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Quantification of urea-spray non-uniformity effects on the H₂-assisted NO reduction and NH₃ slip over an Ag/Al₂O₃ catalyst

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Abstract

Selective catalytic reduction of nitrogen oxides (NO_x) with ammonia (NH₃-SCR) is an efficient technology for lean NO_x removal in automotive applications. In the current work, a kinetic model for hydrogen-assisted NH₃-SCR over a silver-alumina (Ag/Al₂O₃) monolith catalyst is adapted to the corresponding experimental results. The degree of non-uniformity in the NH₃ dose to individual catalyst channels during operation of a urea-SCR system is also investigated and the NH₃ dose probability distribution functions are derived. The effects of NH₃ non-uniformity on the NO conversion and NH₃ slip are studied over an otherwise optimal Ag/Al₂O₃ system. Above the stoichiometric point, the NH₃ slip is shown to increase almost linearly with increasing NH₃ dosage. Channels that receive significantly lower NH₃ dose than the stoichiometric one exhibit low NO conversion, whereas there is no discernable increase in the NO conversion above an NH₃ dose four times the average. These results highlight the importance of the interaction between the design of the NH₃ dosing system and the performance of the catalytic system.

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Keywords: Ag/Al₂O₃; NH₃-SCR; NO_x reduction; NH₃ slip

1. Introduction

Global warming and rising oil prices motivate the development of more fuel-efficient engines, operating under lean conditions. However, excess of oxygen makes an ordinary three-way catalyst inefficient for NO_x reduction, which calls for development of other abatement techniques. Among the most attractive alternative techniques for NO_x reduction one finds selective catalytic reduction with ammonia or hydrocarbons (NH₃-SCR or HC-SCR). Much interest has been directed towards the

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Ag/Al₂O₃ catalyst, which exhibits SCR activity both with NH₃ [1, 2] and HC [3]. The catalytic performance of this catalyst can be further improved by the addition of small amounts of hydrogen [1, 2], which, for example, can be produced on board [4]. Also NH₃ is produced on board, to avoid storage and handling problems. A urea-water solution can be used since it decomposes to NH₃ when sprayed into the exhaust stream. Furthermore, Al₂O₃ is well suited for urea-SCR as it catalyzes this decomposition [2].

Lundström and Ström [5], and Lundström et al. [6] performed detailed computational fluid dynamics (CFD) investigations of the performance of a commercial urea-spray for urea-SCR applications in various exhaust gas aftertreatment configurations. It was found that the extent of urea decomposition into NH₃ and the uniformity of the produced NH₃ at the catalyst inlet are sensitive to the location of the spray injector in the exhaust gas system. More specifically, they observed that insufficient urea decomposition and NH₃ mixing might very well occur also under realistic operating conditions.

In the current work, H₂-assisted NH₃-SCR is investigated experimentally in a synthetic gas bench flow reactor and numerically using the kinetic model by Tamm et al. [7], which is adapted to the experimental results obtained here. The degree of non-uniformity in the NH₃ dose to individual catalyst channels during operation of a urea-SCR system is investigated and NH₃ dose probability distribution functions are derived from the raw data of Ström and Lundström [8]. The effects of this non-uniformity on the NO conversion and NH₃ slip are investigated over an otherwise optimal Ag/Al₂O₃ system, to isolate the effects from the NH₃ delivery strategy. The effects of NH₃ dosing non-uniformities for H₂-assisted NH₃-SCR are then quantified and discussed.

2. Methods

2.1. Experimental section

A 2 wt% Ag/Al₂O₃ catalyst was prepared by incipient wetness impregnation of γ -Al₂O₃ (PURALOX[®] SBa 200, Sasol) using silver nitrate (AgNO₃ \geq 99.0% Sigma-Aldrich) as precursor for the Ag-phase. After impregnation, the powder sample was frozen in liquid nitrogen, subsequently freeze-dried and then calcined in air at 600°C for 4 hours. A cordierite monolith (\varnothing =20 mm, l=20mm, 188 channels and 400 CPSI) was dip-coated with the Ag/Al₂O₃ catalyst until an amount approximately equal to 20% of the total monolith mass was attached. Subsequently, the monolith was calcined in air at 600°C for 1 hour.

The catalytic performance was evaluated using the synthetic gas bench reactor previously described by Kannisto et al. [9]. The experiments were carried out during temperature ramps of 10°C/min between 500 and 100°C at a GHSV of 33,400 h⁻¹. Prior to the measurements, the samples were oxidized in 10% O₂ (Ar-balance) by 500°C for 30 min. During the experiments, the gas composition was 500 ppm NO, 500 ppm NH₃, 1000 ppm H₂, 10% O₂ and 5% H₂O (Ar-balance). The outlet gas composition was analyzed using a gas phase FTIR (MKS 2000) analyzer.

The concentration of acidic sites in the catalyst was measured with temperature programmed desorption (TPD) of NH₃. The catalyst was pretreated in O₂ and then H₂ at 550°C to remove carbonaceous impurities and reduce the silver surface. Thereafter, the temperature was reduced to 100°C and 1000 ppm NH₃ (Ar-balance) was allowed to chemisorb onto the catalyst (GHSV 9,500 h⁻¹). After NH₃-saturation of the catalyst, the system was flushed with argon to remove excess NH₃. Subsequently, the temperature was linearly increased to 550°C by 20°C/min and desorbed NH₃ was measured using the FTIR equipment described above.

It should be noted that, in the development of their kinetic model, Tamm et al. [7] used a pre-sulfated catalyst with higher silver loading (6 wt%) compared to the present work. Exposure of the Ag/Al₂O₃-catalyst to a sulfur-containing gas affects the structural stabilization of the catalyst but also causes loss of

activity due to sulfate formation [10]. In the present work, we choose to focus on the behavior of a Ag/Al₂O₃ catalyst with 2 wt% Ag-loading, which has previously been shown to be a suitable loading for H₂-assisted urea-SCR over Ag/Al₂O₃ [2].

2.2. Numerical methods

The uniformity of the NH₃ dose at the catalyst inlet was obtained from CFD simulations using the computational setup reported by Ström et al. [8] and the urea decomposition model proposed by Lundström et al. [11]. The complete set of equations and boundary conditions is given by Lundström and Ström elsewhere [5]. The micro-kinetic model of Tamm et al. [7] was used in the numerical evaluations of the NO reduction and NH₃ slip for the different monolith channels. Each channel is modeled as five continuously stirred tank reactors in series and a film model describes the mass transfer from the gas bulk to the catalyst surface. There are two different sites (denoted S1 and S2) that bind reactants with different adsorption energies. In a somewhat simplified interpretation of the meaning of these two types of sites, the strong adsorption site S1 could be thought to represent silver and the weaker adsorption site S2 would then represent alumina. The kinetic model contains eight reactions, which are listed in Table 1.

Table 1. Reactions included in the model

Reaction number	Reaction
r1, r2	$\text{NH}_3 + \text{S1} \leftrightarrow \text{NH}_3\text{-S1}$
r3, r4	$\text{NH}_3 + \text{S2} \leftrightarrow \text{NH}_3\text{-S2}$
r5	$2\text{NH}_3\text{-S1} + 1.5 \text{O}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O} + 2 \text{S1}$
r6	$2 \text{NH}_3\text{-S1} + 2.5 \text{O}_2 \rightarrow 2 \text{NO} + 3 \text{H}_2\text{O} + 2 \text{S1}$
r7	$2 \text{NO} + 2 \text{NH}_3\text{-S1} + 2.5 \text{O}_2 + 4 \text{H}_2 \rightarrow 2 \text{N}_2 + 7 \text{H}_2\text{O} + 2 \text{S1}$
r8	$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$

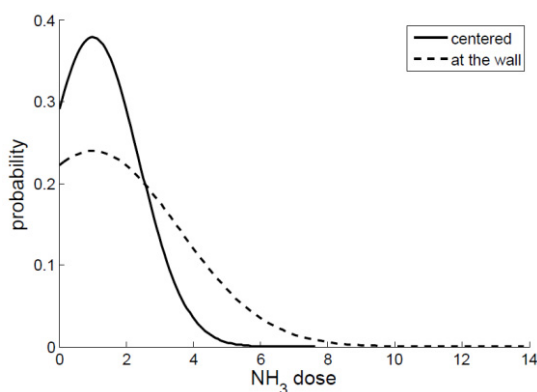


Fig. 1. NH₃ dose probability distribution functions for a urea-spray located at the exhaust gas pipe wall or centered inside the pipe. An NH₃ dose equal to unity corresponds to the average NH₃ dose at the catalyst inlet.

3. Results and discussion

Lundström and Ström [5] quantified the degree of non-uniformity in the NH_3 dose to each individual catalyst channel in a urea-SCR system with the spray situated either in the center of the exhaust pipe or at the pipe wall. In the present work, contour plots of the NH_3 dose over the catalyst inlet from that work were analyzed by deriving the corresponding Gaussian probability distribution functions. The result is shown in Fig 1, where the probability that a catalyst channel receives a certain NH_3 dose is plotted versus the range of doses seen in the raw data. The NH_3 dose is here normalized by the average dose, so that an NH_3 dose of two indicates that the channel in question receives twice the amount of NH_3 that the average channel does. It is clear that the arrangement with the spray situated in the center of the exhaust pipe produces more even NH_3 inlet conditions to the catalyst than does the arrangement with the spray originating from the exhaust pipe wall, however both arrangements produce a large spread in the dose.

Fig 2 shows the NH_3 -TPD and the model calculations for the same experiment. Here, the concentrations of active sites have been fitted to obtain the best possible agreement between the experimental data and the model prediction. The concentration of S1 sites is $0.11 \text{ mol/kg}_{\text{cat}}$ and that of S2 sites is $0.28 \text{ mol/kg}_{\text{cat}}$, which is 2.7 and 1.4 times larger, respectively, than the concentrations reported by Tamm et al. [7] for their pre-sulfated catalyst. As expected, the pre-sulfated catalyst is less active, and the largest difference is observed for the “silver” sites (S1). It can therefore be concluded that the present work investigates the effects of urea-spray non-uniformities in an otherwise optimal catalyst system, in accordance with the intention of the study.

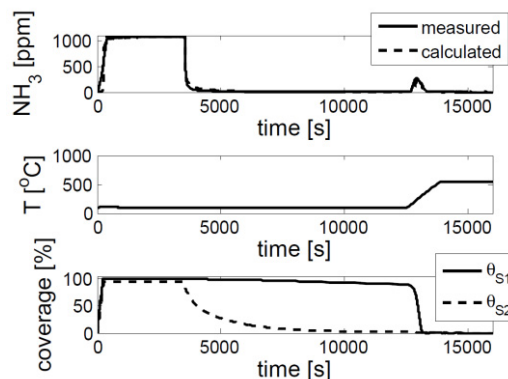


Fig. 2. Results from the NH_3 -TPD: NH_3 signal (top), catalyst temperature (middle) and coverages of the active sites (bottom).

The kinetic model is used to calculate the steady-state NO conversion at a range of different temperatures to allow for a comparison with the flow reactor experiments. It is found that the agreement is very good for low temperatures, but that the model predicts significantly less NO conversion at the higher temperatures. The experimental results of the present work agree with the observations of Shimizu and Satsuma [2], who obtained over 90% NO conversion in the interval $300\text{--}500^\circ\text{C}$ in both $\text{H}_2\text{-NH}_3\text{-SCR}$ and $\text{H}_2\text{-urea-SCR}$ over $\text{Ag/Al}_2\text{O}_3$. The discrepancies observed in Fig 3 could possibly be due to that the kinetic model has been tuned to reproduce the behavior of a pre-sulfated catalyst. However, temperatures above 400°C are not representative of typical lean exhaust gas temperatures. As the quantification of the effects of NH_3 non-uniformity on the catalyst performance are to be carried out at 300°C , the model is deemed appropriate for the purpose of the current work.

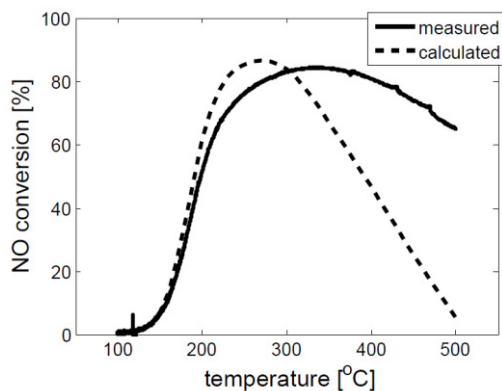


Fig. 3. NO conversion as a function of temperature, as measured in the flow reactor experiments and as calculated with the model.

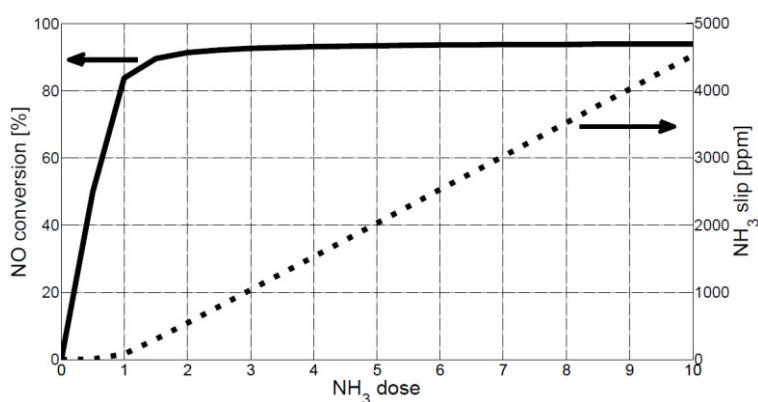


Fig. 4. NO conversion (left) and NH_3 slip (right) for an individual catalyst channel as a function of the incoming NH_3 dose at 300°C.

Finally, the NO conversion and the NH_3 slip at 300°C are calculated with the kinetic model using the input parameters of the present catalyst. In Fig 4, the result is plotted as a function of the NH_3 dose that reaches the catalyst channel inlet. It is assumed that an average dose implies dosing 500 ppm NH_3 (and 1000 ppm H_2) to reduce the 500 ppm NO, which is consistent with the fact that the global stoichiometry between $\text{NO}:\text{NH}_3:\text{H}_2$ is 1:1:2 during the SCR reactions [1]. The NO conversion increases rapidly with increasing the dose from zero to unity, and then increases another 10 percent units up to a dose of approximately four times the average, after which no further improvement in NO conversion is observed for increasing NH_3 dosing. At the same time, the NH_3 slip increases almost linearly after an NH_3 dose equal to unity and reaches 4500 ppm for a channel that receives 10 times the average NH_3 dose. For doses lower than unity, the NH_3 slip is insignificant.

4. Conclusions

In the current work, a kinetic model for H_2 -assisted NH_3 -SCR over $\text{Ag}/\text{Al}_2\text{O}_3$ monolith catalysts is adapted to the experimental results for an optimally Ag-loaded catalyst. The non-uniformity in the NH_3

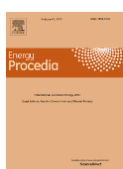
dose to individual catalyst channels during operation of a urea-SCR system is investigated and NH₃ dose probability distribution functions are derived. Channels that receive significantly less than the stoichiometric dose of NH₃ exhibit low NO conversion, whereas there is no discernable increase in the NO conversion above an NH₃ dose four times the average. Significant NH₃ slip is present for channels receiving large doses. These results highlight the importance of the interaction between the design of the NH₃ dosing system and the performance of the catalytic system.

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Biography

Linda Ström is a PhD student at the Competence Centre for Catalysis. The aim of her research is to gain a deeper understanding of the catalytically active sites and the reaction mechanisms, including the promotion of H₂, during lean NO_x reduction over Ag/Al₂O₃ catalysts.