

N₂O Formation and Mitigation in Diesel Aftertreatment Systems

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ABSTRACT

The high global warming potential of nitrous oxide (N₂O) led to its recent inclusion in the list of regulated pollutants under the emerging greenhouse gas regulations. While N₂O can be present in small quantities among the combustion products, it can also be generated as a minor byproduct in various types of aftertreatment systems. In this work, a systematic review of sources of N₂O is presented, along with the potential mechanisms of formation in a typical selective catalytic reduction based diesel exhaust aftertreatment system. It is demonstrated that diesel oxidation catalysts (DOC), selective catalytic reduction (SCR) catalyst, and ammonia slip catalyst (ASC) can all potentially contribute to N₂O formation, depending on the catalyst material and exhaust gas conditions, as well as aftertreatment operation strategies. Furthermore, catalysts used in SCR aftertreatment system are also shown to decompose and/or reduce N₂O to N₂ under select conditions. However, the temperature windows of N₂O formation and decomposition/reduction do not overlap. This requires that N₂O control be focused on reducing its formation by means of optimizing catalyst formulation, system architecture, and operation strategies.

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1. INTRODUCTION

Nitrous oxide (N₂O) is a common minor byproduct of the combustion of various fossil fuels, and of various processes in exhaust aftertreatment systems [1, 2, 3]. N₂O has not been regulated until recently, since it is not considered harmful to human health directly and does not contribute to smog formation; however with a global warming potential (GWP) of ~300 times that of CO₂, it was included in the recent Greenhouse Gas (GHG) regulations [3]. Recognizing that N₂O emissions are not harmful by themselves, but need to be considered in the context of GHG, the regulation established a threshold limit, beyond which N₂O starts counting as CO₂ equivalents, reducing the allowed CO₂ emissions.

Until the recent advent of diesel aftertreatment, the main sources of N₂O in transportation included the byproducts of combustion itself and of NO_x reduction on three-way catalysts (TWC). A good understanding of the nitrous oxide formation mechanism on TWCs has been developed over several decades of their commercial application, enabling progressive reduction in the N₂O levels. In particular, for these applications N₂O is predominantly formed during cold-

start operation. New catalyst materials and operation strategies have evolved over time, minimizing N₂O production [1, 2, 3]. In contrast, N₂O from SCR systems was found to form during various parts of the emissions cycle, due to contribution from several catalytic components in these complex systems.

In this paper a systematic review of various sources of N₂O and its potential formation mechanisms in a typical diesel, SCR aftertreatment system is presented. This system includes a DOC, SCR and ASC. Among these three types of catalytic elements, the chemical processes responsible for potential N₂O formation on DOCs is relatively well understood, being a byproduct of lean NO_x reduction [4]. On the other hand, understanding of N₂O formation on zeolite-based SCR catalysts is only evolving, leading us to focus on it in this study. In addition, the catalytic behaviors of ASC, being a hybrid between DOC and SCR functionalities, are particularly complex and will be also addressed here. Finally, Fe-zeolite and Cu-zeolite, being common to both SCR and ASC catalysts, are known to be capable of decomposing and reducing N₂O under certain conditions, leading us to evaluate

Table 1. List of catalyst samples evaluated for N_2O formation and mitigation.

Catalyst Technology	Catalysts	Comments
DOC	DOC-1	These three research-grade formulations were developed for SCR applications and differed in their composition
	DOC-2	
	DOC-3	
SCR	Cu-zeolite-1	~0.6 times of reference Cu loading
	Cu-zeolite-2	Reference Cu loading
	Cu-zeolite-3	~3 times of reference Cu loading
	Fe-zeolite	Research formulation
	Vanadium-based (V-based)	Commercial formulation
ASC	ASC-1	~0.2 times of reference Pt loading
	ASC-2	Reference Pt loading
	ASC-3	~ 2 times of reference Pt loading

their potential for mitigating N_2O produced by the combustion or by the upstream catalytic elements.

2. EXPERIMENTAL DETAILS

2.1. CATALYST MATERIALS

All the DOC, SCR, and ASC catalysts used in this work were kindly provided by Johnson Matthey or purchased from commercial sources. The list of catalyst formulations, used in this study, is presented in Table 1. All of these catalysts were washcoated on 300 or 400 cpsi cordierite substrates. Cylindrical samples of 1" diameter and 1", 2" or 3" length were used for the laboratory reactor performance evaluation. Prior to the testing, all the 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 h at or above 500°C ("degreened"), or up to 100 h at or above 500°C ("aged"), as noted in the text.

2.2. EVALUATION SETUP AND PERFORMANCE CONDITIONS

The experimental data presented in this work were collected using a bench-flow reactor system, described in detail elsewhere [5, 6, 7, 8]. Synthetic exhaust gas was supplied to the catalyst sample at volumetric flow adjusted to the catalyst core size, maintaining the gas hourly space velocity of approximately 20,000 to 100,000 h^{-1} , as reported for each experiment. The base gas feed for all the experiments included the following molar concentrations of diesel exhaust species: 10% O_2 , 8% CO_2 , 7% H_2O with the balance of N_2 . Specific pretreatment and evaluation conditions are given with the respective figure descriptions. Gas composition analysis was performed using the high-speed model of the MKS MultiGas 2030 FTIR. 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 HC and NH_3 at high temperatures. Unless otherwise indicated, conversion and selectivity values are derived from steady-state measurements.

3. RESULTS AND DISCUSSION

3.1. N_2O FORMATION OVER DIESEL OXIDATION CATALYSTS (DOC)

As illustrated by Figure 1, N_2O is formed on DOCs primarily as a by-product of NO_x reduction by hydrocarbons, the process known as lean NO_x catalysis or hydrocarbon selective catalytic reduction (HC-SCR) [4]. The formation of N_2O occurs in a narrow temperature window, with its peak typically coinciding with high yet incomplete conversion of the reductant(s). At lower temperatures, the catalyst not yet activated the HC reductant, while at higher temperatures it loses its selectivity, due to predominant oxidation of reductant(s) by O_2 .

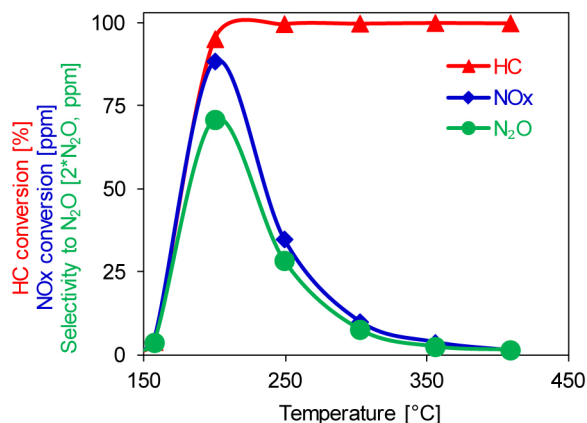


Figure 1. Reduction of NO_x by HC-SCR over DOC-1 under steady-state conditions. Reaction conditions: C_3H_6 = 400 ppm, NO = 200 ppm, SV = 60 h^{-1} .

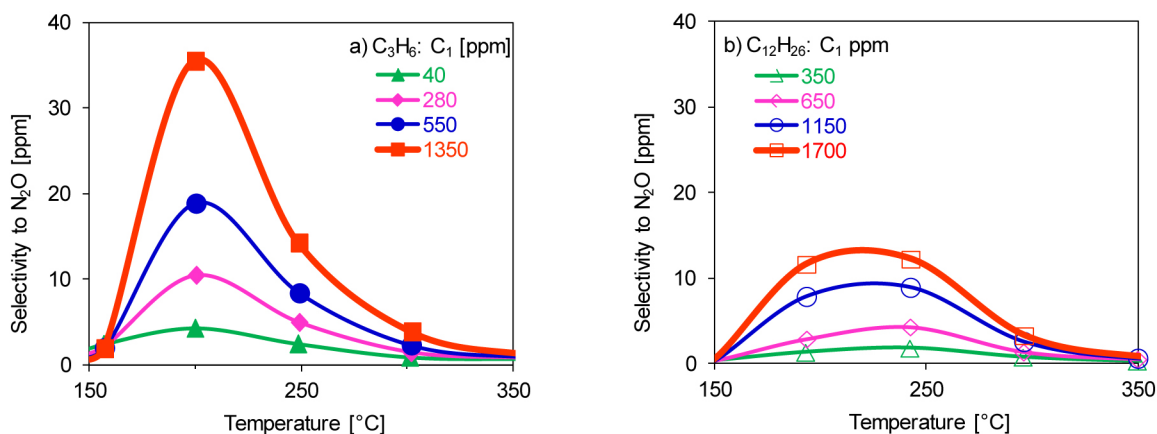


Figure 2. Selectivity to N_2O in reduction of NO_x by HC-SCR over DOC-1 under steady-state conditions. Reaction conditions: HC = as indicated, $NO = 200$ ppm, $SV = 60$ kh^{-1} .

Although the total NO_x conversion via lean NO_x catalysis is quite limited, N_2O rather than N_2 could be its major product, depending on the catalyst and conditions [4]. In fact, the example shown in Figure 1 was selected because it illustrates the most egregious case, with essentially all of the reduced NO_x being converted to N_2O .

The type and concentration of hydrocarbons are among the key parameters, affecting N_2O selectivity over DOCs. In Figure 2 we compare the N_2O selectivity over DOC-1 in response to different concentration of two model HC species - propylene representing the light and highly reactive alkenes and dodecane representing the less reactive long-chain alkanes. The former shows higher N_2O yields, and in both cases the yield increased with HC concentration.

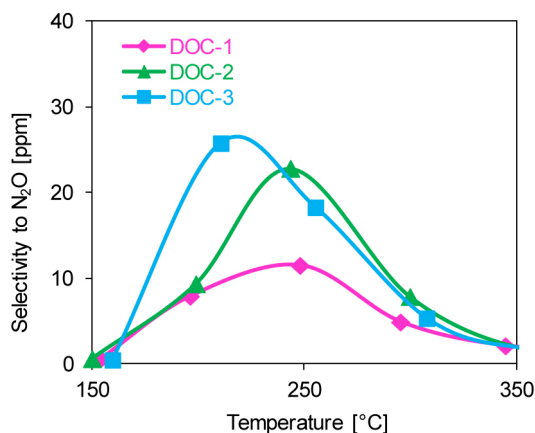


Figure 3. Selectivity to N_2O in reduction of NO_x by HC-SCR over DOCs as indicated under steady-state conditions. Reaction conditions: $C_3H_6 = 400$ ppm, $NO = 200$ ppm, $SV = 60$ kh^{-1} .

DOC formulation is another important parameter which can affect its N_2O production via HC-SCR. To illustrate this effect, in Figure 3 we compare three different DOC formulations, all of which were developed for SCR-type applications and therefore only differed to a limited degree with regards to their composition. N_2O production by these three DOCs varied substantially with regards to the N_2O quantities and their peak temperatures.

3.2. N_2O FORMATION ON SCR CATALYSTS

The bulk of this study was focused on understanding the N_2O -specific behavior of the SCR, because it carries out most of the NO_x conversion, and therefore a small selectivity to N_2O could translate into a significant yield of this species. It is well known that for three major types of SCR catalysts used commercially, namely Cu-zeolite, Fe-zeolite and V-based, N_2O is produced through the following two key mechanistic routes:

- i). Formation of ammonium-nitrate-like surface species (AN_s) and their subsequent decomposition [9], and
- ii). NH_3 oxidation with O_2 [6, 7, 9].

In this study we have addressed these two mechanisms separately, from the perspective of their response to such key catalyst and operating parameters as temperature, exhaust gas composition, catalyst formulation and hydrothermal aging.

We would like to point out, that reporting N_2O selectivity in percent for the NH_3 -SCR reaction presents an inherent challenge, associated with two separate sources of nitrogen atoms (NO_x and NH_3), which could both contribute to the formation of the N_2O . To avoid the ambiguities which may arise when choosing the basis for calculating the percent selectivity, we are reporting below the N_2O formation in the form of concentration in parts per million.

3.2.1. N_2O formation via ammonium nitrate (AN_3) route

Decomposition of AN_3 -like intermediate species, formed from the reaction between surface nitrates and NH_3 , is known to be a major route for N_2O formation under SCR conditions [9]. It is not surprising then that concentration of the key reactants for the ammonium nitrate formation NO_2 and NH_3 , have a major impact on the rate of N_2O production. In fact, Figure 4 illustrates the impact of NO_2 gas-phase concentration, while Figure 5 attests to the impact of NH_3 stored on the catalyst surface.

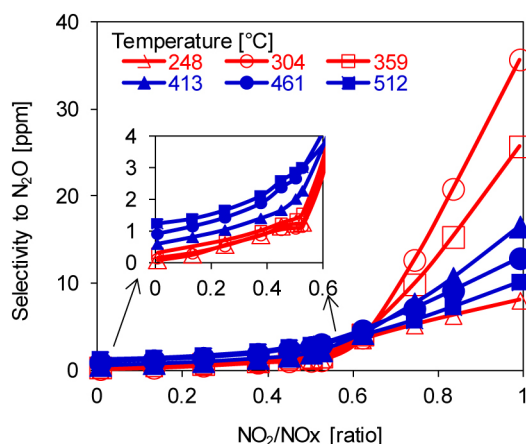


Figure 4. Steady state NH_3 -SCR selectivity to N_2O over Cu-zeolite-1. Reaction conditions: $NO_x = 200$ ppm, $NH_3 = 200$ ppm, $SV = 20$ kh^{-1} .

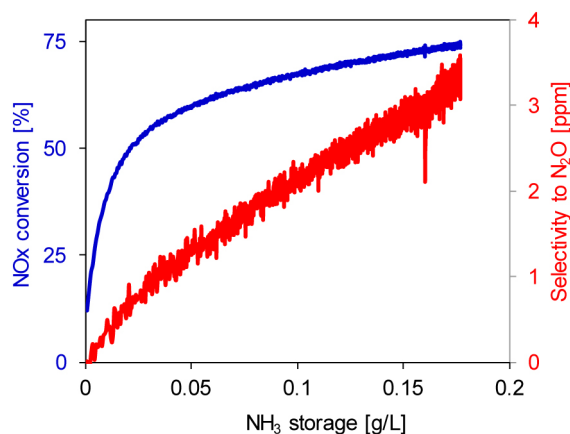


Figure 5. NH_3 storage dependent NO_x conversion and selectivity to N_2O in NH_3 -SCR over Cu-zeolite-1. Reaction conditions: $NO_x = 200$ ppm, $NO_2/NO_x = 0.75$, $NH_3 = 200$ ppm, Temperature = $250^\circ C$, $SV = 40$ kh^{-1} .

As shown in Figure 4, N_2O production changes little with the NO_2/NO_x ratios below ~ 0.5 across the range of temperatures studied in this work. This can be easily explained, based on the “fast” SCR reaction consuming the equimolar mixture of NO and NO_2 . As a result, the NO_x reactant present in deficit is typically consumed very rapidly along with the equivalent quantity of the other NO_x reactant. Thus, until NO_2/NO_x ratio exceeds the equimolar ratio, there would be little or no NO_2 available to contribute to the ammonium nitrate formation. On the other hand, at higher NO_2/NO_x , above the equimolar ratio, the amount of N_2O should grow rapidly, due to excess NO_2 beyond that required for the fast SCR reaction. This was indeed the case in the experiments reported in Figure 4

Figure 5 further illustrates the impact of NH_3 , the second reactant required for the surface formation of NH_4NO_3 , on N_2O production. In this experiment, the catalyst was first stabilized at the target temperature ($250^\circ C$) in the presence of 150 ppm NO_2 and 50 ppm NO ($NO_2/NO_x = 0.75$). Then NH_3 was introduced in the gas feed, and NO_x conversion was tracked with time, along with N_2O and NH_3 . Furthermore, the amount of NH_3 stored on the surface was derived from these data using nitrogen balance calculations, as reported in [6, 7]. It should be noted that NO_x conversion and N_2O selectivity did not increase in unison with the NH_3 build-up on the catalyst surface, since the former has a complex dependence on the ammonia coverage [6, 7], while the latter increased linearly. In other words, when one of the required reactants, NO_2 , was easily available due to high NO_2/NO_x ratio, the rate of N_2O formation via the ammonium nitrate route was limited by the availability of the second reactant NH_3 .

3.2.2. N_2O formation via NH_3 oxidation

When comparing the NH_3 oxidation activity and the N_2O selectivity for different SCR catalysts, representative of the key classes of commercial SCR materials, reported in Figure 6, it is clear that the connection between the two is not obvious. In fact, Cu-zeolite-2, being the most active among these catalysts with regards to NH_3 oxidation, had virtually no selectivity to N_2O in the NH_3 oxidation region (250 – $450^\circ C$). The Fe-zeolite catalyst, which was the least active for NH_3 oxidation also showed minimal N_2O selectivity. However, both the Cu-zeolite-3 and V-based catalysts had a significant selectivity to N_2O . These differences are not specifically tied to their ammonia oxidation activity, but are a complex relationship between that activity and other reactions governed by the chemistry of the various catalyst types and their specific formulation details. In later section, we will further explore one instance of catalyst chemistry on Fe-zeolite and specific aspect of the