Analysis of the NO_x storage behaviour during cold start of modern SCR flow-through substrates and SCR on-filter substrates

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Abstract

Selective catalytic reduction (SCR) systems are the state-of-the-art technology to reduce nitrogen oxide emissions (NO_x) of modern diesel engines. The system behaviour is well understood in the common temperature working area. However, the system properties below light-off temperature are less well known and offer a wide scope for further investigations. Vehicle measurements show that under specific conditions during cold start, NO_x can be partially stored and converted on on-filter and flow-through SCR catalysts. The purpose of this work was in a first step to analyse the main influence parameters on the NO_x storage behaviour. Therefore, synthetic gas test bench measurements have been carried out, varying the gas concentrations, temperature, and gas hourly space velocity (GHSV). These investigations showed that the NO_x storage effect strongly depends on the NH₃ level stored in the catalyst, GHSV, the adsorbed water (H₂O) on the catalyst, and the temperature of the catalyst. Further influence parameters such as the gas composition with focus on carbon monoxide (CO), short-chain hydrocarbons and long-chain hydrocarbons have been analysed on a synthetic gas test bench. Depending on operating conditions, a significant amount of NO_x can be stored on a dry catalyst during the cold start phase. The water vapor from the combustion condenses on the cold exhaust pipe during the first seconds, or up to a few minutes after a cold start. As the water vapor reaches the surface of the catalyst, it condenses and adsorbs onto it, leading to a sudden temperature rise. This exothermal reaction causes the stored NO_x to be desorbed, and furthermore it is partially reduced by the NH₃ stored in the catalyst.

Keywords NO_x storage behaviour · NO_x reduction · NO_x adsorption · NO_x desorption · SCR catalyst · Cold start behaviour · Temperature

Abbreviations

ASC	Ammonia slip catalyst
C ₁₀ H ₂₂	Decane
C ₃ H ₆	Propene
CH ₄ N ₂ O	Urea
CO	Carbon monoxide
CO ₂	Carbon dioxide
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
FTIR	Fourier-transform infrared spectroscopy
GHSV	Gas hourly space velocity
H ₂ O	Water
HNCO	Isocyanic acid
N ₂	Nitrogen
N ₂ O	Nitrous oxide

NDIR	Nondispersive infrared sensor
NH ₃	Ammonia
NO	Nitrogen monoxide
NO ₂	Nitrogen dioxide
NO _x	Nitrogen oxides
O ₂	Oxygen
PID	Proportional–integral–derivative controller
PMA	Paramagnetic analyser
RDE	Real driving emissions
SCR	Selective catalytic reduction
TPD	Temperature programmed desorption

1 Introduction

Even though the market share of electrically powered passenger cars has increased in the European market over the last few years, the share of diesel engines in new passenger cars was still 30.5% in the year 2018. Petrol-driven cars

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showed even a higher share for new registered cars in the European Union in the year 2018 of almost 60%. [1]

The fact that a diesel engine has lower CO₂ emissions than a petrol-powered passenger car, resulting from its significant advantage in thermodynamic efficiency, underpins its importance to reach overall CO₂ fleet emission targets [2].

One of the main development targets for future diesel vehicles is to fulfil new emissions regulations such as Euro 7 including real driving emissions legislations (RDE). Main targets are NO_x and particulate matter emissions, causing a need for a complex exhaust aftertreatment system for modern diesel vehicles. These systems typically consist of a diesel oxidation catalyst (DOC), a diesel particulate filter (DPF) with SCR coating, a selective catalytic reduction catalyst (SCR), and eventually an NH₃ slip catalyst (ASC) [3–5].

The DPF with SCR coating has major advantages compared to two separate systems, such as a better packaging, as well as an improved heating up of both subsystems due to the possible closed-couple position. These facts lead to an improved cold start emission performance. Furthermore the use of a DPF with SCR coating and a normal SCR catalyst offers a greater overall functional SCR volume, which is essential to assure high NO_x reduction rates at high exhaust mass flows, respectively high gas hourly space velocities (GHSV). The SCR on filter catalyst is a state-of-the-art technology for NO_x and particulate matter emission reduction in passenger vehicles [6–8].

The main design criterion of a DPF with SCR coating is a good urea mixture preparation in the exhaust system upstream of the catalyst. In addition to that requirement, the chosen temperature to start the urea dosing is also a key performance indicator. In general urea depositions are not relevant if those two criteria are met. Moreover the clogging of the filter pores by means of solid urea decompositions are in general, neglectable. Further studies show that for lower temperatures a soot loaded catalyst shows a lower NO_x conversion rate compared to a soot free catalyst [9, 10].

A second thermally decoupled underfloor SCR catalyst offers a further increase of the NO_x reduction potential. This is particularly the case during high temperature phases, such as a particulate-filter regeneration and high load operation. A double dosing aftertreatment system with two separate SCR catalysts enables a more efficient use of urea, thus causing a lower urea consumption. The double dosing systems allows an independent operation of the close-coupled SCR and underfloor SCR systems [8].

The carbon-monoxide and hydrocarbon emissions of a diesel vehicle can be reduced by a diesel oxidation catalyst. A three-way catalyst cannot be used to tackle the NO_x emissions due to the lean combustion in a diesel engine. Well over a decade now, the diesel particulate filter has been the state-of-the-art technology to reduce particulate matter emissions. Up to now one of the major development challenges

has been to meet future NO_x limitations. Currently a close-coupled SCR system combined with an underfloor SCR system is used. Furthermore, depending on the vehicle size either one or two urea dosing systems are used [11].

Over the past years, each of these components has been developed further with respect to system performance and overall understanding of the reaction mechanisms by several research groups. In the SCR itself a lot of different reactions can take place, the most regarded reaction path is the so called “standard” SCR reaction ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$) [12–14]. The presence of NO₂ in a ratio of 1:1 for NO:NO₂ enables the “fast” SCR reaction ($NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$), which is quicker than the “standard” SCR reaction and starts at lower temperatures. Another reaction is the so called “NO₂” SCR reaction ($6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$), which has two significant drawbacks: on the one hand the “NO₂” SCR reaction requires a higher amount of ammonia, and the reaction itself is also slower [12–18].

The SCR system behaviour as well as the underlying reactions are well understood and can be predicted with adequate models in the common operating temperature range from approx. 175 °C up to 650 °C [15, 19]. For the system evaluation, catalyst temperatures below 175 °C are often not considered, because SCR reactions play a minor part in the NO_x reduction in this temperature area. At temperatures below 175 °C NH₃ is only available as stored NH₃ in the catalyst itself, due to the fact that the urea dosing needs a certain temperature level to ensure complete thermolysis reaction ($(NH_2)_2CO \rightarrow NH_3 + HNCO$) and the following hydrolysis reaction ($HNCO + H_2O \rightarrow NH_3 + CO_2$) to create NH₃. However, SCR catalysts can store NH₃ up to a certain amount, depending on its zeolite structure and chemical composition [19–24].

Current studies have investigated the NO_x storage behaviour and point out the negative effect of water. Water inhibits the oxidation of NO and has a negative effect on the NO_x storage itself. Beyond that even a small amount of water is detrimental on the NO_x storage behaviour. The presence of water during the adsorption causes a lower peak in temperature during the NO_x desorption phase, leading to a lower NO_x reduction potential. Furthermore these papers aim to enhance the NO_x storage effect by improving the storage material, as well as getting a better understanding of possible influence parameters [4, 25, 26].

Several reasons such as the lower exhaust gas temperatures due to higher engine efficiency and more stringent emissions regulations move the field of interest of the SCR system behaviour to lower catalyst temperatures (< 175 °C). Vehicle measurements for a commercial Cu-zeolite SCR catalyst show that during cold start a variety of effects interact and influence the SCR system behaviour. The aim of this work is on the one hand to get a better understanding of

the interactions and the effect mechanisms itself, and on the other hand to create a basis to be able to design a model which predicts the system behaviour at these temperatures. Lab scale tests with a synthetic gas test bench have been carried out with the aim to understand the main influence parameters on the adsorption and desorption processes of the NO_x emissions on the SCR catalyst. Beyond this, NO_x reduction in the low temperature range has been analysed with the main focus on the gas composition as an influence parameter.

2 Vehicle measurements

2.1 Methods

During cold start vehicle measurements, a NO_x storage effect as well as a water adsorption effect were observed. These measurements indicate that there is a coherence between the NO_x storage effect and the water adsorption effect. In order to validate the NO_x storage behaviour and detect further influence parameters, vehicle measurements were carried out with the same catalyst technology, parallel to the lab scale tests on the synthetic gas test bench (Fig. 4). The test vehicle was equipped with a 3.0 l common-rail diesel engine, a close-coupled SCR system and an underfloor SCR system. The gas sampling points as well as the additional temperature sensors can be seen in Fig. 1. At the gas sampling ports, the gas phase was analysed with additional commercially available NO_x and NH_3 sensors, whereby the NO_x sensors were already active at the start of the vehicle tests.

For the vehicle measurements a conditioning cycle was carried out, which enhanced the repeatability for each measurement. After a soak time of at least 8 h to guarantee catalyst temperatures below 50 °C, the actual measurement cycle was driven. The measurement cycle represents a city cycle, which is followed by extra-urban driving that acts as the conditioning cycle for the next measurement, with a total distance of 42 km. The temperature profile and the vehicle speed are shown in Fig. 2. The entire vehicle measurements were carried out on public roads.

3 Results and discussion

The measurement cycle described above was carried out with focus on the first few hundred seconds of the cycle only. The reason for this is that the NO_x adsorption and desorption cycle is completed after the first few hundred seconds. The NO_x concentrations engine out, after the close-coupled SCR system, and downstream of the underfloor SCR system for the first 300 s after a cold start are depicted in Fig. 3. For the first 75 s all the NO_x emissions stay absence after the close-coupled SCR system. After 75 s engine out NO_x emissions are well below 100 ppm, at about 95 s a NO_x emission peak occurs after the close-coupled SCR system. This sharp NO_x -emissions increase is caused by the temperature rise due to water adsorption in the catalyst, as it can be seen in various literature [4, 25, 27].

Furthermore, the NO_x emissions after the underfloor SCR system stay zero for the first 130 s. After 130 s a slow increase of NO_x emissions downstream of the underfloor SCR system can be noticed, which results in a sharp NO_x emissions peak at 170 s. The slow increase of the NO_x emissions can be explained through NO_x slip caused by a peak in the exhaust mass flow. The following sharp NO_x -emissions peak is caused by the temperature rise.

Beyond 200 s the NO_x emissions of both SCR catalyst sampling points are nearly the same, however, the engine out NO_x emissions values are slightly higher. In general, the behaviour of the close-coupled and the underfloor SCR systems are the same, but the effect is pronounced stronger for the latter. There could be several reasons for this difference such as volumetric varieties, substrate types, or the surface-to-volume ratio of the catalysts. The exhaust gas during the NO_x peaks downstream of both SCR systems consists entirely of NO only.

The cold start temperature behaviour for the entire vehicle setup with its additional thermocouple elements can be seen in Fig. 3. The engine out exhaust-gas temperature increases continuously as it would be expected for a heating-up process of the exhaust system. The temperature measurements in the catalysts show a rather untypical temperature profile for the first few hundred seconds, the behaviour is similar

Fig. 1 Schematic overview of the vehicle exhaust system with the gas sampling points

Fig. 2 Vehicle and temperature profile of the measurement cycle

Fig. 3 Measurement data for the first 300 s during a cold start of the measurement cycle in accordance to the measurement setup in Fig. 1

to that of the NO_x emissions for each catalyst. The trend of the temperature profile as well as the NO_x -emissions profile corresponds to already existing literature, however, absolute

values cannot be compared due to a lack of data concerning the catalyst composition and volume [4]. For the first 80 s the temperature in the close-coupled SCR system (blue

Fig. 4 Simplified overview of the synthetic gas test bench

line) stagnates at ca. 20 °C. Between 80 and 115 s a sudden increase in temperature of more than 100 K occurs. After the sudden temperature rise the temperature decreases till it reaches 90 °C, before slowly increasing again at 275 s.

The temperature profiles (for the thermocouples) in the underfloor SCR system follow the same principle as for the close-coupled SCR system. With the two thermocouples an unequal distribution in the temperature rise for the inlet and the outlet area can be determined. The lift in temperature is nearly double the amount (130 K) in the outlet section of the catalyst than compared to the inlet area (68 K). The underfloor catalyst reaches a maximum temperature during the first 300 s of 156 °C in the depicted measurement cycle. As already shown for the NO_x peak, the temperature profile in the underfloor SCR system behaves in a much more pronounced way than in the close-coupled SCR system. Between 300 and 600 s the outlet temperature decreases and subsequently rises with the other measured temperatures.

The temperature behaviour is caused by the water in the exhaust gas. Whereby the behaviour over the SCR catalysts must be an exothermic H₂O-adsorption reaction, followed by an endothermic H₂O-desorption. The temperature rise is due to H₂O-adsorption on the small pores of the zeolite. Afterwards an endothermic H₂O-desorption occurs, caused by the evaporation of the condensed water. The entire temperature behaviour can be seen in Fig. 2. This effect can be found similarly during water dosing over different zeolite types in other literature [27, 28].

There are two main sources of water in the exhaust gas, on the one hand water contained in the intake air and on the other hand water from the combustion itself. Typical water content in the exhaust gas is between 6 and 12% by volume. During cold start, water in the exhaust gas can condense

on the cold components of the exhaust manifold, as well as on the piping, DOC and so on. This condensation process continues as long as the exhaust pipes and monoliths are below the condensation temperature. The condensed water reduces the moisture content in the exhaust gas, enabling the delayed temperature increase in the SCR systems. As the exhaust components upstream of the close-coupled SCR system are saturated with water, the moist exhaust gas reaches the surface of the SCR catalyst. Furthermore, the water content in the exhaust increases due to the heating up of the upstream exhaust parts by evaporating the previously condensed water. Due to the high surface area and the cold temperature of the SCR catalyst, a high amount of water can condense and secondly adsorb on the catalyst, causing the sharp temperature increase in the catalyst. The higher rise in temperature at the outlet area of the underfloor SCR system compared to the inlet section can be explained by the fact that the exhaust gas that reaches the rear part of the catalyst is already preheated by the inlet area, and the increased humidity in the exhaust gas due the evaporation in the upstream components.

In regard to the NO_x emissions behaviour an adsorption and desorption process describes the activities best. Moreover, only a certain amount of the adsorbed NO_x desorbs during the temperature rise, leaving a NO_x reduction. A possible way to explain the NO_x reduction is that the local temperature, during water adsorption is much higher than the measured one. In combination with NH₃ adsorbed on the surface of the catalyst enables a functional NO_x reduction process. These topics are investigated in the synthetic gas test bench measurements. Additionally, a time-dependent correlation between the temperature rise and the NO_x desorption peaks is found.

4 Synthetic gas test bench measurements

4.1 Methods

To analyse the results of vehicle measurements, more precisely a detailed study of several parameters was done on a synthetic gas test bench. Methods and Results are discussed in the following section.

4.2 Catalyst samples

For the synthetic gas test bench catalyst samples with a diameter of 1 inch were core drilled out of a conventional SCR catalyst. To achieve higher space velocities the bore sample was cut to a length of 3 inch. The SCR catalysts analysed in this work are monolithic Cu-zeolites with a cell density of 400 cells per square inch.

4.3 Synthetic gas test bench

To determine the main influence parameters on the adsorption, desorption, and NO_x reduction behaviour the usage of a synthetic gas test bench is the first choice, due to its high repeat accuracy and the possibility to adapt each variation parameter independently from each other. The layout of the synthetic gas test bench with its subcomponents and gas compositions can be seen in Fig. 4. The synthetic gas test bench uses mass flow controllers to compile the individual gas mix. Water and C₁₀H₂₂ are the only two components which are dosed as a liquid in combination with an evaporator device, the other components are added gaseous. Nitrogen acts as a carrier gas to define the needed gas flow.

For temperature regulation a PID controller is used, which defines how much gas must be heated by the gas heater, the rest is bypassed to the mixing unit. The gas temperature sensor upstream of the catalyst sample acts as an input variable for the temperature regulation. To evaluate the temperature behaviour over the catalysts length, two

additional thermocouple elements were placed in the sample, which can be seen in Fig. 5. The reactor itself is made from quartz glass. The catalyst sample is placed in a ceramic sample holder, which is attached to a stainless-steel mounting unit. The synthetic gas is analysed after the catalyst sample by means of a Fourier-transform infrared spectroscopy (FTIR), a paramagnetic analyser (PMA) and a nondispersive infrared sensor (NDIR). The FTIR is used to analyse NO_x, NH₃, H₂O and so on. The NDIR measures the CO and CO₂ content in the synthetic gas and the PMA determines the oxygen content.

Before each test a conditioning procedure was carried out by heating the sample up to 450 °C in a gas mixture of 8% O₂, 8% CO₂ in N₂ as a filler gas at a space velocity of 25,000 [1/h]. The temperature of 450 °C was kept for at least 500 s, to guarantee that the piping and the catalyst sample were free of water. The gas concentration range as well as the dosed components fed to the reactor are depicted in Table 1.

The low temperature range below 150 °C was the main scope of investigation, which is typical during a cold start of an engine. However measurements started at 50 °C for the reactor setup to secure a proper temperature regulation. The NO_x storage effect was also evaluated for higher starting temperatures such as 75, 100 and 150 °C. The piping up- and downstream of the reactor were heated to

Table 1 Gas composition for the synthetic gas test bench experiments

Dosed component	Concentration range
N ₂	0–100%
CO ₂	0–8%
O ₂	0–8%
H ₂ O	0–12%
NO	0–50 ppm
NH ₃	0–50 ppm
CO	0–5000 ppm
C ₃ H ₆	0–1250 ppm
C ₁₀ H ₂₂	0–250 ppm

Fig. 5 Placement of the thermocouples in the catalyst sample and for the temperature regulation

115 °C in order to avoid water condensation, therefore only in the quartz glass tube water condensation could occur. The space velocity was varied between 15,000 and 50,000 [1/h], whereas the very low and high space velocity was only selected to analyse the influence of space velocity. The test setups carried out in this paper to evaluate the different influence parameters are shown in Table 2. Furthermore a test series was conducted to determine the water adsorption and desorption behaviour. The test procedure is shown in Fig. 6 and consisted of an optional preloading step, during which NH₃ and/or water was loaded on the catalyst. In the adsorption step the GHSV, the catalyst temperature, gas temperature, as well as the gas composition were varied.

5 Results and discussion

5.1 Adsorption/desorption behaviour of water

The H₂O adsorption/desorption test setup raises several questions like: is there an influence of the water concentration on the adsorption behaviour, or what is the maximum temperature rise under the given boundary conditions of the synthetic gas test bench in a lab scale format. For the given test setup, the lowest possible test starting temperature is 50 °C, at a space velocity of 25,000 1/h. The gas composition for the adsorption/desorption tests can be seen in Table 3. The preconditioning guarantees a water

Table 2 Variation parameters shown in this paper to determine the NO_x storage behaviour

Variation parameter during NO _x storage (Adsorption phase)	Variation range	During Adsorption		Additional information
		GHSV	Temperature	
NO _x slip limit	10/45 ppm	25,000 1/h	50 °C	NO dosing shut off at different NO _x slip
Substrate type	SCR flow through / SCR on filter	25,000 1/h	50 °C	
Catalyst temperature during adsorption	50/75/100/150 °C	25,000 1/h	Variable	Variation of the temperature during adsorption phase
Gas hourly space velocity	15,000/25000/50000 1/h	Variable	50 °C	GHSV is changed during the entire test
CO concentration	0/2000/5000 ppm	25,000 1/h	50 °C	Addition of CO during adsorption phase
C ₃ H ₆ concentration	0/25/50/250/1250 ppm	25,000 1/h	50 °C	Addition of C ₃ H ₆ during adsorption phase
C ₁₀ H ₂₂ concentration	0/250 ppm	25,000 1/h	50 °C	Addition of C ₁₀ H ₂₂ during adsorption phase
NH ₃ concentration	0.1/0.2/0.3/0.4/0.5 g/l	25,000 1/h	50 °C	Time dependent addition of NH ₃ during preloading phase
H ₂ O concentration	Time variation of H ₂ O dosing: 0/5/10/15/20/25/30/50/100 s	25,000 1/h	50 °C	Time dependent addition of H ₂ O during preloading phase

Fig. 6 Test procedure of the synthetic gas test bench

free piping and test sample, the total time with a temperature above 100 °C is over 55 min. Before the adsorption phase begins the starting temperature is adjusted to 50 °C. During the adsorption phase 10% water is dosed for 70 s. After this soak period the water dosage is shut off again and the sample is flushed with dry synthetic gas until the measured water content after the sample drops below 500 ppm. This step removes the loosely bound water from the quartz glass reactor and the catalyst sample. After this debouncing phase a temperature programmed desorption (TPD) is started with an increase of 25 K/min up to 450 °C.

The synthetic gas test bench measurement (Fig. 7) confirms the theory that the adsorption of water leads to a distinctive exothermic behaviour, a temperature rise of 121 K can be detected. Additionally, the endothermic performance can be seen as the water dosing is shut off during the debouncing as well as desorption phases. The desorption of the loosely bound water only leads to a temperature drop of 12 K downstream of the catalyst sample, whereas during the TPD a maximum temperature difference of 77 K can be determined. Overall the temperature profile after the catalyst sample is in accordance with vehicle measurements. Additional measurements show that the temperature rise

significantly decreases to 50 °K for a water dosing of 2%, displaying that the water concentration has a major influence on the exothermic behaviour.

5.2 Principal adsorption/desorption behaviour of NO_x

To validate the NO_x adsorption and desorption behaviour a test setup similar to the water adsorption/desorption test has been established. The test setup (Table 4) consists of a preconditioning phase, followed by a phase of constant temperature where 50 ppm of NO is dosed until a NO_x breakthrough of 45 ppm is measured. The starting temperature of 50 °C for the NO_x storage test is the same as for the water storage test, as well as the space velocity of 25,000 [1/h] and the entire preconditioning phase.

During the adsorption phase only NO is dosed due to the fact that the NO_x composition during cold start vehicle measurements also show only NO upstream of the catalyst. The entire test is carried out without water dosing to replicate the adsorption phase of the vehicle measurements, where a lack of water is observed. As can be seen in Fig. 8, the NO_x concentration downstream of the catalyst slowly increases, while NO_x concentrations upstream

Table 3 Overview of the gas composition and the waiting conditions for each test phase for the 10% water adsorption test

Test phase	Inlet gas composition	Waiting condition
Preconditioning	8% CO ₂ , 8% O ₂ , balance N ₂	450 °C for 250 s
Adsorption	10% H ₂ O, 8% CO ₂ , 8% O ₂ , balance N ₂	70 s
Debouncing	8% CO ₂ , 8% O ₂ , balance N ₂	Measured H ₂ O content after the sample < 500 ppm
TPD Desorption	8% CO ₂ , 8% O ₂ , balance N ₂	Temperature ramp to 450 °C at 25 K/min

Fig. 7 Temperature behaviour for the inlet and outlet section over the SCR catalyst sample as a function of the water dosing; 10% H₂O, 25,000 1/h

Table 4 NO_x adsorption and desorption behaviour at 50 °C, 25,000 l/h

Test phase	Inlet gas composition	Waiting condition
Preconditioning	8% CO ₂ , 8% O ₂ , balance N ₂	450 °C for 250 s
Adsorption	50 ppm NO, 8% CO ₂ , 8% O ₂ , balance N ₂	Until 45 ppm NO _x slip
TPD Desorption	8% CO ₂ , 8% O ₂ , balance N ₂	Temperature ramp to 450 °C at 25 K/min

of the catalyst are constant. After a NO_x breakthrough of 45 ppm is reached, the NO dosage is shut off and the TPD begins. During the adsorption and the desorption phase a mass balancing of the dosed and measured NO_x concentrations is carried out to validate the storage potential of the catalyst sample. During the desorption phase, two major NO_x desorption peaks occur, the first peak reaches its maximum at an inlet temperature of 164 °C and the NO_x composition is mainly NO. The second NO_x desorption peak reaches its maximum at an inlet temperature of nearly 400 °C and primarily consists of NO₂. The presence of these two desorption peaks leads to the assumption, that more than one storage site is available on the SCR catalyst.

The observation of two storage sites could not be validated by current literature [26], furthermore the desorption temperature of the stored NO_x differs from the temperature range compared to other papers [4]. A possible explanation for this diverse behaviour is that different catalyst compositions have been used, suggesting that the desorption temperature also strongly depends on the catalyst coating.

Furthermore, the temperature driven desorption underpins the thesis that the adsorbed NO_x desorbs by the rise in temperature caused by adsorption of water rather than competing storage sites. These findings are consistent with other literature [4, 24].

To evaluate the maximum storable amounts of NO_x emissions for this technology the dosed NO has been integrated (1) during the adsorption phase as well as the desorbed NO_x during the TPD (2).

$$\text{Adsorbed NO}_x [\text{g/l}] = \int_{t_{\text{beginads.}}}^{t_{\text{endads.}}} \frac{(\text{NO}_{x_{\text{in}}} - \text{NO}_{x_{\text{out}}} - \text{N}_2\text{O})}{V_{\text{sample}}} dt \quad (1)$$

$$\text{Desorbed NO}_x [\text{g/l}] = \int_{t_{\text{beginTPD}}}^{t_{\text{endTPD}}} \frac{(\text{NO}_{x_{\text{out}}} + \text{N}_2\text{O})}{V_{\text{sample}}} dt \quad (2)$$

For the measurement seen in Fig. 8, 3.043 g/l NO_x can be stored on the catalyst sample, the desorbed amount is with 3.281 g/l a little bit higher, this difference can be explained by measurement noise due to the longer adsorption phase. Such high NO_x storage capacity could not be noticed in [vehicle measurements](#). One possible reason is that during the vehicle measurements the exothermic water adsorption occurs and therefore stops the NO_x adsorption earlier compared to the synthetic gas test bench measurements.

To evaluate the lower storage capacity of NO_x during vehicle measurements, a test setup with a lower slip limit of 10 ppm NO_x instead of 45 ppm during the adsorption phase has been carried out. The results for this test setup are shown in Fig. 9. Remarkable for this measurement is that for the lower NO_x slip limit of 10 ppm, only the low temperature desorption peak is present. This leads to the assumption that the storage site with the lower desorption temperature and mainly consisting of NO is addressed first. This behaviour corresponds to the vehicle measurements, where the desorption peak also mainly consists of NO and the temperature range of the desorption is similar. Furthermore, the amount

Fig. 8 NO adsorption and desorption behaviour of the flow-through substrate; 50 ppm NO, 50 °C and 25,000 l/h; some measurement curves can only be seen partially due to overlapping

of stored NO_x is significantly lower (0.265 g/l), but still considerable higher compared to vehicle data. In contrast to the measurement seen in Fig. 8 the adsorption phase only takes 13.5 min for the lower NO_x slip limit instead of 106 min.

5.3 Parameter influence study for NO_x storage behaviour

The measurements carried out to this point aimed to get a principal understanding of the NO_x adsorption and desorption mechanisms, as well as the thermal behaviour of the catalyst caused by water adsorption and condensation. To get a wider insight of possible influence factors a parameter study has been carried out, therefore the test setup presented in Fig. 8 has been further adapted depending on the influence parameter. If not stated otherwise the gas composition for the following tests is 8% O_2 , 8% CO_2 in N_2 as a filling gas, at a space velocity of 25,000 1/h and an adsorption temperature of 50 °C.

5.4 Influence of the substrate type on NO_x storage behaviour

To validate the impact of different substrate types on the NO_x storage behaviour, the same test setup as shown in Fig. 8 for the flow-through SCR catalyst was carried out with an on-filter SCR catalyst, the result is visualized in Fig. 10.

The total amount of adsorbed NO_x reaches a value of 0.835 g/l, which is significantly lower compared to the flow-through substrate. Furthermore, the first desorption peak reaches its maximum at a temperature of 200 °C and the second one is reached at 385 °C. The general NO_x storage behaviour is comparable to the flow-through substrate, a possible reason for the lower storable NO_x could be the lower amount of washcoat loading of the on-filter catalyst. The main design criterion for the close-coupled SCR system and the underfloor SCR system has already been mentioned in the introduction section, it is noteworthy that the NO_x storage is up to now not a major design criterion for exhaust

Fig. 9 NO adsorption and desorption behaviour until 10 ppm NO_x slip; 50 ppm NO , 50 °C and 25,000 1/h; some measurement curves can only be seen partially due to overlapping

Fig. 10 NO adsorption and desorption behaviour for on-filter substrates; 50 ppm NO , 50 °C and 25,000 1/h; some measurement curves can only be seen partially due to overlapping

Fig. 11 Temperature variation NO_x storage values at 45 ppm NO_x slip, 25,000 1/h

system development. Despite the fact of the lower NO_x storage capacity of the SCR-on-filter catalyst, both catalyst types combined offer a greater NO_x storage potential than a stand-alone version. Because the absolute amount of storable NO_x scales with the total amount of washcoat available in the entire exhaust system, therefore a greater NO_x reduction potential during the cold start is possible. The reason for the lower washcoat loading of the SCR-on-filter catalyst is that there is a trade-off between backpressure and washcoat loading.

5.5 Influence of the adsorption temperature on NO_x storage behaviour

For the next variation parameter, the temperature during adsorption in the catalyst was varied to evaluate the sensitivity towards different cooling phases for vehicle application. The results for the temperature variation are visualized in Fig. 11. The results show that the NO_x storage has a strong dependency on the catalyst temperature, this confirms the observations that the NO_x adsorption occurs preferably at lower temperatures. The TPD (not illustrated) shows that both NO_x desorption peaks are affected equally with increasing adsorption temperature.

5.6 Influence of the space velocity on NO_x storage behaviour

Another influence parameter which has been detected in vehicle measurements is the space velocity in the catalyst. To tackle the severity of this variable, synthetic gas test bench measurements with different space velocities were carried out. As can be seen in Fig. 12, the space velocity plays a minor role with regard to the maximum NO_x adsorption potential. However, doubling the space velocity

from 25,000 to 50,000 1/h leads to a significant reduction of the time needed to reach a NO_x slip of 10 ppm during the adsorption phase by more than 75%. This indicates that a higher space velocity leads to a disproportionate earlier NO_x slip. The underlying cause of this phenomenon could potentially be that the time needed for a NO_x molecule to adsorb on the catalyst increases as the saturation point of the possible storable amount of NO_x is reached. Thus, a higher space velocity makes it impossible for some NO_x molecules to adsorb on the catalyst and reduces the maximum storable NO_x emissions for the same NO_x slip limit. Moreover, the same test setup has been carried out with a space velocity of 15,000 1/h, this measurement points out that the time needed to cross the 10 ppm NO_x slip point does not change compared to the setup with a space velocity of 25,000 1/h. This indicates that a certain minimum time is required for the NO_x molecules for the adsorption process.

5.7 Influence of the exhaust gas composition on NO_x storage behaviour

To evaluate the influence of other typical exhaust gas components during cold start such as short-chain hydrocarbons, long-chain hydrocarbons, and carbon monoxide, further lab scale measurements were carried out. Therefore, optionally C₃H₆, C₁₀H₂₂ and CO are added to the inlet gas composition during the NO_x adsorption phase and shut off again during the desorption phase.

In Fig. 13 the NO_x storage behaviour in combination with 2000 ppm of CO dosing is shown. A total amount of 1.714 g/l NO_x can be stored, whereby CO dosing primarily affects the storage site with the higher NO_x release temperature. Furthermore, both desorption peaks mainly consist of NO, which implies that the CO inhibits the oxidation of NO to NO₂. The calculated mass balance reveals that a

Fig. 12 Space velocity variation NO_x storage values at 45 ppm NO_x slip, 50 °C NO_x adsorption temperature

significant amount of the dosed CO oxidises to CO_2 . This reduces the available oxygen potentially causing the reduced oxidation of NO to NO_2 during the adsorption phase, also leading to a reduced storage amount of NO_x . Additionally, a test with 5000 ppm CO dosing was carried out, with similar results. Furthermore, the calculated mass amount of NO_x during adsorption and desorption was the same for both tests.

In the next step, the influence of short-chain hydrocarbons was evaluated. For that purpose C_3H_6 was added in various concentrations during the NO_x adsorption phase. The measurement results for 50 ppm C_3H_6 dosing are illustrated in Fig. 14. Like for the CO tests, the NO_x desorption peaks mainly consist of NO, furthermore the second desorption peak is significantly lower than the first one.

It is notable that the C_3H_6 dosing slightly reduces the amount of stored NO_x to 2.854 g/l and cuts the desorbed NO_x to less than one third of the adsorbed NO_x amount to 0.927 g/l. The adsorbed C_3H_6 on catalyst enables the

reduction of stored NO_x during the TPD. The low temperature NO_x reduction is due to the following reaction (3) [29, 30].

In Fig. 15 the NO_x mass balance during adsorption and desorption for different C_3H_6 dosing concentrations are shown. The difference in the mass balance for the first case without C_3H_6 dosing is traced back to measurement inaccuracies due to the long duration of the adsorption phase. Overall for low C_3H_6 concentrations the amount of adsorbed NO_x is not significantly influenced, though C_3H_6 enhances the reduction of the adsorbed NO_x considerable. The reduced storability of NO_x with higher C_3H_6 concentrations can be caused by a blocking effect of the NO_x storage sites by the C_3H_6 molecules.

The same measurement procedure was carried out with $\text{C}_{10}\text{H}_{22}$ instead of C_3H_6 . For the 250 ppm $\text{C}_{10}\text{H}_{22}$

Fig. 13 NO adsorption and desorption behaviour; 2000 ppm CO and 50 ppm NO, 50 °C and 25,000 l/h; some measurement curves can only be seen partially due to overlapping

Fig. 14 NO adsorption and desorption behaviour; 50 ppm C_3H_6 and 50 ppm NO, 50 °C and 25,000 l/h; some measurement curves can only be seen partially due to overlapping

dosing measurement, a total NO_x amount of 0.853 g/l can be stored on the catalyst, whereby just 0.616 g/l of NO_x desorb during the TPD. An explanation for this sharply reduced storage capacity is the larger molecule size of $\text{C}_{10}\text{H}_{22}$ compared to C_3H_6 and thus blocking the storage sites of NO_x more easily. The reduction takes the formula (4) as a basis [29, 30].

Fig. 15 NO_x adsorption and desorption behaviour; 0/25/50/250/1250 ppm C_3H_6 and 50 ppm NO , 50 °C and 25,000 1/h

Fig. 16 Preloading of NH_3 on the catalyst; 405 s 100 ppm NH_3 , 200 °C and 25,000 1/h

5.8 Influence of NH_3 on NO_x storage behaviour

A test series with focus on the influence of NH_3 preloading on the catalyst sample was executed. The preloading of NH_3 was achieved by adding an additional phase step before the NO_x adsorption phase. A time-dependent NH_3 dosing with a gas composition of 100 ppm NH_3 , 5% H_2O , 8% CO_2 and 8% O_2 in N_2 at 200 °C and a space velocity of 25,000 1/h was chosen to guarantee a valid mass balance for the NH_3 storage level. As an example a preloading of 0.2 g/l NH_3 is shown in Fig. 16, the space velocity and temperature were chosen in a way so that no NH_3 slip occurs. The initial overshoot of the NH_3 concentration at the start of the NH_3 dosing is caused by the mass flow controller.

The addition of water during the NH_3 dosing prevents the deposition of NH_3 on the piping of the synthetic gas test bench. The NO_x storage results for different NH_3 loadings are visualized in Fig. 17. As soon as NH_3 is stored on the catalyst, the NO_x storage capacity drops from 3.043 g/l to about 1.4 g/l. It is noteworthy that for a NH_3 storage level between 0.2 and 0.5 g/l the amount of stored NH_3 reveals no significant influence on the NO_x storage capacity. During the TPD a NO_x reduction of 0–100 mg/l occurs, whereby the maximum NO_x reduction is reached at a NH_3 storage level of 0.5 g/l. This behaviour corresponds to the general understanding from the vehicle measurements that a higher NH_3 storage level leads to a higher NO_x reduction potential during cold start. During the NO_x desorption phase and simultaneous NO_x reduction phase not all the stored NH_3 is used

for NO_x reduction, the remaining NH_3 is available on the catalyst. For example if 100 mg of NO_x is converted, a total amount of 57 mg of NH_3 is consumed by the reaction. This corresponds to a NH_3 storage level reduction of about 11.5% at an NH_3 storage level of 0.5 g/l. It is assumed that the NO_x reduction takes predominantly the standard SCR reaction path ($4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$) and partially the fast SCR reaction path ($\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$) [12–14]. This is the reason for the results of the lower NO_x slip limit test, where only one desorption peak occurs, which mainly consists of NO. That behaviour is similar to vehicle measurements.

5.9 Influence of adsorbed H_2O on NO_x storage behaviour

The last topic of the synthetic gas test bench experiments was to evaluate the influence of water adsorption on the

Fig. 17 NO storage capacity at 45 ppm NO_x slip; NH_3 storage level variation; 50 ppm NO dosing, 50 °C and 25,000 1/h

Fig. 18 NO adsorption and desorption behaviour; 2% 100 s H_2O preloading and 50 ppm NO , 50 °C and 25,000 1/h; some measurement curves can only be seen partially due to overlapping

NO_x storage behaviour. Vehicle measurements showed a strong inhibition effect due to stored water on the NO_x storage activities. A similar preloading phase like that for the NH_3 synthetic gas test bench measurements described above was introduced. The water preloading phase utilizes a time dependent H_2O dosing of 2% H_2O , 8% CO_2 and 8% O_2 in N_2 at 100 °C and a space velocity of 25,000 1/h. The general behaviour for the maximum storable NO_x mass coincides very well for the vehicle measurements and the synthetic gas test bench measurements. The NO_x adsorption and desorption behaviour with a preloading of 2% H_2O for 100 s is plotted in Fig. 18. A slight shift towards a higher desorption temperature can be noticed for the second desorption peak. Furthermore the H_2O dosing shows no influence on the gas composition of the desorption peaks, with the first emissions peak consisting predominantly of NO and the second one mainly of NO_2 .

The results for the complete water adsorption test series are depicted in Fig. 19 and demonstrate that the slightest amount of water strongly inhibits the storable amount of NO_x . However, during real vehicle measurements the idealized case of no water preloading will hardly occur, because in every operating condition water will reach the surface of the catalyst. Despite the strong gradient for low water dosing it is noteworthy that a kind of saturation of minimum NO_x storage is reached for longer water dosing periods. This behaviour is contrary to that seen in vehicle measurements, where the NO_x storage effect completely disappears as the amount of preloaded water exceeds a certain value.

6 Summary and conclusion

This paper aimed to experimentally analyse and evaluate the NO_x storage behaviour as well as the water adsorption/desorption behaviour on SCR catalyst systems during vehicle

Fig. 19 NO storage capacity at 45 ppm NO_x slip; H₂O preloading variation; 50 ppm NO dosing, 50 °C and 25,000 l/h

cold start. In vehicle measurements the overall behaviour could be classified in the mentioned sub-effects, furthermore the effects have been replicated on a synthetic gas test bench. The lab scale investigations provide a detailed overview for each influence parameter.

The investigated SCR catalysts show a sharp temperature rise during cold start in dry condition, this effect can be traced back to the exothermic adsorption behaviour of H₂O on the surface of the catalyst. A higher water preloading on the catalyst causes a significantly decreased temperature rise. The exothermic behaviour can be subject to a time-based decoupling, traceable to the condensation of the gaseous water upstream of cold exhaust components. In addition, the catalyst analysed is capable of adsorbing NO_x emissions at low temperatures, causing zero NO_x emissions after the catalyst. The temperature rise was reproduced on the synthetic gas test bench and it is proofed that the rise in temperature causes the previously adsorbed NO_x to desorb. It is assumed that locally much higher temperatures are reached enabling a partial reduction of the stored NO_x if NH₃ is available.

Preloaded amounts of water on the catalyst and the catalyst temperature were identified to be the main influence parameters on the NO_x storage behaviour with regards to the storage capacity. Additionally the impact of CO, C₃H₆ and C₁₀H₂₂ was verified, whereby a NO_x reduction effect for the short- and long-chain hydrocarbons was determined. CO in the exhaust gas primarily affects the storage sites with the higher NO_x release temperature by inhibiting the oxidation of NO to NO₂ during the adsorption phase. C₃H₆ increases the reduction potential of NO_x stored on the catalyst during the NO_x desorption. Long-chain hydrocarbons significantly decrease the storable amount of NO_x on the catalyst, due to a blocking effect of the NO_x storage sites on the catalyst. Furthermore, synthetic gas test

bench measurements revealed that the space velocity predominantly affects the adsorption behaviour. An increasing mass flow causes a disproportionate earlier NO_x slip, due to a shorter dwell time of each NO_x molecule on the catalyst. The influence of the catalyst temperature shows that a higher temperature reduces the NO_x storage behaviour, therefore the NO_x storage effect is available only during cold starts.

The different behaviour of a flow-through substrate and an on-filter substrate was analysed. It is assumed that, with a higher amount of washcoat the storable amount of NO_x increases. The seen behaviour corresponds very well to that of vehicle measurements. Additionally the influence of stored NH₃ on the catalyst was analysed, showing that the presence of NH₃ reduces storable amount of NO_x on the one hand, but on the other hand increases the NO_x reduction potential.

Overall, it was possible to outline the main influence parameters on the NO_x storage effect as well as their effect mechanisms on the synthetic test gas bench. To increase the accuracy of an already existing SCR system model, an empirical NO_x storage model will be developed and implemented. This model will be able to give a prediction whether a NO_x storage potential is available and if so, how much NO_x reduction will occur under the given boundary conditions during the cold start phase.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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References

1. ACEA. <https://www.acea.be/statistics/article/Share-of-diesel-in-new-passenger-cars>. Accessed 19 May 2021
2. Mittrecker, H., Wieser, M., Weißbäck, M., et al.: The diesel engine as an important component for CO₂ fleet target achievement. *MTZ Worldwide*. **79**, 38–43 (2018)

3. Reşitoğlu, İ.A., Altinişik, K., Keskin, A.: The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. *Clean Techn. Environ. Policy* **17**, 15–27 (2015). <https://doi.org/10.1007/s10098-014-0793-9>
4. Schmeisser, V., Weibel, M., Sebastian Hernando, L., et al.: Cold start effect phenomena over Zeolite SCR catalysts for exhaust gas aftertreatment. *SAE Int. J. Commer. Veh.* **6**, 190–199 (2013). <https://doi.org/10.4271/2013-01-1064>
5. Lao, C.T., Akroyd, J., Eaves, N., et al.: Investigation of the impact of the configuration of exhaust after-treatment system for diesel engines. *Appl. Energy* **267**, 114844 (2020). <https://doi.org/10.1016/j.apenergy.2020.114844>
6. (2017) SAE Technical Paper Series. SAE Technical Paper Series. SAE International400 Commonwealth Drive, Warrendale, PA, United States
7. Mihai, O., Tamm, S., Stenfeldt, M., et al.: Evaluation of an integrated selective catalytic reduction-coated particulate filter. *Ind. Eng. Chem. Res.* **54**, 11779–11791 (2015). <https://doi.org/10.1021/acs.iecr.5b02392>
8. Bayer T, Samuelsen D, Bareiss S et al. (2018) Double injection SCR–Bosch’s development for future emission regulations. In: Bargende M, Reuss H-C, Wiedemann J (eds) 18. Internationales Stuttgarter Symposium. Springer Fachmedien Wiesbaden, Wiesbaden, pp 579–593
9. Olowojebutu S, Steffen T (2017) A Review of the Literature on Modelling of Integrated SCR-in-DPF Systems. In: SAE Technical Paper Series. SAE International400 Commonwealth Drive, Warrendale, PA, United States
10. Purfürst, M., Naumov, S., Langeheinecke, K.-J., et al.: Influence of soot on ammonia adsorption and catalytic DeNO_x-properties of diesel particulate filters coated with SCR-catalysts. *Chem. Eng. Sci.* **168**, 423–436 (2017). <https://doi.org/10.1016/j.ces.2017.04.052>
11. Steinparzer F, Hiemesch D, Kranawetter E et al. (2020) Die Technik der neuen BMW 6-Zylinder-Dieselmotoren der zweiten Baukastengeneration/The Technical Concept of the New BMW 6-Cylinder 2nd Generation Modular Diesel Engines. In: Geringer B, Lenz H-P (eds) 41. Internationales Wiener Motorensymposium 22–24. April 2020. VDI Verlag, II-34-II-53
12. Beale, A.M., Gao, F., Lezcano-Gonzalez, I., et al.: Recent advances in automotive catalysis for NO_x emission control by small-pore microporous materials. *Chem Soc Rev* **44**, 7371–7405 (2015). <https://doi.org/10.1039/C5CS00108K>
13. Brandenberger, S., Kröcher, O., Tissler, A., et al.: The State of the art in selective catalytic reduction of NO_x by ammonia using metal-exchanged zeolite catalysts. *Cataly Rev.* **50**, 492–531 (2008). <https://doi.org/10.1080/01614940802480122>
14. Chen, L., Janssens, T.V.W., Vennestrøm, P.N.R., et al.: A Complete Multisite Reaction Mechanism for Low-Temperature NH₃-SCR over Cu-CHA. *ACS Catal* **10**, 5646–5656 (2020). <https://doi.org/10.1021/acscatal.0c00440>
15. Yim, S.D., Kim, S.J., Baik, J.H., et al.: Decomposition of Urea into NH₃ for the SCR Process. *Ind Eng Chem Res* **43**, 4856–4863 (2004). <https://doi.org/10.1021/ie034052j>
16. Ebrahimian, V., Nicolle, A., Habchi, C.: Detailed modeling of the evaporation and thermal decomposition of urea-water solution in SCR systems. *AIChE J* **58**, 1998–2009 (2012). <https://doi.org/10.1002/aic.12736>
17. Devada, M., Krocher, O., Elsener, M., et al.: Influence of NO₂ on the selective catalytic reduction of NO with ammonia over Fe-ZSM5. *Appl. Catal. B* **67**, 187–196 (2006). <https://doi.org/10.1016/j.apcatb.2006.04.015>
18. Ciardelli, C., Nova, I., Tronconi, E., et al.: Reactivity of NO/NO₂–NH₃ SCR system for diesel exhaust aftertreatment: Identification of the reaction network as a function of temperature and NO₂ feed content. *Appl. Catal. B* **70**, 80–90 (2007). <https://doi.org/10.1016/j.apcatb.2005.10.041>
19. Roppertz, A., Föger, S., Kureti, S.: Investigation of Urea-SCR at Low Temperatures. *Top Catal* **60**, 199–203 (2017). <https://doi.org/10.1007/s11244-016-0597-8>
20. Chen, L., Janssens, T.V.W., Skoglundh, M., et al.: Interpretation of NH₃-TPD Profiles from Cu-CHA Using First-Principles Calculations. *Top Catal* **62**, 93–99 (2019). <https://doi.org/10.1007/s11244-018-1095-y>
21. Kwak, J.H., Tonkyn, R.G., Kim, D.H., et al.: Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH₃. *J. Catal.* **275**, 187–190 (2010). <https://doi.org/10.1016/j.jcat.2010.07.031>
22. Schmieg, S.J., Oh, S.H., Kim, C.H., et al.: Thermal durability of Cu-CHA NH₃-SCR catalysts for diesel NO_x reduction. *Catal. Today* **184**, 252–261 (2012). <https://doi.org/10.1016/j.cattod.2011.10.034>
23. Gao, F., Walter, E.D., Karp, E.M., et al.: Structure–activity relationships in NH₃-SCR over Cu-SSZ-13 as probed by reaction kinetics and EPR studies. *J. Catal.* **300**, 20–29 (2013). <https://doi.org/10.1016/j.jcat.2012.12.020>
24. Lundström, A., Snelling, T., Morsing, P., et al.: Urea decomposition and HNCO hydrolysis studied over titanium dioxide, Fe-Beta and γ-Alumina. *Appl. Catal. B* **106**, 273–279 (2011). <https://doi.org/10.1016/j.apcatb.2011.05.010>
25. Sella, T., Gramigni, F., Nova, I., et al.: A PGM-free NO_x adsorber + selective catalytic reduction catalyst system (AdSCR) for trapping and reducing NO_x in lean exhaust streams at low temperature. *Catal Sci Technol* **8**, 2467–2476 (2018). <https://doi.org/10.1039/C8CY00343B>
26. Gramigni, F., Sella, T., Nova, I., et al.: Analysis of AdSCR Systems for NO_x Removal During the Cold-Start Period of Diesel Engines. *Top Catal* **62**, 3–9 (2019). <https://doi.org/10.1007/s11244-019-01138-5>
27. Storch JGC (2009) Materialwissenschaftliche Untersuchungen an zeolithischen Adsorbentien für den Einsatz in offenen Sorptionssystemen zur Wärmespeicherung. Dissertation, Technische Universität München
28. Hauer A (2002) Beurteilung fester Adsorbentien in offenen Sorptionssystemen für energetische Anwendungen. Dissertation, Technische Hochschule Berlin
29. Shelef, M.: Selective catalytic reduction of NO_x with N-free reductants. *Chem Rev* **95**, 209–225 (1995). <https://doi.org/10.1021/cr00033a008>
30. Iwamoto, M., Yahiro, H., Tanda, K., et al.: Removal of nitrogen monoxide through a novel catalytic process. 1. Decomposition on excessively copper-ion-exchanged ZSM-5 zeolites. *J Phys Chem* **95**, 3727–3730 (1991). <https://doi.org/10.1021/j100162a053>

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