Dierk Grunwaldt: grunwaldt@kit.edu
Abstract

With stricter regulations and decreasing exhaust gas temperature due to more efficient engine management, NO$_x$ abatement remains a critical issue despite many technical and catalytic advances. To counterbalance these challenges the positioning of exhaust gas aftertreatment systems in front of the turbocharger has gained significant interest in recent years. In this context, we report a systematic study on the impact of propylene, $n$-dodecane, and $o$-xylene as well as of SO$_2$ on the gas phase reactions and NH$_3$-SCR activity of a conventional vanadium-based catalyst at increased pressure. An elevated pressure is shown to dramatically promote homogeneous reactions of hydrocarbons, which subsequently contribute to an increased NO oxidation but also to parasitic NH$_3$ overconsumption. The hydrocarbons are also faster catalytically oxidized at elevated pressure and affect NO$_x$ reduction at all investigated temperatures. Their presence in the exhaust gas further leads to the formation of the toxic byproducts HCHO and HCN. Upon short term exposure of 20 ppm SO$_2$ in the feed gas, strikingly no significant catalyst poisoning was observed. However, for longer exposure times an enhanced formation of sulfur containing deposits was observed at low temperature for elevated pressures. Notably, their poisonous effect was reversible after heating to elevated temperature.

Keywords. Selective catalytic reduction, vanadium, pre-turbo, catalyst poison, elevated pressure
1. Introduction

As internal-combustion engines play a significant role both for stationary and mobile application, finding efficient technologies for reducing pollutants in the exhaust gas is of great importance. In particular, the abatement of nitric oxides (NO\textsubscript{x}), which are the cause of airways irritation, photochemical smog formation, ozone depletion and acidic rains, has become increasingly important in recent decades and a variety of techniques have been developed. Efficient paths are exhaust gas recirculation, modified fuel injection or using alternative tailor-made fuels with superior combustion characteristics.[1] Nevertheless, these techniques are limited to a certain extent and the implementation of catalytic systems is mandatory to meet increasingly stricter emission regulations. One of the most effective ways to decrease NO\textsubscript{x} emissions in lean combustion engines is the ammonia assisted selective catalytic reduction (NH\textsubscript{3}-SCR). NH\textsubscript{3}-SCR is widely applied for stationary as well as mobile applications, especially heavy-duty vehicles. Vanadium based catalysts and ion-exchanged zeolites are the most efficient catalysts for this process.[2] While Cu-exchanged zeolites are the preferred catalysts for low temperature applications and their good hydrothermal stability is well known, Fe-exchanged zeolites and vanadium-based catalysts are used due to their good overall activity and resistance against sulfur poisoning.[3] With the help of NH\textsubscript{3}-SCR catalysts a significant decrease of NO\textsubscript{x} emissions was achieved in recent years. However, due to the improved engine efficiency that causes a decrease in the exhaust gas temperatures better technical solutions are required. One possible approach would be to reduce the distance between the catalytic system and the engine. Studies from Presti et al.[4] showed that a significant increase of pollutant conversion could be achieved by locating the catalyst closer to the engine. An even more attractive methodology is to place the aftertreatment system in front of the turbocharger, directly after the engine. Previous investigations showed an
up to 180 °C higher exhaust gas temperature compared to that measured at typical catalyst locations.[5] Besides the advantage of higher exhaust gas temperatures, this configuration of the exhaust aftertreatment system would also result in increased pressures and therefore higher residence times. Particularly, the last aspect has attracted increasing interest and several studies were already conducted. For diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) a high potential to decrease the catalyst volume (down to 50%) without having the drawback of a significant pressure drop was reported.[5, 6] More recently, the application of the SCR catalysts under pre-turbine conditions was investigated. Kröcher et al.[7] showed for a V-based catalyst that an increased pressure grants a significantly smaller catalyst volume but also that the decreased diffusion and increased partial pressures can hinder the standard SCR reaction. Experimental and modeling studies of Rammelt et al.[8] and Christensen et al. [9] indicated no change in catalytic activity and kinetics at elevated pressures, and only an increased adsorption of NH₃ for V-based catalysts. In one of our earlier studies we reported the positive influence of pressure as well as the negative impact of propylene and SO₂ for a Cu-SSZ-13 SCR catalyst.[10] The last two aspects, HCs and SO₂ impact, are particularly important if no DOC is implemented in front of the SCR catalyst or if, due to limited space, a too short DOC is used to fully convert the catalyst poisons. Furthermore, the influence of elevated pressures on the gas phase reactions is an essential parameter. As shown in our previous study NOₓ significantly promotes the oxidation of light alkanes under pre-turbo conditions.[11] An analogous effect was observed even at ambient pressure.[12-14] At the same time, a reciprocal sensitization of NO oxidation to NO₂ via low and high temperature mechanisms involving alkyperoxy or HO₂ radicals, respectively, has been reported.[15, 16] Furthermore, Hazlett and Epling[13] have demonstrated that such homogeneous reactions occur within the monolithic channel of a DOC and might promote the NO oxidation.
Hence, with this study we aimed at a systematic investigation on the impact of pressure on the catalytic activity of a conventional V$_2$O$_5$-WO$_3$/TiO$_2$ NH$_3$-SCR catalyst, including the presence of hydrocarbons (HCs) and SO$_2$. Additionally, the impact of the gas-phase reactions was investigated. In order to represent the full diversity of hydrocarbons and their impact, several model compounds were used: propylene (short chain HCs), $n$-dodecane (long chain HCs) and $o$-xylene (aromatic HCs). During the SO$_2$ poisoning tests, the focus was especially on the low temperature formation of sulfur-containing deposits as a function of pressure variation. This study thus contributes to a holistic view on the benefits and limitations of a pre-turbo SCR application under more realistic reaction conditions.

2. Experimental

2.1 Catalyst Preparation

For this study a V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst was prepared with a 2.0 wt.% V$_2$O$_5$ and a 9.0 wt.% WO$_3$ loading. The vanadium catalyst was synthesized by incipient wetness impregnation (IWI) of commercially purchased TiO$_2$ (Alfa Aesar) like in the work of Zheng et al.[17] The resulting powder was coated on a cordierite honeycomb (cell density 400 cpsi) via dip coating. For each testing condition a new honeycomb was prepared. Each catalyst core had a 2.54 cm in diameter and 3 cm in length. These dimensions were selected to reach a high gas hour space velocity, i.e. 100,000 h$^{-1}$, similar as in real applications. The catalyst slurry was prepared by mixing the catalyst powder with 10 wt.% Disperal P2 (Sasol) of the total mass in demineralized water. After several coating and drying steps, the desired amount of washcoat was achieved. The coated honeycomb was calcined in static air at 550 °C for 4 hours. For each catalyst poison a different honeycomb was used. The amount of washcoat on the different honeycombs is summarized in Table S1.
2.2 Catalyst Characterization

The prepared catalyst powder was characterized before coating to ensure that the powder has the desired composition and properties of a common vanadium catalyst. X-ray diffraction measurements were performed on a Bruker D8 Advance diffractometer using Cu-Kα radiation. The scans were recorded over a 2θ range of 20-80° with steps of 0.017°. A Belsorp Mini II (Bel Japan Inc.) was used to determine the surface area and the pore volume of the catalyst. Approximately 80 mg of the sample were degassed at 300 °C under vacuum for 2 hours. Afterwards adsorption and desorption of N₂ was measured and evaluated with the Belsorp Adsorption/Desorption Data Analysis Software assuming a Brunauer-Emmet-Teller isotherm. The elemental composition was identified by X-ray fluorescence (XRF) analysis at the Institute for Applied Materials - Applied Materials Physics (IAM-AWP, KIT). For characterization of the washcoat after the SCR reactions and the formation of deposits Raman spectroscopy was used during the tests in presence of SO₂. Raman spectra were recorded with a Renishaw inVia Reflex Raman Spectrometer System equipped with Leica microscope and a 532 nm laser. The laser was defocused to a line and an area of 80 µm x 268,8 µm was scanned with a raster step size of 3,2 µm, resulting in 2210 individual spectra. Finally, all obtained spectra were averaged.

2.3 Catalyst Test Bench Measurements

The catalytic activity tests as well as the temperature programmed desorption experiments were performed on a test bench which is described in detail in a study by Günter et al.[10] In short, a stainless steel reactor was used for safety reasons, particularly, to avoid leaking of the setup at the high pressures applied. The reactor, gas pipes and FTIR gas cell were entirely coated by chemical
vapor deposition with a Si-based coating by SilkoTek (225 PennTech Drive, Bellefonte, PA 16823), which to our knowledge is one of the most inert coatings that are currently commercially available. A coating layer thickness of 800 nm was used not only protect the stainless steel against corrosion, which might occur due to the presence of corrosive gases (NOx, SO2), but also to prevent reactions catalyzed by the reactor wall (see also blank reactor tests). In addition to gaseous compounds, the testing setup allowed the dosage of liquid hydrocarbons like n-dodecane and o-xylene. For this purpose, an additional heated saturator with varying flows of nitrogen was used adjusting the saturator temperature, dependent on the amount and kind of dosed hydrocarbon.

To determine the effect of possible reactions in the gas phase, systematic empty reactor tests were conducted for each gas mixture and pressure variation. For the calculation of the residence time, the total reactor volume (inner and outer tubes of the countercurrent flow reactor) corresponding to a constant temperature zone (±5 K) was used. Temperature profiles along the inner tube for two reactor temperatures (200 °C and 650 °C) and two pressures (1 and 5 bar) are given in Fig. S2. The temperature gradient especially observed at high temperatures (up to 85 K lower at 650 °C) is due to the colder gases entering the reactor, as the gas lines were heated to 180 °C to prevent uncontrolled gas phase reactions in front of the catalytic reactor. The residence time of the gas mixture increased from 0.2 to 4.4 s depending on pressure and temperature (Table S2). For the catalytic reactions, the monolithic catalyst (3 cm length) was always placed within the constant temperature zone of the reactor (> 20 cm for all test conditions, Fig. S2).

Before each series of catalytic tests, the coated monoliths were heated up to 550 °C in 14% O2/N2 for one hour to clean the catalyst surface. The conditioning and activity tests were conducted under a total flow of 25.3 L min⁻¹ which is equal to a gas hour space velocity of 100,000 h⁻¹. For measurements in absence of hydrocarbons and SO2 the catalyst was heated up to 550 °C and exposed to
relevant gas mixtures. The tested reaction mixtures are standard-SCR (350 ppm NO, 350 ppm NH₃) and fast-SCR (175 ppm NO, 175 ppm NO₂, 350 ppm NH₃). Each condition also involved 14% O₂, 4.5% H₂O and 2% CO₂ in N₂ as balance. For measurements in the presence of hydrocarbons no CO₂ was added to the gas feed to determine also the selectivity towards CO₂. To exclude an influence of CO₂ on the reaction, test measurements with and without CO₂ were compared showing no significant difference. The different gas mixtures were fed at a stationary temperature point until the conversion reached a steady state. The temperature was decreased stepwise with 50 °C steps and the procedure was repeated until the lowest temperature of 150 °C was reached. After finishing for 1 bar pressure the experiment was carried out for 3 and 5 bar as well. The measurements in the presence of hydrocarbons were performed by using HCs concentration selected so that the total carbon number was 600 ppm, e.g. 200 ppm C₃H₆. In addition, the hydrocarbon oxidation with 14% O₂ and 4.5% H₂O in N₂ balance was determined.

Besides the effect of hydrocarbons also the influence of SO₂ under varying pressure was investigated. For these tests 20 ppm of SO₂ were dosed in a standard SCR gas mixture. As for the first measurements, temperatures from 550 to 150 °C and all three pressures were investigated. After each test at certain pressure the catalyst was heated up to 550 °C in presence of O₂ to remove the formed residues or decompose the sulphated species. To investigate the influence of pressure on formation of such residues the catalyst was exposed to a standard SCR gas mixture in presence of SO₂ over an extended period. For this investigation different temperatures as well as different pressures were tested. Subsequently, a temperature programmed desorption in N₂ was performed to determine the amount of deposits. In addition, also catalytic activities right after extended exposure to SO₂ were conducted. Note that in this case the NOₓ conversion was determined measuring from 150 to 550 °C to see the impact of possible sulfur residues on the catalytic activity.
Afterwards the NO\textsubscript{x} conversion was measured a second time to clarify whether the catalyst showed any irreversible changes.

3. Results and Discussion

3.1 Gas-phase reactions involving HCs, SO\textsubscript{2}, NO and NH\textsubscript{3}

The effect of the temperature and pressure variation on the gas-phase reactions was studied systematically for all gaseous components and their mixtures. Only a minor effect of the pressure increase was observed during NO and NH\textsubscript{3} oxidation above 450 °C (Fig. S3a and b). Under standard SCR conditions, NH\textsubscript{3} oxidation is slightly promoted at high temperatures and 5 bar pressure (Fig. S3c). Propylene oxidation increases as well at temperatures higher than 400 °C and pressures above 3 bar, and is similarly promoted in the presence of NO and standard SCR conditions (Fig. 1 and Fig. S4) but is inhibited in a gas mixture containing only C\textsubscript{3}H\textsubscript{6}, NH\textsubscript{3} and O\textsubscript{2}.

![Fig. 1 Gas phase reaction in absence of a catalyst under standard SCR conditions (350 ppm NO, 350 ppm NH\textsubscript{3}, 14% O\textsubscript{2} and 4.5% H\textsubscript{2}O in N\textsubscript{2}) at 1 bar/ambient, 3 bar and 5 bar pressure in presence of a) 200 ppm C\textsubscript{3}H\textsubscript{6} or b) 50 ppm C\textsubscript{12}H\textsubscript{26}.](image)

The mechanism of gas-phase hydrocarbon oxidation has been described as a chain radical reaction with degenerative branching[18] initiated by an oxidizing compound, such as O₂, HO₂· or OH·. The formation of HO₂·, OH· and R· radicals was suggested to involve O₂ and also NOₓ, if the latter are present in the gas mixture.[11, 14] The next stage is the formation of an hydroperoxide ROOH, which further reacts with the hydrocarbons, free radicals or oxidation intermediates.[18] In the presence of NO₂ the formation of an alkyl nitrites was proposed by Otsuka et al.[12]

Additionally, the alkylperoxy radicals might undergo isomerization or thermal decomposition into smaller alkyl radicals and olefin species, a path especially promoted at high temperatures.[19, 20] These different reaction paths, with oxygenates formation favored at low temperatures and alkene formation at high temperature, are supported by the various oxidation byproducts detected during propylene oxidation in a standard SCR gas mixture (Fig. S5), i.e. CO, formaldehyde and ethylene. In addition to the effects observed during propylene conversion, a promotion of the NH₃ and NO oxidation was measured at high pressure and temperature, which is in line with our previous study.[10] Under standard SCR conditions 30% NO conversion to NO₂ was recorded at 550 °C and 5 bar (Fig. 2a) as compared to only 9% measured in a C₃H₆ free gas mixture of 350 ppm NO, 4.5% H₂O, 14% O₂ in N₂. A similar increase of the NO oxidation beyond the equilibrium of NO₂ formation with O₂ as oxidizing species was reported by Zalc et al.[14] during homogenous methane oxidation. Under such conditions, NO₂ has been proposed to form by NO reaction with oxidizing radicals such as HO₂· or ROO·.[21, 22]
Fig. 2 NO/NO$_2$ ratio after the empty reactor with a standard SCR gas mixture containing a) C$_3$H$_6$ and b) C$_{12}$H$_{26}$ at 1/ambient, 3 and 5 bar pressure.

For a longer carbon chain, as present in $n$-dodecane, a significantly earlier oxidation onset was obtained under all reaction conditions. This result is in line with previous studies which demonstrated a lower oxidation temperature with increasing chain length and furthermore a lower oxidation temperature for straight-chain hydrocarbons in comparison with branched chain or aromatic hydrocarbons.[13, 19, 23] Almost regardless of the pressure variation, the oxidation of $n$-dodecane started above 250 °C in 50 ppm C$_{12}$H$_{26}$, 4.5% H$_2$O, 14% O$_2$/N$_2$ and is completed around 350 °C (Fig. S6a). In contrast to propylene oxidation, NH$_3$ has a minor effect on $n$-dodecane conversion but the reaction is inhibited by the presence of NO (Fig. S6b and c), which led to a shift of the ignition temperature with about 50 °C. NO and NO$_2$ seem to act as an oxidation
chain terminator, probably by reacting with HO· radicals following a mechanism analogous to that suggested in previous studies [11, 21, 24] or via the formation of nitroalkanes at low temperatures.[12] As reaction byproducts several compounds were detected: CO, HCHO, HCOOH, and C₂H₄ (Fig. S7).

In a NO/C₁₂H₂₆ gas mixture a positive impact of n-dodecane presence on the NO oxidation to NO₂ was noticed already at atmospheric pressure (Fig. S8). Starting at 350 °C a sharp increase and approximatively 43% NO conversion to NO₂ was observed at 400 °C. A similar effect was recently reported for HCs rich diesel exhaust gas mixtures, as for example present during the low temperature combustion of diesel.[13, 16] The oxidation reaction was only slightly affected by the temperature increase (48% NO conversion at 550 °C). At 1 bar the NO₂ concentration also showed a two-maxima profile as the temperature increased. This behavior could be linked to the two reaction pathways involving alkylperoxy or HO₂ radicals at low and high temperatures, respectively.[25] On the contrary, the elevation of pressure dramatically promoted the homogeneous reaction. For a pressure of 5 bar 81% NO to NO₂ oxidation activity was measured already at 400 °C and almost complete NO oxidation at 550 °C. Such a high NO to NO₂ conversion due to HCs promoted gas phase reactions at elevated pressures, as revealed in this study for propylene and n-dodecane, could have a substantial positive effect on downstream SCR or DPF catalytic components in the exhaust pipe, which perform at lower exhaust gas temperatures. Hence, the possibility of deliberately dosing small amounts of HCs at the pre-turbine position to passively regenerate the downstream DPF or to sustain the fast SCR reaction on a following NH₃-SCR catalyst via homogeneously generated NO₂ could be regarded as a promising path for further improvement of the emission control system.
As an additional effect, a small difference was noticed when comparing the total NO\textsubscript{x} amount resulting for the different measurement points with the NO concentration at reactor inlet, especially at low temperatures (Fig. S8). As mentioned above, this behavior could be due to the formation of nitroalkanes,[12] which decompose at higher temperatures.[12, 26] The promoting effect of \textit{n}-dodecane oxidation intermediates on NO oxidation was also observed in a standard SCR gas mixture (Fig. 1 and Fig. 2b).

However, in this case a lower NO to NO\textsubscript{2} conversion was measured at 1 bar (only 12% NO oxidation at 550 °C) in comparison to that observed in a NO/C\textsubscript{12}H\textsubscript{26} oxidation feed, which was due to the additional presence of NH\textsubscript{3}. Radical formation boosted also the conversion of NH\textsubscript{3} above 350 °C, apparently with a high selectivity towards N\textsubscript{2} formation, leading to 10% NH\textsubscript{3} conversion at 550 °C (Fig. 1). The pressure increase resulted in a pronounced overconsumption of NH\textsubscript{3} as well as higher N\textsubscript{2}O emissions (up to 65 ppm) above 400 °C. Nevertheless, the formation of NO\textsubscript{2} was tremendously enhanced at high temperature resulting in NO to NO\textsubscript{2} oxidation of up to 74% between 400-550 °C at 5 bar. All these effects dramatically affected the performance of a following SCR catalyst, as it will be shown in the following sections.

An incomplete conversion and also the lowest influence on NO and NH\textsubscript{3} oxidation were observed in the presence of \textit{o}-xylene at all investigated pressures (Fig. S9 and Fig. S10). \textit{O}-xylene conversion was mainly detected at higher pressure above 300 °C, reaching about 80% at 550 °C and 5 bar. The mechanism of \textit{o}-xylene partial oxidation is rather complex and not yet completely elucidated. Several studies have reported numerous reaction products, formed either by oxidation of the methyl groups at lower temperature or via benzene ring rupture at higher temperatures.[27, 28] During our tests the detected products included mainly formaldehyde and propylene. However, the formation of additional byproducts cannot be excluded, since such could not be detected due
to the FTIR calibration method boundaries, which to some extent applies also to propylene and $n$-dodecane oxidation. As shown in Fig. S9, $o$-xylene oxidation seems to be inhibited by NO and to a lesser extent by NH$_3$ presence. Under standard SCR conditions only 32% $o$-xylene were converted at 550 °C and 5 bar. For the same reaction parameters 20% NH$_3$ were overconsumed whereas a decrease in NO oxidation was noticed (Fig. S10 vs. Fig. S3c). Since gas phase reactions between $o$-xylene or its oxidation intermediates and NO or NH$_3$ took place to a lower extent as compared to propylene and $n$-dodecane, it is expected that these processes only moderately influence the subsequent catalytic reactions even at elevated pressure and high temperatures.

In order to rule out the possible influence of the SO$_2$ homogeneous oxidation or reactions with SCR gas components at high pressure, e.g. formation of ammonium sulfates, empty reactor tests were carried out also in this case. The results obtained for gas mixtures containing SO$_2$ showed almost no decrease in NO, NH$_3$ and SO$_2$ concentrations and no additional emissions during heating up the reactor at the end of the testing procedures (Fig. S12). Hence, the formation of additional gaseous byproducts or deposits due to gas phase reactions can be excluded for the testing conditions used in this study.

3.2 Influence of hydrocarbons on catalytic NH$_3$-SCR at elevated pressure

To evaluate the catalytic performance of V$_2$O$_5$-WO$_3$/TiO$_2$, a catalyst containing 2.0 wt.% V$_2$O$_5$ and 8.8 wt.% WO$_3$ (74 m$^2$/g BET surface area and 0.25 cm$^3$/g pore volume) was prepared and subsequently coated on honeycombs. Additional information on washcoat-loadings and composition can be found in the ESI (Fig. S1, Table S1). For each series of tests a freshly prepared catalyst core was used. In a first step, the NH$_3$-SCR activity was determined in the absence of hydrocarbons to observe only the influence of pressure. As depicted in Fig. 3, the NO$_x$ conversion
increased over the entire temperature range, reaching 100% at around 350 °C and at the higher pressure of 5 bar.

**Fig. 3** a) NO\textsubscript{x} conversion over a V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst during standard SCR conditions (350 ppm NO, 350 ppm NH\textsubscript{3}, 14% O\textsubscript{2}, 4.5% H\textsubscript{2}O in N\textsubscript{2}) under ambient and elevated pressures. Comparison of hydrocarbon induced change in NO\textsubscript{x} conversion at b) 1 bar/ambient, c) 3 bar and d) 5 bar.

This behavior is in line with literature [7, 8] and emphasizes the positive effect of elevated pressure on the performance of a V-based SCR catalyst. Several studies [8, 9] have shown that the pressure does not change the reaction kinetics and that the increased conversion with elevated pressure is affected by the negative impact of decreased diffusivity. For the small hydraulic diameter (1.27 mm) of the monolithic channels used in the present study, the higher residence time was the dominant factor leading to significantly improved NO\textsubscript{x} conversion. However, once the
hydrocarbons were added to the standard SCR gas mixture different effects were observed, as summarized in Fig. 3b, c and d. More detailed figures, showing the NO\textsubscript{x} conversion and N\textsubscript{2}O emissions in the presence and absence of hydrocarbons, can be found in the supplementary information (Fig. S13-S15).

3.2.1 Impact of propylene on NH\textsubscript{3}-SCR of NO\textsubscript{x}

At atmospheric pressure, the short chain model compound propylene had a minor effect on NO\textsubscript{x} reduction up to 400 °C. These findings agree with our previous studies [17, 29] and also with those of Watling et al.,[30] who showed an influence on NO\textsubscript{x} conversion only above the onset temperature of propylene oxidation. Hence, with increasing the temperature and especially the pressure, the negative impact on NO\textsubscript{x} conversion was enhanced. This could be a joint effect of parasitical ammonia oxidation above 300 °C in presence of propylene [31] and the competition for active sites of SCR species and propylene oxidation intermediates.[17, 30] Furthermore, propylene could slightly hinder the reoxidation of V-species, as shown in one of our previous studies.[32] According to our results (Fig. 4 and Fig. S13), at elevated pressure NH\textsubscript{3} overconsumption increases significantly, suggesting side reactions with propylene and its intermediates. The results of the empty reactor tests (Fig. 1) indicate that both C\textsubscript{3}H\textsubscript{6} and NH\textsubscript{3} start to convert around 500 °C and more pronounced at 3 and 5 bar. This trend aligns as well with the enhanced NH\textsubscript{3} conversion as measured during the catalytic reaction.
**Fig. 4** Additional NH$_3$ conversion in presence of hydrocarbons relative to NH$_3$ oxidation without hydrocarbons during standard SCR at 1, 3 and 5 bar pressure: 200 ppm C$_3$H$_6$, 50 ppm C$_{12}$H$_{26}$ and 75 ppm C$_8$H$_{10}$.

Propylene conversion during standard SCR and the corresponding product selectivity are shown in Fig. 5. The conversion started at 300 °C and increased up to 50% at 550 °C and 1 bar pressure. The main products were CO and CO$_2$ with a shift in selectivity towards CO formation at higher temperatures. This emission profile was observed in several studies in literature [33] and has been attributed to the decomposition of formic acid (HCOOH) into H$_2$O and CO.[34]

The formation of HCOOH could not be observed in presence of C$_3$H$_6$. On the one side this could be due to the low propylene conversion below 300 °C while at higher temperatures HCOOH is not stable.[35] Besides CO and CO$_2$, also other emissions like HCHO and HCN were observed. These compounds are particularly critical as they pose a serious health hazard.[36, 37]
Fig. 5 Selectivity of formed carbonaceous species (left axis) and hydrocarbon conversion (right axis) at 1 (solid), 3 (dashed) and 5 bar (dotted) over a temperature range from 200 to 550 °C during standard SCR conditions (350 ppm NO, 350 ppm NH₃, 14% O₂, 4.5% H₂O in N₂) with a) 200 ppm C₃H₆, b) 50 ppm C₁₂H₂₆ and c) 75 ppm C₈H₁₀.
Regarding the mechanism of byproducts formation, recent studies showed that HCN can be formed over SCR catalysts via the reaction between NH$_3$ and HCHO.[38-40] Therefore, also in the present case the observed HCN could originate from the same process. The conversion of 200 ppm propylene over the vanadium catalyst resulted in a maximum emission of 18 ppm HCN and 9 ppm HCHO at ambient pressure and 550 °C (Fig. S16). By increasing the pressure up to 5 bar an enhancement in propylene conversion was observed, which is probably the effect of increased residence time. Additionally, the product selectivity changed: An increased amount (Fig. S16) and higher selectivity (Fig. 5) towards HCHO formation was detected at lower temperatures whereas a higher selectivity for CO or CO$_2$ was observed above 450 °C, showing a more complete conversion of propylene as the temperature increases. At the same time, the selectivity towards HCN decreased with increasing pressure, even below the emissions recorded at ambient pressure. Furthermore, the formation of small amounts of ethylene was observed at high pressure and temperature. In general, although increased pressure improves the propylene conversion (up to 92% at 5 bar and 550 °C), the formation of side products like HCHO, HCN and CO could represent a challenge for downstream catalysts. Especially HCN emissions could be problematic since the oxidation of HCN over Pt-based DOC can be incomplete at low temperatures and might lead to additional NO$_x$ and N$_2$O formation.[41]

### 3.2.2 Impact of n-dodecane on NH$_3$-SCR of NO$_x$

In comparison to propylene, the long chain hydrocarbon (n-dodecane) showed a negative impact on the catalytic activity over the entire temperature window (Fig. 3). At ambient pressure and 150 °C, where almost no n-dodecane is converted, already a decrease in NO$_x$ conversion could be observed (Fig. 3b). The interaction of n-dodecane with the catalyst surface seems to not affect the
adsorption/desorption profile of NH₃, which applies also to α-xylene (Fig. S17 and Fig. S18). This suggests the possible blockage of the catalytic sites by n-dodecane conversion intermediates. Additionally, the presence of hydrocarbons might impede the reoxidation of V-species during the NH₃-SCR reactions.[32] The deactivation became more pronounced with increasing temperature up to 300 °C. At this temperature the catalyst started to convert the majority of C₁₂H₂₆, thus leading to a competition for active sites between n-dodecane oxidation intermediates and SCR reactants.[17, 30] Simultaneous to the onset of n-dodecane conversion, additional NH₃ consumption was measured, indicating side reactions of n-dodecane oxidation intermediates with NH₃ (Fig. 4). For instance, the observed HCN formation was due to the reaction between NH₃ and HCHO over the SCR catalyst.[38] This process is supported by the highest concentration peak of HCN (45 ppm) observed at 450 °C that replicates the NH₃ overconsumption profile (Fig. S19). After reaching full conversion at 400 °C and 1 bar, the negative influence of C₁₂H₂₆ on the NOₓ conversion became less pronounced, which is in line with the study of Ura et al.[42]

At higher pressure the decrease in NOₓ conversion due to n-dodecane presence was more pronounced at lower temperatures as compared to that measured for C₃H₆ (Fig. 3b vs. Fig. 3c), which is linked to the conversion of n-dodecane at lower temperature with formation of byproducts that could block the catalyst surface (Fig. 5). At 250 °C the negative impact reached a maximum at both 3 and 5 bar. With further temperature increase the SCR activity significantly dropped (almost no NOₓ conversion at 5 bar and 550 °C), suggesting a different cause for deactivation of the vanadium catalyst. At the same time as the conversion was declining, the N₂O emissions rose hinting to a change of selectivity during SCR or to additional side reactions. As shown earlier by the gas phase reaction tests, this significant change in selectivity and decrease in activity might be explained by parasitic gas phase reactions (Fig. 1), which led to additional NH₃ overconsumption
at high pressure and temperature. In fact, when comparing the emission profile of the gas phase reactions with that of the NH₃-SCR activity and of the byproducts detected after the catalyst (Fig. S14), the link between the loss of activity and the lack of NH₃ due to its homogeneous conversion is evident. Furthermore, the N₂O emissions can be associated to gas phase reactions as well.

Regarding the conversion of n-dodecane in the presence of the SCR gas mixture over the V-catalyst, it increased steadily up to 40% at 350 °C and ambient pressure. Above this temperature a steeper increase in conversion was observed, which is probably due to the simultaneous gas-phase conversion of n-dodecane before reaching the catalyst (Fig. 1 and Fig. 5). In comparison to propylene, the oxidation of n-dodecane led to the formation of significantly more CO₂ than CO emissions at low temperatures. This selectivity towards CO₂ decreased with rising temperature to almost equal amounts of CO and CO₂ at 550 °C. However, one should also consider that gas phase reactions lead to CO emissions which add up to the amount formed over the catalyst (Fig. S7), as vanadium catalysts are not able to oxidize CO to CO₂.[43] Furthermore, beside CO and CO₂ also other carbonaceous species like HCOOH, HCHO, C₂H₄ and HCN were detected during catalytic n-dodecane oxidation (Fig. S19). Formic acid was formed below 250 °C in small amounts, but decomposes to H₂O and CO at elevated temperatures.[44] HCHO and HCN were emitted as well starting with low temperatures and their concentration reached a maximum value around 400-450 °C, i.e. 13 ppm HCHO and 45 ppm HCN. At temperatures above 350 °C, traces of ethylene could be observed (up to 9 ppm at 550 °C).

At higher pressures n-dodecane oxidation was considerably promoted and complete conversion was reached at 350 °C for 3 and 5 bar pressure. The increase in pressure resulted also in lower HCN and HCHO emissions at high temperatures. In contrast, high CO amounts were detected.
Analogous to propylene catalytic oxidation, the observed outcome was influenced by the concurrent gas phase reactions and should be carefully interpreted.

### 3.2.3 Impact of o-xylene on NH₃-SCR of NOₓ

At ambient pressure the impact of hydrocarbons with an aromatic ring, in this study represented by o-xylene, was similar to that observed for n-dodecane. The SCR activity decreased especially up to 300 °C and recovered above this temperature (only 8% activity diminishment at 550 °C). The decrease in the low temperature activity was accompanied by an increased NH₃ overconsumption relative to the standard SCR reaction in the absence of o-xylene (Fig. 4). As shown in Fig. 3, an increase in pressure resulted in a less pronounced catalyst deactivation, which was most probably due to the higher o-xylene oxidation (Fig. 5). Furthermore, a higher pressure seems to reduce NH₃ overconsumption. In contrast to the impact of propylene and n-dodecane, only a small amount of NH₃ was unselectively converted at higher temperatures (Fig. 4 and Fig. S15). As already seen for the gas-phase reaction tests (section 3.1, Fig. S10), o-xylene is less reactive under these conditions and, therefore, did not affect the SCR reactions.

During o-xylene oxidation in the SCR gas mixture several species were detected at the different pressures investigated in this study, i.e. formic acid, formaldehyde, HCN, propylene, CO and CO₂ (Fig. 5 and Fig. S20). However, at 1 bar their concentration at 200 °C corresponded to less than 40% of the expected amount based on the total carbon in the inlet feed. This indicates that further compounds were formed, as e.g. ketones, aldehydes and phthalic anhydrides,[45, 46] which could not be detected during our tests due to technical limitations. With rising temperature, the total selectivity increased up to approximatively 80% at the highest temperature and ambient pressure, with CO₂ as the most prominent product (Fig. 5). In comparison to propylene and n-dodecane...
oxidation, the CO fraction was very small even at high temperatures. Additionally, formic acid could be observed at low temperatures and C₃H₆ was detected above 250 °C (22 ppm C₃H₆ at 450 °C, Fig. S20). Under these conditions, the formation of HCHO was minor with a maximum concentration of 2 ppm at 550 °C. However, HCN emissions were observed also in this case, with the highest concentration of 17 ppm measured at 500 °C and ambient pressure.

At higher pressure, a strong increase in CO and CO₂ formation as well as a shift of side product emission maximum towards lower temperatures was observed (Fig. 5 and Fig. S20). Furthermore, HCN (6 ppm maximum) and C₃H₆ (15 ppm maximum) emissions decreased and almost vanished completely at high temperatures. Therefore, a higher pressure seems to positively affect the conversion of o-xylene and its oxidation intermediates leading to a more complete oxidation to CO and CO₂ (Fig. 5).

3.3 Influence of SO₂ on the NH₃-SCR and impact of pressure

The results of the standard SCR catalytic tests in the presence of 20 ppm SO₂ are shown in Fig. 6. Contrary to the results reported by Magnusson et al.[47] and Shi et al.[48] an improvement in catalytic activity even at low temperatures was observed in this study. However, a much lower SO₂ concentration was used during our experiments. Up to 450 °C the conversion of NOₓ increased for all tested pressures if SO₂ was present. Only at temperatures above 500 °C a small negative impact on NOₓ conversion and an increase of N₂O emissions were observed. The increase in activity could be explained by several potential processes. On one side, the sulfating of catalyst surface by SO₂ adsorption, e.g. on the TiO₂ support and V-OH groups, could increase the Brønsted acidity and therefore the storage of ammonia.[49, 50] On the other side, the formation of ammonium sulfate is promoted under these conditions. Such deposits could initially increase
surface acidity and also react directly with NO.[51, 52] Consequently, both pathways could improve the catalytic activity during short term catalyst exposure.

Although ammonium sulfate formation is boosted by the presence of water to such an extent that the deposits begin to cover both the surface and the active centers,[47] no deactivation was observed during the relatively short steps of the steady activity tests conducted in our study. This could be due to relatively lower SO\textsubscript{2} concentration in the gas stream in comparison to previous studies.[47, 48, 50]

![Fig. 6](image)

**Fig. 6** Catalytic activity of VWTi during standard SCR conditions (350 ppm NO, 350 ppm NH\textsubscript{3}, 0/20 ppm SO\textsubscript{2}, 14% O\textsubscript{2}, 4.5% H\textsubscript{2}O, 2% CO\textsubscript{2} in N\textsubscript{2}) with carrying pressure and a GHSV of 100,000 h\textsuperscript{-1} in absence/presence of SO\textsubscript{2}.

To uncover if a prolonged exposure time at elevated pressure could lead to a significant loss of activity, systematic SO\textsubscript{2} poisoning tests were additionally performed at selected temperatures. In Fig. 7 the evolution of the NO\textsubscript{x} conversion over 4 h period of SO\textsubscript{2} exposure is shown for 1 and 5
bar pressure. The results indicate an increase in NO\textsubscript{x} conversion at low temperatures and elevated pressures (approx. 3% at 250 °C and 5 bar) whereas the activity remained the same during the test at 350 °C. A similar trend could be observed at 150 °C and 5 bar during the first minutes of SO\textsubscript{2} feeding. However, a pronounced decrease of activity was detected during the following time period. Such an evolution of the SCR activity might be due to an initial increase in surface acidity, which promotes NO\textsubscript{x} conversion, followed by the formation of excessive amounts of ammonium sulfate that blocks the catalyst surface.[53] To verify this assumption, temperature programmed desorption measurements and NO\textsubscript{x} conversion tests (two consecutive cycles between the poisoning temperature and 550 °C) were conducted at ambient pressure directly after the different poisoning steps.

**Fig. 7** Catalytic activity during standard SCR in the presence of sulfur (350 ppm NO, 350 ppm NH\textsubscript{3}, 20 ppm SO\textsubscript{2}, 14% O\textsubscript{2}, 4.5% H\textsubscript{2}O, 2% CO\textsubscript{2} in N\textsubscript{2}) over 4 h with different temperature and pressure: a) 350 °C at 1 bar, b) 250 °C at 1 bar, c) 150 °C at 1 bar, d) 350 °C at 5 bar, e) 250 °C at 5 bar and f) 150 °C at 5 bar.
As depicted in Fig. 8a and Fig. 8b, the TPD measurements show that the increase of pressure resulted in enhanced deposit formation especially at low temperatures. The recorded NH\textsubscript{3} and SO\textsubscript{2} evolution during TPD indicate minor deposit formation at 250 °C and increased pressure. In contrast, significantly higher amounts of SO\textsubscript{2} were desorbed from the catalyst poisoned at 150 °C. Especially for the sample treated at 150 °C and 5 bar pressure up to 10 times the amount of NH\textsubscript{3} and SO\textsubscript{2} was desorbed as compared to the sample poisoned at 250 °C. The desorption profiles of these deposits suggest the presence of ammonium sulfate, which decomposes in several steps and is completely converted up to 480 °C.[53]

![Fig. 8](image)

**Fig. 8** Temperature programmed desorption in 5 L min\textsuperscript{-1} N\textsubscript{2} after poisoning the sample at a) 150 °C and b) 250 °C with 1 and 5 bar pressure, c) improvement of NO\textsubscript{x} conversion during the first run after different poisoning conditions.

To identify the nature of formed deposits, the SO\textsubscript{2}-poisoned samples exposed for 4 h to 20 ppm SO\textsubscript{2} at various temperatures and pressures were characterized with Raman spectroscopy. The
A comparison of the Raman spectra obtained for the fresh and the most severe poisoned catalyst (150 °C, 5 bar) are shown in Fig. 9. The most prominent bands at 144 cm\(^{-1}\), 197 cm\(^{-1}\), 394 cm\(^{-1}\), 516 cm\(^{-1}\) and 639 cm\(^{-1}\) were previously attributed to anatase TiO\(_2\).\([54]\) The bands at 798 cm\(^{-1}\) and 979 cm\(^{-1}\) can be assigned to WO\(_3\) and V\(_2\)O\(_5\) species, respectively.\([55]\) In comparison to the spectra of the fresh sample, additional bands at 452 cm\(^{-1}\), 975 cm\(^{-1}\) and 3153 cm\(^{-1}\) appeared after SO\(_2\)-poisoning. These bands can be assigned to (NH\(_4\))\(_2\)SO\(_4\)\([56]\] as confirmed also by measurements on reference compounds (Fig. S21). For the other poisoned samples, no bands corresponding to ammonium sulfate could be detected (Fig. S22). For higher SO\(_2\)-poisoning temperatures and varying pressure only a small decrease of the characteristic bands for anatase at 394 cm\(^{-1}\) and 516 cm\(^{-1}\) could be observed. Hence, all these findings unravel the pronounced effect of pressure particularly at low temperatures despite of the rather low SO\(_2\)-concentration. According to the results of the TPD measurements after poisoning (Fig. 8a and Fig. 8b), the pressure mainly influences the amount of sulfur-containing species formed during poisoning.

**Fig. 9** Comparison of Raman spectra from V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) before (black) and after 4 h sulfur poisoning at 150 °C and 5 bar pressure (red): a) Range Raman shift: 80-1100 cm\(^{-1}\), b) Range Raman shift: 2500-3700 cm\(^{-1}\).
In order to correlate the results from Raman spectroscopy with those observed in catalytic performance, the difference in NO\(_x\) conversion as measured before and after SO\(_2\) poisoning at different temperatures and pressures is summarized in Fig. 8c. In most cases, an increase in catalytic activity was achieved in the low to medium temperature range. Only for the sample exposed to SO\(_2\) at 150 °C and 5 bar, a notable decrease in activity was detected up to 300 °C (approx. 13% activity loss at 250 °C). Above 300 °C a significant increase of catalytic activity was observed which was maintained up to 550 °C. The low-temperature behavior is in line with the results of the long-term SO\(_2\)-exposure measurement at 150 °C (Fig. 7), which showed a deactivation after the first few minutes due to the surface coverage with ammonium sulfate deposits. The increase in activity between 350 and 450 °C can be explained by the decomposition of (NH\(_4\))\(_2\)SO\(_4\) and release of the active centers. The conversion could be further increased by the reaction between NO and ammonium bisulfate at temperatures above 300 °C.[52] Above 450 °C almost no alteration of the SCR activity was found for all samples. When repeating the measurement in a 2\(^{nd}\) consecutive run, the activity detected at 1 bar corresponded to the initial profile. Hence, all poisoned samples are completely recovered upon heating to 550 °C (Fig. S23).

4. Conclusions

A systematic study has been conducted to reveal the impact of elevated pressure on the gas phase reactions and NH\(_3\)-SCR activity of a V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) catalyst under pre-turbine conditions. Particularly, the effect of hydrocarbons and SO\(_2\) presence was investigated, which to the best of our knowledge is for the first time reported here for high pressure conditions. The experiments revealed pronounced conversion of short and long chain hydrocarbons as well as of aromatic hydrocarbons already in the gas phase above 300 °C. The homogeneous oxidation reaction,
especially of long chain hydrocarbons, contributes to NH₃ overconsumption at high temperature and pressure. This parasitic reaction seems not to be promoted by the presence of SO₂. At the same time, the mutual sensitization of HCs and NO oxidation is highly promoted by the pressure increase as well. Almost full conversion of NO to NO₂ was observed at 5 bar and 550 °C in a gas mixture containing NO and n-dodecane. Gas phase NO oxidation is enhanced by the radical n-dodecane oxidation also under standard SCR reaction conditions, reaching up to 74% conversion of NO between 400-550 °C at 5 bar. Exploiting such a high NO to NO₂ conversion already in the gas phase by dosing small amounts of hydrocarbons, i.e. n-dodecane, at the pre-turbine position could be an interesting alternative for supporting the low temperature activity of subsequent catalytic systems in the exhaust pipe.

The NH₃-SCR catalytic activity of a state-of-the-art vanadium catalyst itself is also strongly influenced by pressure. Both, the low and high temperature activity are positively affected by the prolonged residence time at elevated pressure. However, the presence of any kind of hydrocarbon in the gas mixture influences and diminishes the beneficial effect of pressure due to blockage or competition for active sites and due to gas phase NH₃ overconsumption. The latter was found to dominate especially at high temperature and pressure, and particularly during simultaneous oxidation of n-dodecane. Among the different classes of hydrocarbons, o-xylene showed the lowest influence under the same conditions. At low temperatures propylene has only a minor effect on the SCR activity but slightly promotes NH₃ overconsumption as the temperature and pressure increases. In all cases the concurrent hydrocarbon oxidation leads not only to CO₂ and CO but also to small amounts of hazardous byproducts like HCHO and HCN, which would make a following oxidation catalyst necessary.
Even though the presence of SO\textsubscript{2} does not affect the homogeneous reactions significantly, it has a dual role during the catalytic process. No catalyst deactivation has been observed at all investigated temperatures during short term SO\textsubscript{2} exposure, as an increase of the Brønsted acidity is initially induced via catalyst surface sulfation. In contrast, the formation of sulfur containing deposits, i.e. (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, is promoted over the catalyst surface at high pressure during prolonged SO\textsubscript{2} feeding at temperatures below 250 °C.

Overall, the study offers a holistic view on the implications of more complex gas mixtures containing hydrocarbons and low sulfur concentrations on the activity of a V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst at pre-turbine position. This allows a more rational system design in future which considers the advantages and disadvantages of a pre-turbo application and therefore is able to exploit its true potential.

ASSOCIATED CONTENT

**Supporting Information.** Additional information on catalyst characterization, test bench parameters, gas phase measurements, catalyst testing and Raman spectra (PDF).

AUTHOR INFORMATION

**Corresponding Author**

*Jan-Dierk Grunwaldt, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany, Tel.: +49 721 608 42120, grunwaldt@kit.edu*

**Author Contributions**
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**Notes**

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**Abbreviations**

DOC, diesel oxidation catalyst; DPF, diesel particle filter; FTIR, Fourier-transform infrared spectroscopy; GHSV, gas hourly space velocity; HC, hydrocarbon; NO\textsubscript{x}, nitrogen oxides; SCR, selective catalytic reduction; TPD, temperature programmed desorption; XRF, X-ray fluorescence.

**References**


