

New Insights into Reaction Mechanism of Selective Catalytic Ammonia Oxidation Technology for Diesel Aftertreatment Applications

2011-01-1314

Published
04/12/2011Krishna Kamasamudram
Cummins IncAleksey Yezerets
Cummins Inc.Xu chen and Neal Currier
Cummins IncMario Castagnola and Hai-Ying Chen
Johnson Matthey Inc

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doi: [10.4271/2011-01-1314](https://doi.org/10.4271/2011-01-1314)

ABSTRACT

Mitigation of ammonia slip from SCR system is critical to meeting the evolving NH_3 emission standards, while achieving maximum NO_x conversion efficiency. Ammonia slip catalysts (ASC) are expected to balance high activity, required to oxidize ammonia across a broad range of operating conditions, with high selectivity of converting NH_3 to N_2 , thus avoiding such undesirable byproducts as NO_x or N_2O . In this work, new insights into the behavior of an advanced ammonia slip catalyst have been developed by using accelerated progressive catalyst aging as a tool for catalyst property interrogation. The overall behavior was deconstructed to several underlying functions, and referenced to an active but non-selective NH_3 oxidation function of a diesel oxidation catalyst (DOC) and to the highly selective but minimally active NH_3 oxidation function of an SCR catalyst. In particular, it was shown that different functions of the ASC degrade independently, resulting in minimal changes to NH_3 conversion with substantial changes to product selectivity.

1. INTRODUCTION

Diesel and lean-burn engines are gaining in popularity, worldwide, due to their superior combination of fuel efficiency and power density, compared to other conventional sources of on-road propulsion. However, their market penetration in the US

and elsewhere depends on their ability to meet the increasingly stringent environmental regulations, while delivering the expected fuel economy benefits. The unprecedentedly stringent US EPA 2010 emission regulations led to the development of aftertreatment systems combining Diesel Particulate Filters (DPF) with highly stable zeolite-based Selective Catalytic Reduction (SCR) catalysts, capable of withstanding active DPF regeneration conditions [1]. Applications of such systems enabled improvements in the overall system fuel economy, while drastically reducing NO_x emissions when compared to the previous tier of regulations [2].

NH_3 slip represents one of the potential concerns with the high efficiency urea-SCR technology. It can occur under different conditions, as illustrated by two example scenarios described below [3,4]. In order to utilize an SCR catalyst of current generation with maximum efficiency, significant amount of NH_3 has to be stored on its surface. This may lead to NH_3 release during high-temperature excursions. Also, over-stoichiometric amounts of NH_3 may need to be injected to maximize NO_x conversion at some conditions, thus increasing the chances for NH_3 slip. Although regulations for NH_3 emissions from SCR systems are only evolving in the US, several manufacturers considered proactive measures to eliminate even small amounts of NH_3 slip from 2010 aftertreatment systems [2,3,4]. One such approach is based on

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integrating an ammonia slip catalyst (ASC) downstream of an SCR catalyst [2, 3].

Ammonia can be very effectively converted by oxidation catalysts containing even small amounts of Pt, however with very poor selectivity towards N_2 . For example, Pt/ Al_2O_3 type catalysts have been shown to produce large quantities of NOx and N_2O from NH_3 [3, 5] and are therefore considered not germane for automotive applications. On the other hand, an effective ASC should possess an activity comparable to such oxidation catalysts, with high selectivity towards N_2 . Emphasizing the challenge, a successful ASC should maintain high activity and selectivity across a very broad range of temperatures, flow rates, and gas compositions; representing wide range of real life duty cycles. It should further be sufficiently robust against various aging factors, in particular exposure to high temperatures under diesel exhaust conditions. While catalytic materials satisfying these challenging requirements are rapidly evolving, little has been published about the underlying mechanisms of their operation and deactivation.

In this article the overall operation of an advanced research grade ASC formulation was deconstructed to its key underlying individual functions, and referenced against DOC and SCR catalysts. The changes in the catalyst functions with progressive hydrothermal aging provided additional insights into ammonia oxidation performance. Excessively high temperatures, beyond those found in the typical applications, have been used to accelerate the aging in order to emphasize the target effects. The findings reported in this work pave the way for more capable ASC materials, enabling high efficiency of NOx conversion with minimal NH_3 slip.

2. EXPERIMENTAL DETAILS

2.1 Catalyst materials

Research-type formulation of ammonia slip catalyst for this work was provided by Johnson Matthey. Its composition included a platinum group metal (PGM)-based oxidation component and zeolite-based ammonia storage component. The catalyst was supported on 400 cpsi cordierite substrate. An Fe-zeolite sample described earlier [6] and a DOC sample, similar to the one used in 2007 aftertreatment applications, were used for comparison.

Cylindrical samples of 1" diameter and 2" length were used for the laboratory reactor performance evaluation of ASC and DOC. Prior to testing catalyst samples were treated in a gas stream containing 10% O_2 , 8% CO_2 , 7% H_2O with the balance of N_2 for 2 hrs at 600°C ("degreened"), or up to 100 hrs at 650°C ("aged"). Such aging temperature, unlikely to be experienced by ASC in real-life applications, was chosen in order to exacerbate any changes in catalyst behavior. The

reference Fe-zeolite catalyst of 1" diameter and 3" length was evaluated under varied experimental conditions, as described in the text.

2.2 Experimental setup and conditions

The experimental data in this work were collected using a bench-flow reactor system with rapid gas transient capabilities. Gas composition analysis was performed using high-speed model of the MKS MultiGas 2030 FTIR. Concentrations of NH_3 , N_2O and NOx were measured, while N_2 was estimated from the mass balance of the measured species. All gas lines in the system were temperature-controlled above 190°C, to minimize adsorption of the reactant and product species. The reactor tube was made of fused silica to avoid parasitic oxidation of NH_3 at high temperatures. Further details of the experimental setup were previously reported elsewhere [6].

Synthetic exhaust gas was supplied to the catalyst sample at a total flow rate of 43 slpm, resulting in the gas hourly space velocity of approximately 100,000 h^{-1} . Unless specifically noted in the text, the base gas feed for all the experiments included the following molar concentrations of the species inherent to diesel exhaust: 10% O_2 , 8% CO_2 , 7% H_2O with the balance of N_2 . When required by the experimental protocol, ≈ 55 ppm of NOx and ≈ 100 ppm of NH_3 were added to the above gas feed.

2.3 Catalyst functional evaluation methodology

The experimental protocol developed in this study includes three segments (labeled as steps 1, 2 and 3), as schematically depicted in [Figure 1](#). Basic components of exhaust gas (10 vol.% O_2 , 8 vol.% CO_2 , 7 vol.% H_2O , balance of N_2) were present during the entire experiment, while NH_3 and NOx and were switched on and off, as shown in [Figure 1a](#). Duration of individual steps was varied depending on the time required to achieve steady-state. The methodology used yielded information about a number of useful catalyst functions. A few of such functions probed by different steps are indicated below:

Step 1. NH_3 oxidation, product selectivity and ammonia storage functions (NH_3 storage estimation is further explained in Section 3.1.5).

Step 2. Oxidation functionality of a PGM component.

Step 3. SCR function and the resulting changes in NH_3 oxidation product selectivity.

The protocol above was employed at different temperatures and at different stages of progressive hydrothermal aging, yielding function-specific information about catalyst performance and degradation.

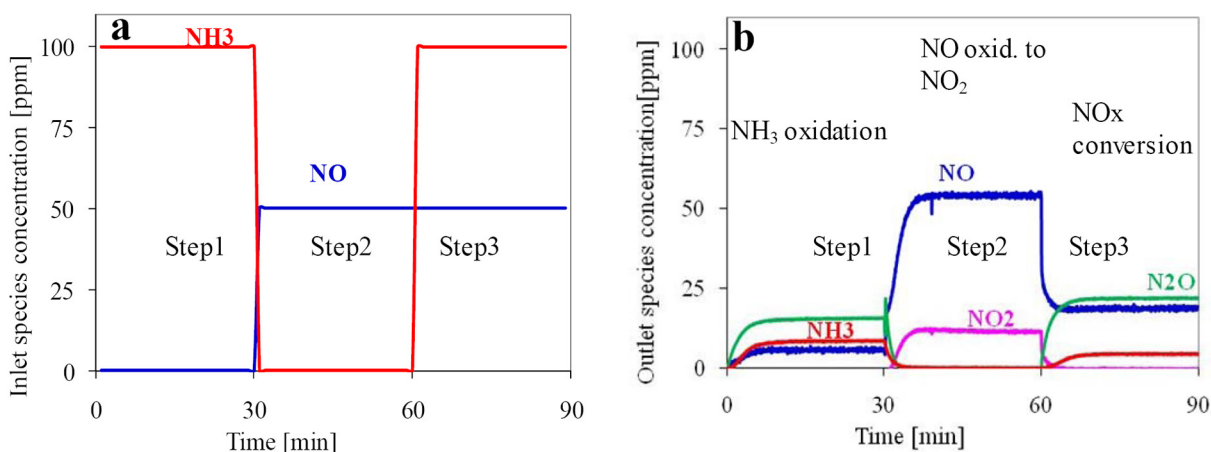


Figure 1. Experimental methodology used for ammonia oxidation catalyst functional evaluation. a) inlet NH_3 and NO , and b) outlet product concentrations. Reaction conditions: $\text{NH}_3 \approx 100 \text{ ppm}$, $\text{NO} \approx 55 \text{ ppm}$, $\text{SV} = 100 \text{ kh}^{-1}$.

3. RESULTS AND DISCUSSION

3.1 COMPARISON OF ASC FUNCTIONALITY TO THE REFERENCE DOC AND SCR CATALYSTS

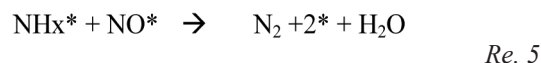
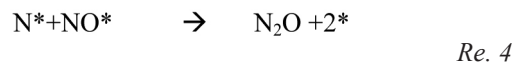
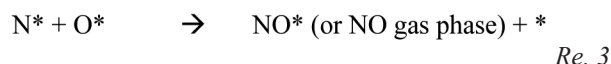
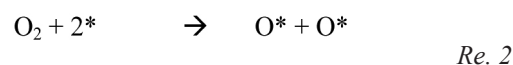
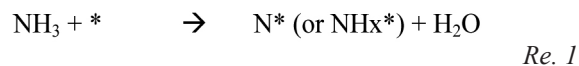
3.1.1 NH_3 conversion

Steady-state NH_3 conversions and product selectivity over DOC, SCR and ASC are plotted in Figure 2. The reference samples, DOC and SCR, were not designed for NH_3 oxidation and are used here for illustration purposes only. As expected, DOC showed the best ammonia conversion (Figure 2a), attaining 100% efficiency substantially below 250°C . On the other hand, Fe-zeolite catalyst showed poor NH_3 oxidation, despite being tested at a lower space velocity. The ASC, having a PGM loading substantially lower than a DOC, exhibited only a small decrease in NH_3 oxidation performance compared to the DOC.

3.1.2 Product selectivity

Although N_2 represents the most thermodynamically favorable product of NH_3 oxidation, the pathways leading to N_2O or NO are thermodynamically feasible as well, as schematically depicted in Figure 3. As a result, the overall selectivity is entirely dependent on the catalyst properties and reaction conditions. Indeed, all three species - N_2 , N_2O , and NOx - can be found among the products of NH_3 oxidation over the catalysts studied in this work, albeit with drastically different selectivity (Figures 2b, c, d). On the precious metal-containing

DOC and ASC, under the reactions conditions used, NH_3 and O_2 decompose on the metal surface leading to several adsorbed intermediate species like NH_x ($x=0-3$), O and NO which further react with each other via the following plausible simplified reaction routes [7,8,9,10], whose rates strongly depend on the reaction temperature, feed gas composition, and catalyst properties.



On the other hand, ammonia oxidation on the SCR catalyst led almost exclusively to N_2 under the conditions studied, even at high NH_3 conversion.

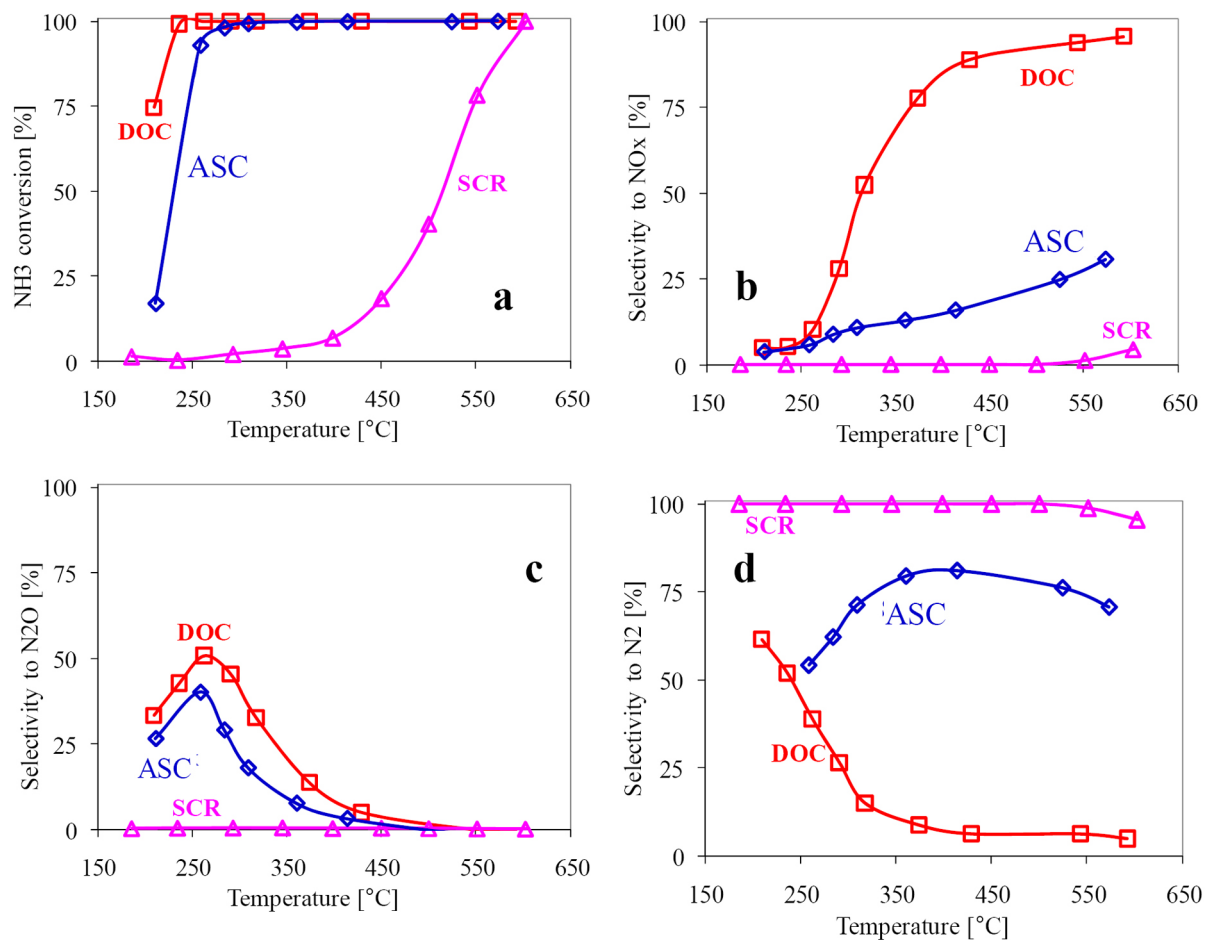


Figure 2. Steady-state NH₃ conversion and product selectivity over the DOC, ASC, and SCR catalysts. Reaction conditions: For DOC and ASC, NH₃ ≈ 100 ppm, SV = 100 kh⁻¹. For SCR catalyst NH₃ ≈ 200 ppm, SV = 40 kh⁻¹.

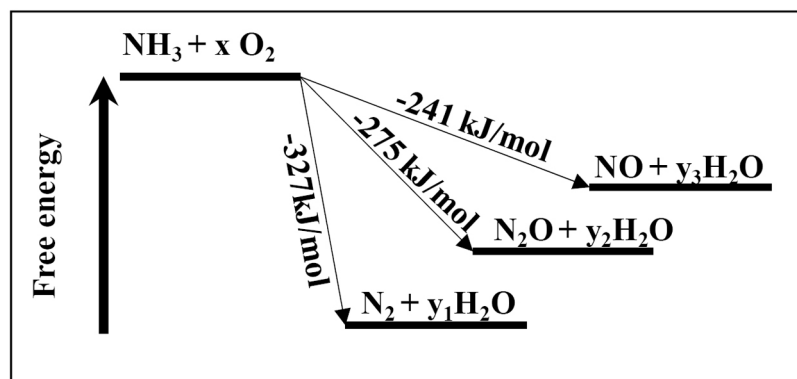


Figure 3. Free energy for ammonia oxidation to different products.

3.1.3 Selectivity to NO_x

Platinum group (PGM) metals are extensively used in chemical industry to oxidize NH₃ to NO_x as a part of nitric acid production process [7,8,9]. Therefore, it was not surprising to find NO_x among the products of ammonia oxidation over the PGM-containing catalysts in this study. The DOC, which

featured the highest PGM content, showed significantly higher selectivity to NO_x than the low-PGM ASC and the PGM-free SCR catalyst (Figure 2b). Also, when compared at the same NH₃ conversion level, ASC showed much lower selectivity to NO_x than the DOC.