

Cold Start Effect Phenomena over Zeolite SCR Catalysts for Exhaust Gas Aftertreatment

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ABSTRACT

NH₃/urea SCR is a very effective and widely used technology for the abatement of NO_x from Diesel exhaust [1]. The SCR mechanism is well understood and the catalyst behavior can be predicted by mathematical models [2,3,4] - as long as operation above the temperature limit for AdBlue® injection is considered. The behavior below this level is less understood.

During the first seconds up to minutes after cold start, complete NO_x abatement can be observed over an SCR catalyst in test bench experiments, together with a significant increase in temperature after the converter (ca. 100 K).

In this work these effects have been investigated over a monolith Cu-zeolite SCR catalyst. Concentration step experiments varying NO, NO₂ and H₂O have been carried out in lab scale, starting from room temperature. Further, the interaction of C₃H₆ and CO with NO_x over the SCR has been investigated. The effects observed during cold start have been reproduced successfully at lab scale, providing insight into the prevailing mechanisms.

It was found that low-temperature NO oxidation proceeds already at room temperature, showing a negative temperature dependence [5]. However, it is strongly inhibited by H₂O. Thus, significant amounts of NO₂ can be produced over the SCR while H₂O of the exhaust condenses on the cold devices upstream. Further, the SCR catalyst can store NO₂ efficiently, so that a major part of NO_x disappears. Finally, upon addition of H₂O-vapor to the gas, it adsorbs on the zeolite, causing a sudden temperature increase due to the heat of adsorption. The results show that this increase forces the stored NO₂ to desorb immediately. However, real engine cold start measurements show NO desorption instead. The reason can be reducing agents like CO and hydrocarbons, that were indeed proven able to reduce NO₂ to NO over the SCR.

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INTRODUCTION

Nowadays, one of the challenges in the development of Diesel vehicles is the limitation in the pollutants emission in order to fulfil new governments regulations, especially in relation to NO_x and particulate matter (PM) [1]. Regarding PM, the application of a Diesel particle filter is an efficient measure to reduce particle emissions from the exhaust gas. Focusing on NO_x, the application of the NH₃/urea SCR system is well established, being one of the most effective DeNO_x systems [1]. Here, Fe- or Cu-exchanged zeolites are an attractive technology, showing high NO_x conversion over a wide temperature range. The SCR performance as well as the continuous soot oxidation on the filter benefit from an

increased NO₂/NO_x-ratio in the exhaust gas, so that a Diesel oxidation catalyst is placed upstream of the filter and SCR. Thus, a modern common Diesel vehicle aftertreatment system consists of the following devices: Diesel oxidation catalyst, particle filter, AdBlue® injection and SCR catalyst, eventually followed by an NH₃ slip catalyst (ASC).

Due to the complexity of the aftertreatment system, optimization of its design and operation is a challenging and expensive task as it affects many topics like temperature and AdBlue® dosing strategy for minimal emissions at reasonable costs. In this context, the application of simulation tools is a key factor in an efficient development process of aftertreatment systems, reducing costs and effort. Model development of the single devices has been carried out

successfully over many years by several research groups, accompanied by appropriate experimental investigation. Regarding the SCR, most effort has been devoted to study and model the “standard” SCR reaction ($2\text{NH}_3 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$), but more recently the other reactions occurring when NO_2 is also present in the exhaust have been analysed into details [6,7,8,9]. The increased NO_2 -fraction greatly enhances the DeNOx efficiency onto the SCR unit as the “Fast” SCR reaction ($2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$) [3,6,7,9,10,11,12] becomes active. Furthermore, in the presence of excess NO_2 in the reacting system the “ NO_2 ” SCR reaction ($8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$) [3,6,7,8,12] can significantly contribute to the overall DeNOx process. This chemistry is well understood and the SCR performance can be predicted by simulation tools in the temperature range of common SCR operation starting from ca. 150°C up to 600°C . On the other hand, SCR reactions at low temperatures are often neglected in discussions or simulations, as it is assumed, that NO_2 is not yet produced over the DOC. Further, NH_3 is not available in significant amounts at the SCR because AdBlue® injection and processing require a certain temperature level, typically above 150°C . However, the low temperature ($T < 150^\circ\text{C}$) SCR behavior is becoming more and more important, as the exhaust temperatures steadily decrease with increasing fuel efficiency of the engine.

Indeed, in reality several phenomena occur at low temperatures, which should not be neglected. From engine test bench experiments with real exhaust gas it can be observed that during the first seconds after cold start, NO_x emissions are completely reduced over the SCR brick. Further, the exhaust gas leaving the SCR shows a significantly higher temperature than the gas entering the catalyst. When the temperature rise is at its maximum, a desorption peak of NO_x can be measured after the SCR, followed by a slow decrease in gas temperature after the SCR. Such results are also presented within this work. The models published in literature are not yet able to describe properly the peculiar SCR behaviour in the period from cold start until common operation temperature is reached, as the related processes have not been yet fully elucidated.

In this contribution such effects, playing a major part in the cold start behavior of the SCR converters, are investigated in dedicated lab scale experiments with synthetic exhaust gas over commercial monolith Cu-zeolite SCR catalysts. It was the goal on the one hand to reproduce the observations from engine test bench measurements under controlled conditions. On the other hand, dedicated experiments should provide results and information leading to the identification of the individual steps and effects that contribute to the overall phenomenon, namely ad- and desorption of H_2O and NO_x , NO oxidation and NO_2 reduction to NO . This is a critical step in order to be able to start the mathematic modeling of the SCR behavior at these conditions.

METHODS

Lab Scale Experiments

The low temperature behavior of Cu-zeolite based SCR converters was investigated over core drilled monolith samples on two different synthetic gas test rigs. As long as not otherwise stated, experiments were carried out on test rig 1. On test rig 2, only the NO_x reduction experiments with CO and C_3H_6 have been carried out.

Test Rig 1

The SCR catalyst sample (around 6 cm^3 volume, 400 cpsi cell density, 5 mils) was taken from a commercial Cu-zeolite, the same technology as used on the engine test bench. The conditioning procedure was carried out by heating the samples up to 550°C for 5 hours in high O_2 and H_2O feed contents (10%) with a GHSV of $81'000\text{ h}^{-1}$. Typical gas phase concentrations fed to the reactor were 0-8 % H_2O , 0-8 % O_2 , 0-500 ppm of NO or NO_2 in N_2 , used as balance gas. The space velocity was set to $100'000\text{ h}^{-1}$ for H_2O adsorption/desorption runs and to $30'000$ for most of the other experiments. A low GHSV value, consistent with rig restrictions, was preferred to better approximate idling conditions at the engine start up. The temperature was monitored by means of a K-thermocouple placed in the central axial and radial position of the core samples. The experiments have been focused in the low temperature region (below 100°C) and most of the experiment started at ambient temperature: an efficient temperature control was realized without heating the reactor and the inlet lines, with the exception of the one for H_2O , which needed to be vaporized. On the contrary, outlet lines were heated to prevent product condensation. Gas phase analysis was performed using an UV-analyzer (ABB LIMAS 11HV) for the analysis of NO , NO_2 , NH_3 and a Non Dispersive IR Analyzer (ABB Uras-14) for the analysis of N_2O . A more detailed description of the experimental rig is provided in [13,14].

Test Rig 2

Principles of this test rig are basically the same as for rig 1. The catalyst was a core drilled monolith sample with a diameter of 20mm and a length of 31mm. GHSV in the experiments was $60'000\text{ h}^{-1}$. The technology used in these experiments was also a commercial Cu-zeolite SCR catalyst (600cps, 5mil), aged hydrothermally at 750°C for 2h, but from a different manufacturer. Still, we believe that the basic behavior of this sample can be transferred to the technology used at test rig 1 and the engine test bench. Gas mixtures containing 200ppm of NO_2 , 10% of O_2 and 2000ppm of CO or 200 ppm of C_3H_6 have been introduced to the reactor (balance N_2). The experiments started at a constant reactor temperature of around 80°C , ramping up to 300°C at a rate of 2 K/min. Gas analysis has been performed with a IR-analyser

for CO and CO₂ (Hartmann&Braun Uras-14), FID-analyser for C₃H₆ (ABB Multi-FID 14), CLD-detector for NO_x (Ecophysics CLD 700 RE ht) and CI-mass spectroscopy for NH₃ (V&F Analysentechnik Airsense).

Engine Test Bench Experiments

The cold start phenomena presented in this work under real exhaust gas conditions have been observed on a heavy duty engine test bench. The exhaust aftertreatment system consisted of a DOC and DPF. The exhaust stream was then split symmetrically into two lines, each equipped with SCR- and ASC-catalysts. Each line contains 2 SCR-bricks (300cps, 5mil) with a total length of 12" and diameter of 10.5". The whole system was thermally insulated against the environment. The first SCR monolith was a commercial Fezeolite, the second brick a commercial Cu-zeolite technology. The latter was washcoated with the same SCR-technology as the lab scale sample on test rig 1. The catalysts were conditioned hydrothermally (air + H₂O) for 5 hours at 600°C in an oven before the test bench runs. Thus their condition is comparable to that of the lab scale sample.

RESULTS AND DISCUSSION

Engine Test Bench Experiments

A World Harmonized Transient Cycle (WHTC) has been run on the engine test bench. In the following we focus on the cold part of the cycle only. In [Figure 1](#) the temperature evolution of the exhaust gas before the SCR (leaving the DPF) and after the SCR is shown over the whole cold part of the cycle. While the entering gas shows a slow, but continuous rise in temperature due to slow heating up of the exhaust aftertreatment system upstream of the SCR, the temperature behavior of the gas leaving the SCR does not correspond to this trend. Instead, it shows a sudden temperature rise of more than 80K, starting at ca. 100s after start. It even exceeds the temperature of the entering gas and reaches its temporarily highest value at ca. 250s, before it slowly decreases over the next 350s. The temperature finally rises again after the time point 600s, showing the conventional heating up behavior of the system.

[Figure 2](#) shows the NO_x content of the exhaust gas after the engine and end of pipe until 500s of the cycle. Obviously, NO_x totally disappear over the first 100s. At the point of time when the temperature peak is observed, a NO_x peak occurs as well. This peak consists of NO only.

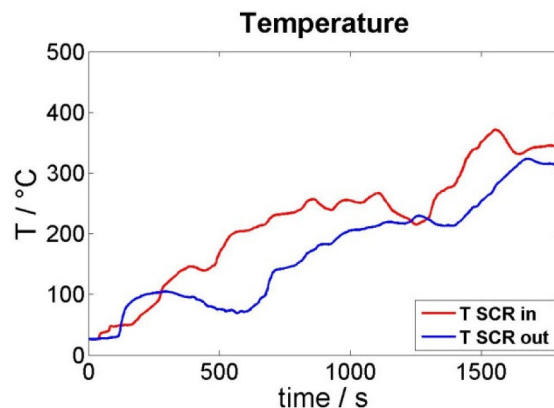


Figure 1. Gas temperature behavior before and after the SCR system during cold part of the WHTC.

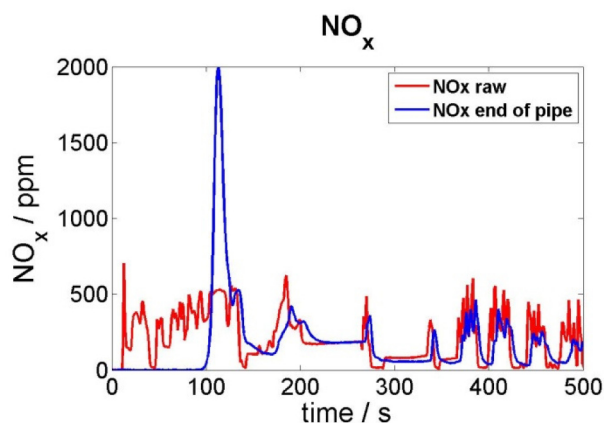


Figure 2. NO_x content engine out and end of pipe during the first 500s of the cold part of the WHTC.

The qualitatively same observations can be made for a SCR system consisting of Fe-zeolite technology only. However, the peaks in temperature and NO_x are of lower extent than in the combination with Cu-zeolite.

The observed temperature rise must be due to a strong exothermal process at the SCR. As such a behavior is not observed to this extent on the other parts (DOC, DPF), it must be closely related to the properties of the SCR catalyst. Exhaust gas contains significant amounts of H₂O in a fraction of around 10% v/v. It is probable that H₂O condensation occurs in the aftertreatment system during the cold start transient. The H₂O generated in the combustion process, in fact, is transported with the exhaust gas along the cold aftertreatment system. As long as the tubes and monoliths are still cold, H₂O will condense at its surfaces. As the monolithic structures provide a very high contact surface area, this process can efficiently take place. The SCR system in the rear part will thus see rather dry exhaust gas right after cold start. When DOC and DPF are saturated with H₂O, the exhaust gas containing H₂O will reach the SCR.