

Brief Investigation of SCR High Temperature N₂O Production

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ABSTRACT

Nitrous Oxide (N₂O) is a greenhouse gas with a Global Warming Potential (GWP) of 298-310 [1,2] (298-310 times more potent than carbon dioxide (CO₂)). As a result, any aftertreatment system that generates N₂O must be well understood to be used effectively. Under low temperature conditions, N₂O can be produced by Selective Catalytic Reduction (SCR) catalysts. The chemistry is reasonably well understood with N₂O formed by the thermal decomposition of ammonium nitrate [3]. Ammonium nitrate and N₂O form in oxides of nitrogen (NO_x) gas mixtures that are high in nitrogen dioxide (NO₂) [4]. This mechanism occurs at a relatively low temperature of about 200°C, and can be controlled by maintaining the nitric oxide (NO)/NO₂ ratio above 1. However, N₂O has also been observed at relatively high temperatures, in the region of 500°C. The ammonium nitrate mechanism is unsatisfactory because ammonium nitrate is not stable above about 210°C, and yet N₂O formation can begin close to 480°C and increase above 500°C for some formulations.

The objective of this brief study was to collect data showing under what conditions high temperature N₂O is formed, and to provide evidence towards understanding the mechanism that leads to high temperature N₂O production.

CITATION: Bartley, G. and Sharp, C., "Brief Investigation of SCR High Temperature N₂O Production," *SAE Int. J. Engines* 5: doi:10.4271/2012-01-1082.

INTRODUCTION

SCR catalysis has been employed in the industrial sector for decades to reduce NO_x stack emissions from applications such as power plants. SCR typically uses ammonia (NH₃) as the reductant to reduce the NO_x to nitrogen (N₂). The most common SCR catalyst type used for a considerable time was composed of vanadium, tungsten and titania, and referred to here as a V/W/TiO₂ catalyst.

Stoichiometric gasoline mobile source NO_x emissions have been successfully converted to N₂ using three-way catalysts (TWC) since the 1970's [5,6]. In recent years, efforts to reduce NO_x emissions from sources that operate under lean, oxidizing conditions have proven more challenging. To address this challenge, industry explored several options, one of which is the application of SCR catalyst technology. The first catalysts investigated were of the industrial V/W/TiO₂ type, that led to today's advanced V/W/TiO₂ catalysts. New SCR catalyst technologies are also being developed, most notably copper-zeolite (Cu-Z) and iron-zeolite (Fe-Z) catalysts that are in use or being considered for use. The work described here used samples of Fe-Z and Cu-Z catalysts. The

actual formulations were proprietary to the suppliers, and not known to SwRI.

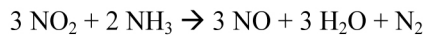
TECHNICAL APPROACH

All of the testing work was performed using Southwest Research Institute®'s (SwRI®) Universal Synthetic Gas Reactor® (USGR®), a model gas reactor that exposes catalyst core samples to simulated exhaust gas mixtures. The catalyst core samples used were 2.54 cm diameter by 2.54 cm length. The base temperature for testing was 500°C, and the space velocity was 60,000 hr⁻¹. At 500°C there was a significant amount of gas phase reaction with certain gas mixtures. Therefore, tests were performed with and without the catalysts to differentiate the catalyst effects. The basic gases used in the testing were NH₃, NO, NO₂, O₂ with balance N₂. In all cases, NO₂/NO did not exceed 0.25, so a significant portion of the SCR reactions were controlled by Standard SCR reaction rates, leading to only moderate activity at lower temperatures. There was no water in any of the tests, and it is recognized that water may have a significant effect on the reactions seen. Actual gas mixtures and conditions for each test type are given in the results and discussion section.

RESULTS AND DISCUSSION

Gas Phase / Reactor

The first series of tests were performed without a catalyst so that the gas phase and reactor surface reactions could be observed. The results are given in [Table 1](#). NO-only shows a small amount of NO₂ impurity in the NO supply, which is common. NO₂-only resulted in a small amount of conversion to NO. This may be due to the thermodynamic equilibrium being in favor of NO over NO₂ at 500°C. NH₃-only exhibited no reactions. When NH₃ and NO were mixed together, there was no apparent reaction, but about 5 ppm of N₂O was observed. Adding 10% O₂ slightly decreased the NH₃ and increased the NO₂, and the N₂O went up to 6 ppm. When NH₃ and NO₂ were mixed together, a significant amount of the NO₂ was converted to NO, some of the NH₃ was reacted, and N₂O was produced at about 6 ppm. Adding O₂ had very little effect. Hence the presence of NH₃ enhanced the reduction of NO₂ to NO, possibly by a reaction like that given as [Equation 1](#)[7].



Equation 1

What may be concluded from these gas phase tests is that N₂O formation does occur at 500°C, even without a catalyst. Furthermore, NH₃ is required to make N₂O, along with an oxidizer that may be NO or NO₂ or O₂.

Fe-Z

In a second series of tests, the Fe-Z catalyst core was installed in the reactor. The catalyst core was preconditioned at 380°C for 4 hours to reach its peak NH₃ storage capacity (as determined in other work). Similar tests were performed as before, and the results are given in [Table 2](#). The effects of the catalyst were very apparent. In all tests with NH₃ in the feedgas, all of the NH₃ was reacted. The SCR reaction was evidenced by a substantial decrease in NO_x. It appears, at this temperature, that some of the NH₃ was being oxidized to NO_x, resulting in full consumption of NH₃, but not NO_x. The Fe-Z catalyst was active for about 39 percent oxidation of NO to NO₂ at 500°C. When NH₃ and NO₂ were both present, the N₂O formation was about 7 ppm. The addition of O₂ only marginally increased the N₂O, indicating that NO₂ is a stronger oxidizer than O₂ under these test conditions. NO was able to produce about 2 ppm N₂O in the presence of NH₃ and O₂, but not in the absence of the O₂, so it is likely that some of the NO was oxidized to NO₂, which then reacted with the NH₃ to form some N₂O. Since NO and NH₃ formed N₂O in the absence of a catalyst, the catalyst may have prevented the formation of N₂O by favoring the SCR reaction.

Cu-Z

A Cu-Z catalyst that had previously been conditioned at 775°C for 16 hours was installed in the reactor. This sample condition was chosen for its high NH₃ storage capacity and high SCR activity. In these tests, a NO_x mixture was used

TABLE 1. NO/NO₂/NH₃/O₂ Tests Results with no Catalyst

Feedgas = 300 ppm NH ₃ , 300 ppm NO, 300ppm NO ₂ , 10% O ₂ , balance N ₂					
Gas Mix, ppm	NH ₃	NO ₂	NO	(NO _x)	N ₂ O
NO only	0	7	293	300	1.25
NO ₂ only	0	280	20	300	0
NH ₃ only	300	1	1	2	0.40
NO/NH ₃	298	1	302	303	4.93
NO ₂ /NH ₃	238	193	119	311	6.01
NO/NH ₃ /O ₂	295	5	316	321	5.94
NO ₂ /NH ₃ /O ₂	241	206	124	330	6.18

TABLE 2. NO/NO₂/NH₃/O₂ Tests Results with Fe-Z Catalyst

Feedgas = 300 ppm NH ₃ , 300 ppm NO, 300ppm NO ₂ , 10% O ₂ , balance N ₂					
Gas Mix, ppm	NH ₃	NO ₂	NO	(NO _x)	N ₂ O
NO only	0	7	302	309	0.14
NO/O ₂	0	120	188	308	0.29
NO/NH ₃	0	0	80	80	0.15
NO ₂ /NH ₃	0.7	40	92	131	6.70
NO/NH ₃ /O ₂	0	26	69	95	1.85
NO ₂ /NH ₃ /O ₂	0.4	59	86	145	7.37

