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Investigation of Urea-SCR at Low Temperatures

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Abstract This paper addresses the NO_x removal from diesel exhaust by using urea-SCR technique with focus on critical operating conditions, particularly low temperatures. The investigations were performed on a special laboratory test bench enabling the supply of aqueous urea solution ("AdBlue") or gaseous NH_3 to practical model exhaust. The SCR tests were made with a commercial $V_2O_5/WO_3/TiO_2$ honeycomb catalyst showing very similar performance between 250 and 400 °C when dosing AdBlue and NH_3. However, below 200 °C the activity of urea-SCR was clearly lower than that of NH_3-SCR due to incomplete conversion of urea and formation of deposits covering the reactor wall. ATR-IR analyses evidenced that these residues consist of urea as well as cyanuric acid originated from side-reactions of isocyanic acid. Furthermore, ramping the temperature upon urea-SCR forced the deposits towards consecutive reactions mainly resulting in cyanuric acid. Consequently, our study provides insights into the dynamic decomposition behavior or urea-related residues relevant for reliable SCR process in diesel exhaust.

Keywords Diesel exhaust · SCR · Deposits · Urea · Isocyanic acid · Cyanuric acid

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1 Introduction

Diesel engines with direct fuel injection provide high efficiency closely related to enhanced fuel economics and reduced CO_2 output. As a consequence, diesel engines are widely used for transportation implying heavy duty vehicles as well as passenger cars and they are also applied for working machines, cranes and power generators. However, a constraint of diesel engines is the emission of pollutants such as carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxide (NO_x) and soot [1]. Therefore, these components are continuously subjected to legal regulations since the late 1970s. In order to meet the emission limits both engine optimization as well as catalytic exhaust after-treatment are considered [2]. For the abatement of CO and HC, diesel oxidation catalysts (DOC) are already introduced into the market, while for soot diminution diesel particulate filters (DPF) are used. For NO_x removal, two techniques are currently available representing NO_x storage reduction catalysts (NSR) and selective catalytic reduction (SCR). In NSR, NO_x is periodically trapped and reduced by switching from lean to rich exhaust conditions induced by engine management systems. Contrary, SCR implies continuous reduction of NO_x by NH_3 on $V_2O_5/WO_3/TiO_2$ or iron and copper containing zeolite catalysts [3, 4]. The required NH_3 is produced on-board from "AdBlue", which is a 32.5 wt % aqueous solution of urea $[CO(NH_2)_2]$ injected into the exhaust pipe by single- or two-fluid nozzles. There, urea is firstly decomposed into ammonia and isocyanic acid (HNCO) followed by hydrolysis of the formed HNCO to yield NH_3 and CO_2. The overall reaction equation of NH_3 production is expressed as $CO(NH_2)_2 + H_2O \rightarrow 2\ NH_3 + CO_2$ reflecting a molar NH_3/CO_2 ratio of 2.

Above 200 °C the conversion of AdBlue into NH_3 is rapid and reliable, but below that the decomposition is decelerated and potentially incomplete, even in presence of catalysts such as TiO_2 [5–7]. As a result, solid urea deposits can cover the exhaust pipe and can even block the SCR catalyst. Additionally, these residues potentially undergo complex networks of consecutive reactions resulting in side-products like biuret, cyanuric acid, ammelide, ammeline and melamine, which boil and decompose above 300 °C only. These reactions were well studied in the literature under defined laboratory test conditions [8–11], but the transfer to real world is difficult, as the formation of the side products strongly depends on dynamics of temperature and composition of exhaust gas.

Thus, the aim of this paper was the evaluation of the urea conversion at low exhaust temperatures under practical operation conditions including the formation of the possible side-products. For this purpose, a special home-made SCR test bench with AdBlue injection was used. Deposits were analyzed by attenuated total reflection IR spectroscopy (ATR IR).

2 Experimental

The employed SCR test bench consisted of four units implying gas dosage, reactor, analytics and controlling (Fig. 1). The silica glass tube reactor (inner diameter: 32.8 mm, length: 1000 mm) contained the AdBlue injection nozzle (Duesen-Schlick, Type 970 S8) as well as the SCR catalyst. For the catalytic tests, a commercial cordierite-supported honeycomb catalyst coated with $V_2O_5/WO_3/TiO_2$ was taken. The cylindrical monolith revealed a length of 90 mm, a diameter of 26 mm and a cell density of 400 cpsi. The total flow was 120 l min^{-1} (STP) resulting in a space velocity of 152,000 h^{-1}. The gas stream was heated up before entering the reactor unit by using a 2 kW flow heater (Dohle XS 20). For NH_3-SCR, the feed consisted of 400 vppm NH_3, 400 vppm NO, 4.7 vol. % H_2O and 19.5 vol. % O_2 and N_2 as balance, while for urea-SCR an AdBlue flow of 25 ml min^{-1} (STP) was dosed instead of gaseous ammonia potentially producing 400 vppm NH_3. The distance between AdBlue injection nozzle and catalyst

was 250 mm corresponding to a residence time of ca. 0.1 s (STP). Dynamic laser scattering analysis provided a most probable AdBlue droplet size of about 15 µm. All gases (air liquide) were fed from independent mass flow controllers (Bronkhorst), while water was adjusted by a home-made evaporation unit. The gas temperature was measured by K-type thermocouples directly placed in front of and behind the catalyst, whereas the difference was always below 5 K. In the catalytic tests, the temperature was decreased from 400 to 150 °C in steps of 50 K and the reactor effluents were recorded after reaching steady state. The gaseous species NO, NO_2, N_2O, H_2O, NH_3 and HNCO were continuously detected by hot measuring FTIR spectrometer (MultiGas 2030, MKS Instruments) at a time resolution of 1 s. Deposits formed during urea-SCR were taken from the reactor unit and were analyzed by ATR IR. For this purpose, a Tensor 27 FTIR spectrometer (Bruker-AXS) equipped with a platinum ATR unit and a MCT detector was used. The measurements were made under ambient conditions without any pre-treatment and dilution of the residues. Spectra were recorded in the range from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, while accumulating 550 scans. Background measurements were taken without sample.

3 Results and Discussion

3.1 Urea- and NH_3-SCR Performance

The NH_3-SCR measurements show that the $V_2O_5/WO_3/TiO_2$ catalyst reveals $deNO_x$ performance, which is very similar to literature data [12]. Note that neither N_2O nor NO_2 is found. When dosing AdBlue instead of NH_3 the same activity is obtained between 250 and 300 °C, whereas beyond this range urea-SCR provides slightly lower activity (Fig. 2). This decrease in $deNO_x$ above 300 °C is associated with the higher flow rate at the elevated temperatures resulting in shorter residence time of AdBlue droplets causing incomplete conversion of urea. As a result, lower NH_3 concentrations appear in the catalyst thus decreasing the rate of SCR. This interpretation is supported by a blank experiment, in which AdBlue is injected in the

Fig. 1 Scheme of test bench including positions of thermocouples (TC), nozzle, catalyst and FTIR analyzer. Locations, at which residues were taken for analysis, are marked as deposit
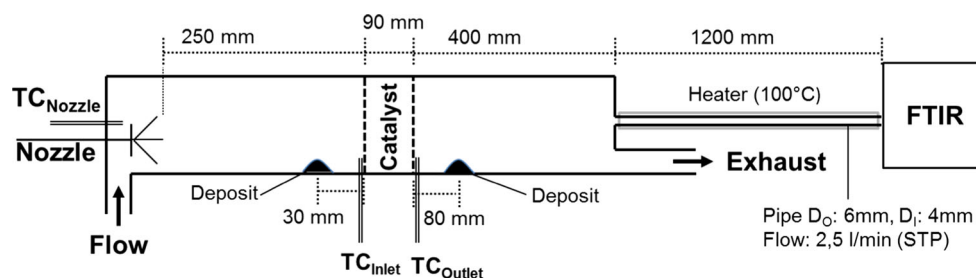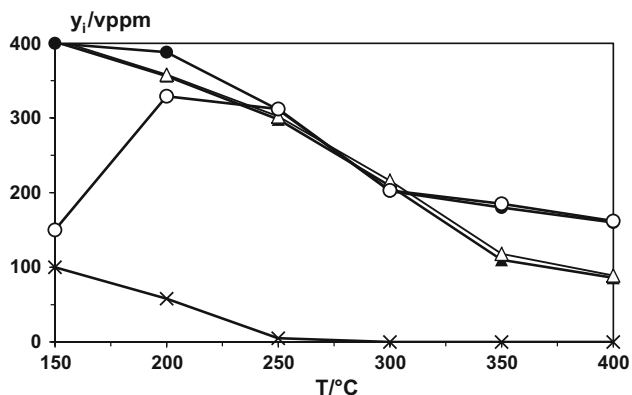
Fig. 2 Activity of $V_2O_5/WO_3/TiO_2$ catalyst in urea-SCR [y_{NO} (*filled circle*), y_{NH3} (*open circle*), y_{HNCO} (*times*)] and NH_3-SCR [y_{NO} (*filled triangle*), y_{NH3} (*open triangle*)]. Conditions: y (urea) = 200 vppm or y (NH_3) = 400 vppm, y (NO) = 400 vppm, y (H_2O) = 4.8 vol. %, y (O_2) = 19.5 vol. %, N_2 balance, S.V. = 152,000 h^{-1} (STP)

absence of the SCR catalyst. In this run, urea is completely decomposed at 300 °C with equimolar yield of NH_3 and HNCO (each ca. 200 vppm), whereas even above that temperature only slight hydrolysis of HNCO occurs, e.g. at 400 °C the NH_3 fraction is just ca. 220 vppm. It may be noted that negligible conversion of urea and HNCO may take place in the pipes (100 °C) feeding the FTIR analyzer.

The minor urea-SCR activity at 200 °C is also referred to limited NH_3 production as indicated by the presence of ca. 60 vppm HNCO (Fig. 2). Since the sum of NH_3 and HNCO fractions is equal to 400 ppm, it is evident that the urea decomposition to HNCO and NH_3 is complete, but temperature and residence time is not appropriate for subsequent hydrolysis of HNCO to yield NH_3 and CO_2. Basically, decomposition of urea starts at ca. 132.5 °C. As expected, no SCR occurs at 150 °C irrespective of the reducing agent dosed. However, when AdBlue is added quantities of 150 vppm NH_3 and 110 vppm HCNO are detected at this temperature evidencing urea conversion of ca. 50 % only. The unreacted urea potentially passes the reactor or forms deposits inside the reactor. Indeed, deposits were found at 150 °C all over the reactor, whereas ATR-IR indicated exclusive presence of urea.

3.2 Critical Operating Conditions During Urea-SCR

As demonstrated in Sect. 3.1, urea-SCR operating below 200 °C potentially results in non-decomposed urea producing deposits in the reactor and the exhaust pipe of a vehicle, respectively. These residues can cover and deactivate the SCR catalyst [13] or they can react to unwanted side-products with high boiling and decomposition temperatures. The deposits can be removed by heating at 400 °C [14], but in practice the exhaust often does not exceed 300 °C, particularly in city traffic. Therefore, a basic experiment was conducted to evaluate the formation and decomposition of residues in a practical temperature regime. For this purpose, the urea-SCR feed was adjusted for 3 h at 150 °C to produce urea deposits. Subsequently, the NO dosage was stopped and three heating (16 K/min)

Fig. 3 Formation of HNCO, CO_2 and NH_3 during heating/cooling cycles performed after exposure to urea-SCR feed performed at 150 °C for 3 h. Urea-SCR conditions:, y (NO) = 400 vppm, y (urea) = 200 vppm, y (H_2O) = 4.8 vol. %, y (O_2) = 19.5 vol. %, N_2 balance, S.V. = 152,000 h^{-1} (STP); conditions of temperature cycles: same as for urea-SCR except dosage of NO, $\Delta T/\Delta t$ = 16 K/min (heating) and 21 K/min (cooling)
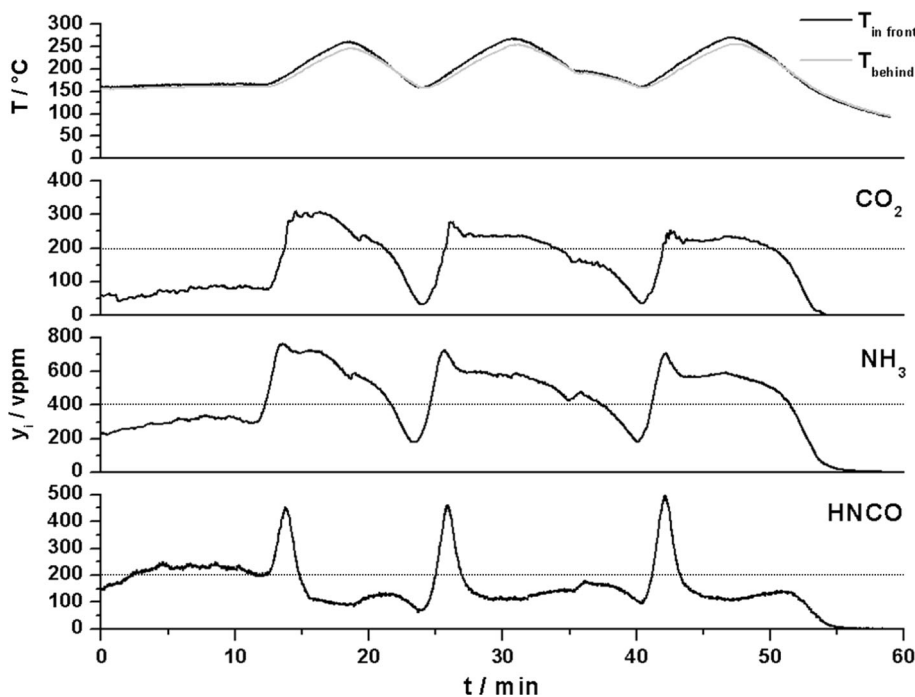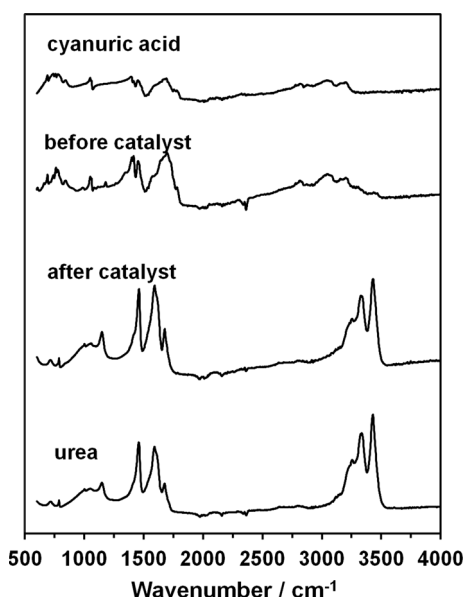
Fig. 4 ATR-IR spectra of deposits formed in front of and behind the catalyst after the heating/cooling cycles. For comparison the spectra of urea and cyanuric acid are shown

and cooling ramps (21 K/min) were run between 150 and 250 °C to check the decomposition of the residues and production of NH_3 and CO_2, respectively. In the heating sequences NH_3 and CO_2 are increasingly formed with molar NH_3/CO_2 ratios up to 5.5 evidencing incomplete urea conversion (Fig. 3). This is substantiated by the strong appearance of HNCO showing peak formation of 480 vppm. Since the quantities of NH_3, CO_2 and HNCO are clearly above that expected for complete conversion of urea fed, it is evident that deposits formed in the 150 °C exposure are additionally decomposed. Finally, the residues remaining after the experiment were removed from the reactor. ATR-IR analysis shows that the deposits taken in front of the catalyst are predominately consisting of cyanuric acid, while the material located behind the catalyst is mainly composed of solid urea (Fig. 4). The deposition of urea downstream to the catalyst may be referred to decreased temperature causing partial condensation; note that the temperature difference of catalyst and sampling point is about 15 K. Contrary, no significant amount of urea or side-products is formed on the catalyst as checked by a temperature programmed desorption experiment performed subsequent to the ramping experiment.

4 Conclusion

Critical operation conditions of the SCR process widely used for diesel vehicles were studied on a special laboratory test bench, which enables the supply of AdBlue (urea-

SCR) as well as gaseous ammonia (NH_3-SCR). As a result, urea-SCR on a commercial $V_2O_5/WO_3/TiO_2$ catalyst provides lower activity at temperatures above 300 °C and below 250 °C. The difference at lower temperatures is attributed to the incomplete urea decomposition and formation of solid urea deposits. The reactivity of residues produced at 150 °C is investigated by adjusting heating/cooling cycles resulting in huge production of NH_3 and HNCO. The later leads to cyanuric acid in front of the catalyst, whereas behind the catalyst urea is predominately deposited. Contrary, no urea or side-products are formed on the catalyst. Thus, this study shows that deposits may cover the exhaust pipe, but they do not necessarily deactivate the SCR catalyst. For complete removal of deposits such as cyanuric acid and urea formed under dynamic conditions thermal exposure above 300 °C is suggested.

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