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Investigating the Effect of NO Versus NO_2 on the Performance of a Model NO_X Storage/Reduction Catalyst

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Abstract The effects of using NO or NO_2 as the NO_X source on the performance of a NO_X storage/reduction catalyst were investigated from 200 to 500 °C. The evaluation included comparison with constant cycling times and trapping the same amount of NO_X during the lean phase. With NO_2 as the NO_X source, better trapping and reduction performance was attained in comparison to NO, at all operating temperatures except 300 °C. This exception, under the conditions tested, was likely due to high NO oxidation activity and rapid trapping of NO_2, although it is expected that extending the trapping time would lead to consistent differences. Several reasons for the observed improvements at 200, 400 and 500 °C with NO_2 relative to NO are discussed. One that can explain the data, for both trapping and release improvement, is treating the monolith as an integral reactor. With NO_2, more NO_X is trapped at the very inlet of the catalyst, whereas with NO, the maximum in trapping during cycling occurs slightly downstream. Thus more of the catalyst can be used for trapping with NO_2 as the NO_X source. The decreased release during catalyst regeneration is similarly explained; with more being released at the very inlet, there is more residence time and therefore contact with downstream Pt sites, but more importantly more interaction between reductant and stored NO_X. NH_3 and N_2O measurements support this conclusion.

Keywords NO_X reduction · NO_X storage · Diesel emissions · Monolith reactor

1 Introduction

Concern over fluctuating fuel prices and depleting fuel reserves has led to increased interest in more fuel-efficient engines, such as lean-burn gasoline and diesel engines. However, the excess oxygen present in lean-burn engine exhaust significantly decreases the reduction of NO_X to N_2 over today's three way catalytic converter (TWC), which was designed to operate efficiently in stoichiometric-burn, near-zero oxygen, engine exhaust. An alternative, emerging catalyst technology for NO_X clean-up from lean-burn engine exhaust is NO_X storage and reduction (NSR). NSR catalysts are typically composed of a high surface area substrate such as γ-alumina, alkali and alkaline metal earth components that trap NO_X in the form of nitrites and nitrates, and precious metals such as Pt, Pd, and Rh for the redox reactions [1–4]. This technology operates in two modes: lean and rich. In the lean mode, which is where the engine normally operates, NO is oxidized to NO_2 over precious metal sites and the NO and/or NO_2 is then stored on the trapping material as a nitrate and/or nitrite [4–8]. When some portion of these trapping materials becomes saturated, the engine exhaust is switched to a reductant-rich mode where reductants such as H_2, CO, and HC are introduced to induce the reduction of the stored NO_X to N_2 [9–11].

Although the trends and mechanisms of NO_X storage, release, and reduction have been investigated [12–15], due to the complexity of the catalyst, process and their sensitivity to experimental conditions, there is still debate regarding the mechanisms and the potential reactions involved in the multiple catalytic steps [15]. However, there is consensus in the literature that improved NO oxidation to NO_2 results in improved NSR catalyst performance. Previous work [16] has demonstrated that

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over a wide range of operating temperatures, NO can not be adsorbed over barium aluminates and barium stannate, even in the presence of O_2, whereas NO_2 is readily absorbed. In a study that investigated the storage of NO and NO_2 over a Pt-containing commercial NSR catalyst [17], no storage occurred when NO was used as the NO_X source below 150 °C, while significant storage was observed when NO_2 was used. However, at 380 °C with a $Pt/Rh/Ba/Al_2O_3$ sample [18], no significant difference was observed in storage capacity when either NO or NO_2 was used. This improvement with NO at higher temperature is likely attributed to one, or all of, three reasons. First, NO oxidation activity in this higher temperature range is significant [19–21]. Second, NO_2 is known to inhibit the NO oxidation reaction [22], and with NO_2 being trapped more rapidly as the temperature is increased, at least until approximately 300–400 °C [13, 23], less is present to inhibit the reaction, thus allowing even more NO oxidation. Finally, thermodynamic equilibrium between NO and NO_2 within this temperature range [18] imposes a constraint on the NO_2 concentration, which is easily achieved over a typical NSR catalyst [19]. Therefore at downstream positions, the same amounts of NO and NO_2 are present, resulting in similar performance no matter the NO_X source. The interaction of NO, NO/O_2, and NO_2 mixtures was also investigated at even higher temperature, 500 °C, over $Pt\text{-}Ba/Al_2O_3$, Ba/Al_2O_3, and Pt/Al_2O_3 [7]. The trapping efficiency followed the order $NO < NO + O_2 < NO_2$. Similar findings were also observed over a commercial NSR catalyst at 400 °C [24]. These results indicate that it must be more than just NO oxidation efficiency that dictates performance, otherwise there would be a consistently decreasing difference as the temperature is increased. Overall, NSR catalysts are more efficient with NO_2 as the NO_X source, or NO_2 may even be a necessary intermediate for NO_X storage.

Several mechanisms have been proposed for NO_X storage when either NO or NO_2 is present in the inlet gas feed. Previous work has proposed that nitrites and nitrates can form, either individually [7, 12, 13, 18, 25–27], or both form simultaneously via $2BaO + 4NO_2 \rightarrow Ba(NO_3)_2 + Ba(NO_2)_2$ [15, 18]. NO_X release mechanisms have also been investigated, with the research indicating that nitrate species decompose releasing NO or NO_2 [7, 13, 18].

There are several reasons that might explain the performance improvements observed when NO_2 is used instead of NO as the NO_X source. First, if trapping is a function of NO_2 partial pressure [6], then when NO_2 is used, the very inlet of the catalyst can participate in trapping whereas with NO, oxidation to NO_2 must occur before efficient trapping is realized. A second possibility involves the presence of multiple types of trapping sites [28–30]. As an example, if one Ba site type is near Pt and another is distant from Pt, NO might only adsorb on the Ba sites which are in close proximity with Pt since it needs to be oxidized to NO_2 prior the adsorption event. While with NO_2, it can be adsorbed on both Ba site types.

Although NO_2 improves NSR catalyst efficiency, increasing NO_2 amounts to the NSR catalyst or within the NSR catalyst requires the addition of more oxidation catalyst. Diesel oxidation catalysts have been added upstream of NSR catalysts to provide higher inlet NO_2, as well as for other functions. These are currently precious metal-based catalysts. To improve NO oxidation within the NSR catalyst, more precious metal can also be added. These obviously come at a cost and therefore it is important to understand the effects of NO_2 and optimize the amount of NO_2 in the inlet. In the present work, we have investigated the performance of a model NSR catalyst as a function of NO_X source at operating temperatures between 200 and 500 °C. Although there are studies that have investigated the influence of NO versus NO_2, as shown above, the NO_X trapping, release, and reduction characteristics as well as N_2O and NH_3 formation when the two are used has not been systematically investigated. Furthermore, a comparison was made between the two when the same amount of NO_X is trapped so that the effects during the regeneration phase could be observed.

2 Experimental Methods

The model $Pt/BaO/Al_2O_3$ sample used in this study was supplied by Johnson Matthey in monolithic form. The model sample contains 2.0 g/in^3 Al_2O_3, 1.45% Pt and 20% BaO relative to the Al_2O_3. The sample was removed from a monolith block that had a cell density of 300 cpsi. The sample used was 0.83″ in diameter with a length of 3″. The sample was inserted into a horizontal quartz tube reactor, which was placed inside a Lindberg temperature-controlled furnace. The catalyst was wrapped with 3 M matting material to cover the gap between the catalyst and the wall of the reactor to ensure that no gas slipped around the sample. Two K-type thermocouples were placed at the radial center of the catalyst; one just inside the inlet face of the catalyst and one just inside the outlet face of the catalyst. A third was placed ~1″ upstream of the sample.

The gases and gas mixtures were supplied by Praxair and were metered with Bronkhorst mass flow controllers. A four-way, fast-acting solenoid valve was used to switch between the lean and rich mixtures, which were made in separate manifolds. After the dry gas mixture had been heated to >120 °C, water was introduced downstream of this valve. Table 1 lists the gas compositions used in the

Table 1 Details of flow conditions used in the experiments

Flow conditions	Trapping (lean) phase	Regeneration (rich) phase
Space velocity	25,000 h^{-1}	25,000 h^{-1}
Concentrations		
NO_2 or NO	330 ppm	0
O_2	10%	0
CO_2	5%	5%
H_2O	5%	5%
H_2	0	3%
N_2	Balance	Balance

cycling experiments. The gas mixture then passed through a high-capacity furnace, achieving the target test temperature prior to entering the furnace holding the sample. This set-up minimized any artificial axial and radial temperature gradients during the experiments.

Before each experiment, the sample temperature was ramped to 500 °C with 5% H_2O, 5% CO_2, and a balance of N_2 and then the catalyst was cleaned/conditioned with a gas mixture consisting of 5% H_2O, 5% CO_2, 1% H_2, and a balance of N_2 for 15 min. The reactor was then cooled to the target test temperature. Experiments were performed at 200, 300, 400 and 500 °C with a space velocity, at standard conditions, of 25,000 h^{-1}. The gases exiting the reactor were maintained at >190 °C to avoid condensation and NH_3 hold-up. The gas compositions were measured using a MKS MultiGas 2030 FT-IR analyzer at approximately a 2 Hz collection rate. CO, CO_2, NO, NO_2, N_2O, NH_3, and H_2O concentrations were measured.

3 Results

3.1 Effect of Inlet NO Versus NO_2, with Identical Cycling Times

The outlet NO_X concentrations when either NO or NO_2 was used as the NO_X source at 200 °C are shown in Fig. 1. For this set of experiments, the lean, or trapping, time was 40 s, the rich, or regeneration, time was 4 s and 3% H_2 was used as the reductant in the regeneration phase. The conversions and amounts of NO_X trapped and released for these experiments are listed in Table 2. All reported values and plotted data were obtained after steady cycle-to-cycle performance was observed. The data plotted in Fig. 1 show that the trapping performance for both cases, when either NO or NO_2 was used, is similar during the first 11 s of the lean phase. Beyond

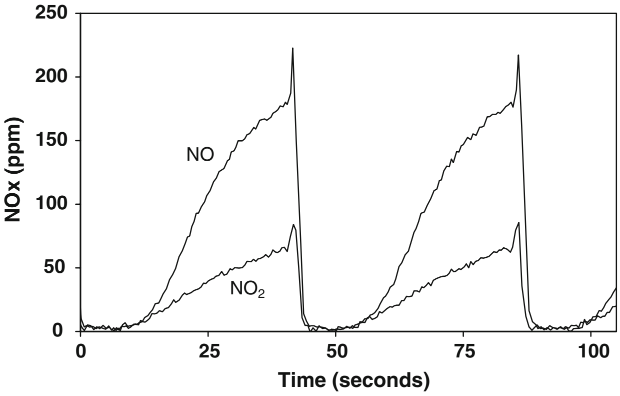

Fig. 1 NO_X outlet concentrations obtained when testing the sample at 200 °C

Table 2 Calculated performance characteristics as a function of temperature, NO_X source, and lean phase time over a $Pt/BaO/Al_2O_3$ catalyst

Temperature (°C)	NO_X source	Time (s)		NO_X trapped (μmoles)	NO_X released (μmoles)	NO_X conversion (%)	N_2O released (μmoles)	NH_3 released (μmoles)
		Lean	Rich					
200	NO	40	4	85	3.5	73	5.2	47
	NO_2	40	4	101	1.5	90	4.1	50.5
	NO_2	35	4	92	1.3	94	3.5	45.6
	NO_2	30	4	80	0.9	95	3.4	39.6
300	NO	100	4	264	1.8	94	0.57	58
	NO_2	100	4	268	1.6	96	0.55	79
	NO_2	95	4	256	1.6	96	0.51	73
400	NO	120	4	278	8	81	0.27	0
	NO_2	120	4	312	6.4	92	0.07	0.80
	NO_2	100	4	277	3	98	0.01	24
500	NO	80	4	163	31	59	0.26	11
	NO_2	80	4	189	23	75	0.19	26.5
	NO_2	62	4	162	19	83	0.11	24

the first 11 s, however, differences in the outlet concentrations were observed. The outlet NO_X concentrations at the end of the lean phase were 63 and 178 ppm with NO_2 and NO, respectively, and the amounts of NO_X trapped were 101 and 85 μmoles. The amounts released as unreduced NO or NO_2 during the rich period were relatively small, but slightly more was actually released with NO as the feed NO_X source although less NO was trapped in the prior lean phase. This is somewhat surprising since the same amount of reductant was added in both cases.

Similar experiments were carried out at 300, 400 and 500 °C, with data shown in Fig. 2, 3, 4. At 300 °C, 100 s of storage and 4 s of regeneration were used for cycling. A summary of the results for all temperatures is also listed in Table 2. At 300 °C, with NO_2, the calculated NO_X conversion was 96%, while with NO, it was 94%. It is apparent from Fig. 2 that the differences in the breakthrough profiles are less than those observed at 200 °C, but with some difference in trapping performance noted after 34 s into the lean phase. However, even at end of the 100-second lean phase, the difference in the breakthrough was only about 10 ppm. The amounts trapped were 268 and 264 μmoles with NO_2 and NO, respectively, and the amounts released were 1.8 μmoles with NO to 1.6 μmoles with NO_2. Overall, using either NO_2 or NO at 300 °C led to similar performance for these cycling conditions.

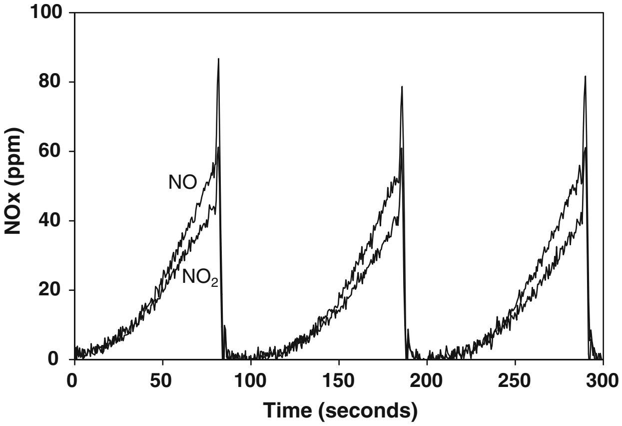

Fig. 2 NO_X outlet concentrations obtained when testing the sample at 300 °C

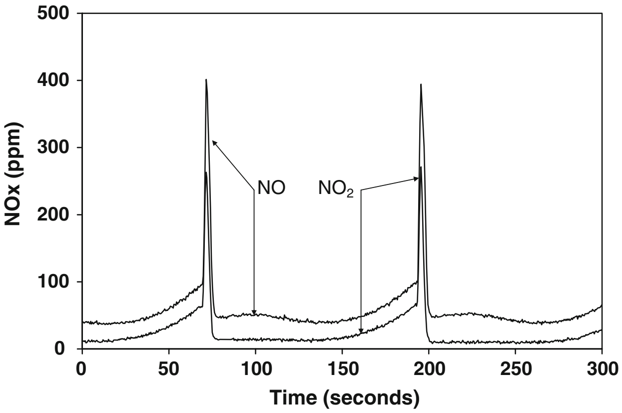

Fig. 3 NO_X outlet concentrations obtained when testing the sample at 400 °C

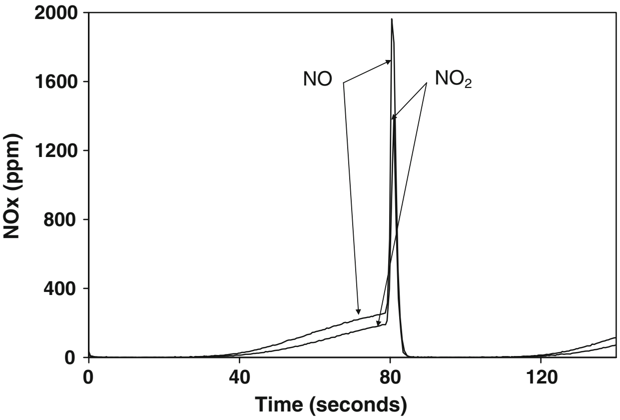

Fig. 4 NO_X outlet concentrations obtained when testing the sample at 500 °C

The outlet NO_X concentration data obtained at 400 °C are shown in Fig. 3. For this set of experiments, the trapping time was 120 s and the regeneration time was 4 s. With NO as the NO_X source, the calculated NO_X conversion was 81%, while with NO_2 the NO_X conversion was 92%. The NO_X released decreased from 8 μmoles with NO to 6.4 μmoles with NO_2, while the trapping performance increased from 278 to 312 μmoles. The data obtained at 500 °C are shown in Fig. 4. The cycle time was 80 s for storage and 4 s for regeneration. The NO_X trapped with NO_2 as the NO_X source was 189 μmoles and 23 μmoles were released during the regeneration phase. When NO was used, 163 μmoles were trapped and 31 μmoles released. From the data shown in Fig. 4, the NO_X breakthrough was similar for the first 38 s of the lean phase and beyond that, differences were observed. At the end of lean phase, the difference in the concentrations exiting the reactor was about 63 ppm.

3.2 Effect of Inlet NO Versus NO_2 with the Same Amount Trapped

In this set of experiments, the catalyst performance when trapping the same, or similar, amount of NO_X, using either NO or NO_2, was monitored. The same reductant amounts during the regeneration phase were delivered, resulting in a constant surface NO_X species-to-reductant amount in the cycles. The conversions and amounts of NO_X trapped and released for these experiments are also listed in Table 2. In this case, although listed for completeness and to demonstrate the more dramatic effects, the conversions are not directly comparable since the lean times for the experiments differ. For example, at 200 °C, when a similar amount is trapped with NO and NO_2, the lean-phase times were 40 s and 30 or 35, respectively. The amount of NO_X in during 30 s is 75% of that in over 40 s, and thus when calculating the conversion, the basis or inlet amount is not the same. At 200 °C, with NO as the NO_X source, the NO_X trapped was 85 μmoles. To achieve a similar trapped amount of NO_X with NO_2 as NO_X source, the lean phase was decreased to 30 and 35 s. For these two times, the NO_X trapped was 80 and 92 μmoles, respectively. For all three experiments, 3% H_2 was used in the 4-second regeneration phase. One would think that since a similar amount of NO_X was trapped with both NO and NO_2 for these experiments, and the same amount of reductant was introduced during the regeneration phase, a similar amount of release might be expected. This was not the case at 200, 400 and 500 °C. For the four experiments run at 200 °C, the NO_X released was 3.5 μmoles with NO (85 μmoles trapped) and 1.5, 1.3 and 0.8 μmoles with NO_2 (101, 92 and 80 μmoles trapped).

At 300 °C, performance was comparable with the same cycling times, therefore extra experiments were not run. At 400 °C, the lean time was reduced to 100 s when testing with NO_2 so that a similar amount was trapped as that with NO for 120 s. When NO was used in the lean phase, the NO_X trapped was 278 μmoles and the NO_X released was 8 μmoles, while with NO_2, the NO_X trapped was 277 μmoles and the NO_X released was 3 μmoles. At 500 °C, when NO was used, 163 μmoles were trapped and 31 μmoles released and with NO_2, the lean phase was shortened to 62 s resulting in 162 μmoles of NO_X trapped and 19 μmoles released. The above results demonstrate that the use of NO_2 as the NO_X source is not merely better for trapping, but also less release occurred.

4 Discussion

In comparing the results obtained at 200 and 500 °C when testing with either NO or NO_2, similar trapping profiles were observed at the onset of the trapping phase. Low initial NO_X out values indicate that active trapping sites were regenerated during the prior rich phase. It has been suggested that there are sites with different relative activities and the more active sites for $Pt/Ba/Al_2O_3$ samples are associated with the outermost layers of Ba particles or are in close proximity to the precious metal sites [28–30]. If the reduction equation is assumed as follows; $Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O$, for 2 moles of NO_X trapped, 5 moles of H_2 are required for reduction to N_2. At 200 °C, the amount of NO_X that enters the reactor during a 40-second lean phase is 0.11 mmoles, so the H_2 required to reduce all of the entering NO_X to N_2 if it all were trapped is 0.28 mmoles. Therefore, 3% H_2, or 1.01 mmoles input during the 4 s of rich, is in large excess. Since the catalyst does not contain any oxygen storage components, such as ceria, this amount will be in excess even if including that needed to consume the very small amount of oxygen stored on the catalyst surface. Hence, excess reductant was delivered during the regeneration phase and therefore similar cleaning might be expected with either NO or NO_2. However, except at 300 °C, the data demonstrate that trapping is significantly more efficient if NO_2 is the NO_X source, and based on the regeneration comparison, is not related to total site availability. Such improvements in overall performance have been repeatedly observed when comparing NO_2 to NO [7, 12, 13, 15, 31–34]. In this study, the differences between the two are especially apparent at the temperature extremes. There are several possible reasons for this trend in trapping.

First, monolith-supported catalysts are integral devices, and introducing NO_2 can increase use of sites at the very inlet of the catalyst if trapping depends on NO_2, or is enhanced via NO_2. With NO, NO_2 becomes available via NO oxidation, and therefore the NO_2 concentration will be relatively low at the very inlet, but increase downstream, meaning that for some distance within the sample, the amount of NO_2 will be significantly less than when introducing NO_2 as the NO_X source. For example, applying previously derived NO oxidation kinetics [22] demonstrates that at steady-state conditions, in other words after the Ba is saturated and no trapping occurs, the conversions of NO to NO_2 at 200 °C and at positions 0″, 1″, 2″ and 3″ from the inlet are 0, 11, 16 and 21%, respectively. This build-up in NO_2 would result in higher nitrate concentrations downstream of the inlet, which has indeed been observed [35]. Note that during trapping, NO_2 would be adsorbed from the gas phase, resulting in higher local NO oxidation rates compared to the absence of trapping. Also, using NO_2 as the NO_X source can result in good trapping performance even in the absence of oxygen in the inlet feed [31]. Thus activation of the O_2 molecule is not required with NO_2, possibly helping reaction at low temperature. Another possible contribution is from different trapping sites having different adsorption affinities for NO_2 and NO. Multiple Ba sites or adsorbing types have been proposed [28–30]. In one example, there are two Ba site types, one proximal to Pt sites and the other further away. With such a scheme, NO might be more likely to be trapped at sites close to Pt, as the Pt would oxidize the NO to NO_2, which would then “spill-over” to an adjacent Ba site. Otherwise, the NO_2 would have to desorb from the precious metal site and re-adsorb to Ba downstream, but as described above, the overall NO oxidation rate is fairly limited at the lower temperatures. NO_2 can be adsorbed on both types of Ba sites, the one proximal to Pt and the one far away from Pt via direct nitrite formation, or via the disproportionation mechanism to nitrates. This of course increases the available amount of trapping sites when NO_2 is introduced, therefore increased trapping will occur and overall higher NO_X reduction performance would be expected. Again, however, this would contribute to more being trapped at upstream sites as well as throughout the catalyst. Another possibility, along the same concept, is that nitrate species and not nitrite species are always, or at least preferentially, formed when NO_2 was used, while a mixture of the two species are formed with NO. The thermal stability of nitrate species is higher than nitrite species [4, 7], and therefore they are less likely to decompose during the lean phase (via an adsorption/desorption like equilibrium) leading to more NO_X trapped. Most evidence, however, suggests that at temperatures below 300 °C, a mixture of nitrites and nitrates form when NO is used, but at higher temperatures, although a mixture may initially form, the nitrites are quickly oxidized to nitrates and have therefore not been observed [6, 7]. This is therefore unlikely to significantly influence higher temperature performance and therefore cannot explain the differences observed at 400 and 500 °C.

At 300 °C, the trapping performance of the catalyst appears only slightly dependent on the NO_X source under the conditions of these tests. NO oxidation initially increases with temperature [36] and most NSR catalyst types attain their maximum oxidation activity between 300 and 400 °C, resulting in high NO_2 amounts, thus leading to more favorable trapping and comparable performance. Again, using previously derived kinetics [22], at 300 °C and in the absence of trapping, 50% NO conversion is predicted. However, the generated NO_2 over a NSR catalyst can be immediately trapped, leading to maintained, higher overall NO oxidation rates due to lesser NO_2 product inhibition, especially in this 300–400 °C range. Additionally, in this temperature range, some thermodynamic equilibrium between NO and NO_2 is being established [18], with a calculated maximum 87% conversion allowed at 300 °C, indicating the kinetics are still responsible for the lower conversion. Even so, based on the data shown in Fig. 2, it is expected that with longer lean time, more difference would be observed, with NO_2 still resulting in improved NO_X trapping at 300 °C. At 400 and 500 °C, more significant differences were observed. It should also be noted that NO_2 was observed in the outlet gas composition at 400 and 500 °C, with NO and NO_2 as the NO_X source, indicating it is not an absence of NO_2 limiting trapping at these high temperatures.

At all temperatures, with NO_2 used, there was also noticeable improvement in the regeneration phase, i.e., less unreduced NO and NO_2 was released. This is based on the data obtained from the experiments where the same amount of NO_X was trapped during the prior lean phase, presented in Table 2, resulting in a constant reductant-to-trapped NO_X ratio for comparison purposes. A likely reason that explains this trend as well, is the integral nature of the NSR catalyst system. As mentioned above, if NO_2 is introduced as the NO_X source, more sites at the front of the catalyst will participate in trapping. Trapping with NO will be limited at the very inlet due to low NO_2 partial pressures, until the extent of NO oxidation is significant enough. Therefore, upon switching from the lean to rich phase, in the case of NO_2, more NO_X is released at the very front of the catalyst giving it more chance to be reduced by downstream Pt sites before exiting the monolith. While with NO, more is released slightly further downstream, and has spent less time in the monolith or less chance to contact the reducing Pt sites. This is compounded by the local reductant-to-NO_X ratio as will be discussed below.

Another impact, still in conjunction with the integral reactor explanation, is the oxygen stored on the catalyst surface affecting the amount of reductant available for NO_X reduction. Previous research [37, 38] has shown that reductant can be used up in reducing the stored oxygen on the catalyst and hence influences the amount of reductant available for regeneration and reduction of NO_X. With NO_2, more NO_X is trapped at the very inlet and upon switching from lean to rich, the reductant will simultaneously be depleted to reduce both oxygen and NO_X stored on the catalyst. Although competitive, this still results in the opportunity for reductant to be consumed in the reduction of NO_X. However, when NO is used, more is trapped slightly downstream and the incoming reductant is first used to deplete the oxygen stored at the very inlet, thereby delaying reductant delivery to downstream Pt and Ba sites where the higher concentrations of stored, or released, NO_X species are. This will likely play an increasing role as the nitrate decomposition reaction becomes more significant, i.e., with increasing temperature. Also, with the catalyst studied in these experiments, although present, little OSC was measured due to the absence of standard OSC components. Therefore, the effect described may be minor with this system, but more significant with commercial formulations that contain ceria and other OSC components.

Further evidence supporting the increased reduction being related to where the NO_X was trapped is the formation of N_2O and NH_3 byproducts during the regeneration event. As shown in Table 2, the formation of N_2O was always higher when NO was used. With more NO_X trapped at the front of the catalyst when NO_2 is used, during regeneration there is more opportunity for complete reduction downstream, leading to decreased selectivity toward N_2O formation, where N_2O can be considered an incomplete reduction product. While with NO, the distribution of trapped NO_X is shifted downstream, and there is therefore less chance for released NO_X to be completely reduced. This is again related to residence time, but can also be related to the reductant-to-NO_X ratio. As the reductant enters, it is consumed by surface oxygen and in reducing the nitrites and nitrates. Therefore, reductant delivery to downstream active sites lags the lean/rich gas transition, and as time increases, or the lean/rich transition front distance into the catalyst increases, this lag increases as well. With NO_2 as the NO_X source, more was trapped at the very upstream Ba sites, and a relatively higher reductant-to-NO_X ratio is achieved, leading to more complete reduction overall. As a matter of fact, NH_3 formation was always higher when NO_2 was used instead of NO (Table 2). NH_3 is formed from the trapped nitrite/nitrate species and the H_2 input during regeneration, and leads to selective catalytic reduction of NO_X over the NSR catalyst [39, 40]. Following the same concept discussed above, if NO_2 is trapped at the very inlet of the catalyst, more NH_3 can be formed due to longer residence time of the released NO_X in the channel with the reductant, as well as a higher reductant-to-NO_X ratio, a key parameter in NH_3 formation on NSR catalysts [41]. Furthermore, with NO_2 leading to more upstream trapping, NH_3 that does form will have less trapped NO_X downstream to react with, contributing to the greater amounts observed with NO_2 as the feed. In the case of NO, the NO_X is trapped slightly downstream relative to the NO_2 case, and therefore less NH_3 is formed, due to the decreased reductant-to-NO_X ratio and decreased residence time. It should be noted that the amount of N_2O, overall, decreased with increasing temperature, while NH_3 did not show a consistent trend. Typically, outlet NH_3 concentrations decrease with increasing temperature, but this was not the case when comparing the data at 400 and 500 °C. But, different lean times were used and less NO_X was trapped at 500 °C, and with the same amount of reductant added, more NH_3 was therefore formed at 500 °C due to a higher reductant-to-NO_X ratio. With the trapped NO_X being different between the temperatures, a direct correlation of NH_3 as a function of temperature cannot be made.

Other than the axial distribution of trapped NO_X explaining the trends, another possibility is the nature of the stored NO_X during the lean phase. Several complex compounds, (e.g., barium aluminates) could be present, which may have different NO and NO_2 dependencies on trapping [18]. Similarly, the decomposition trends of the nitrates or surface NO_X compounds formed might be different. However, these types of sites are typically formed via high temperature treatments [42], which were not done with this sample, making this an unlikely path.

There are other factors that can contribute to the observed trends differentiating NO and NO_2, but these have different levels of significance in different temperature ranges, and therefore do not explain the consistently observed trends in the 200–500 °C range. These possible contributing factors are discussed here. The possibility of nitrates forming at sites near and far from the precious metal sites when using NO_2 was discussed in conjunction with the trapping results. Previous studies [7, 33, 43] have also addressed the influence of Pt on the thermal stability and decomposition of nitrate and/or nitrite species. If with NO, more NO_X is trapped at Ba sites that are near Pt, then there may be higher release associated with NO as the inlet NO_X source as Pt could induce the decomposition of the Ba nitrite/nitrate during the regeneration phase. With a catalyzed release, or simply higher than that compared to sites that are not necessarily near Pt, more will escape unreduced. Along the same concept, nitrates are more thermally stable than nitrites. More nitrates form with NO_2 introduced as compared to NO, which at low temperatures is trapped as a nitrite or nitrite/nitrate pair [5, 6, 15, 44]. Therefore at low temperature, nitrite decomposition could lead to a higher amount of unreduced NO_X, while the nitrates formed with NO_2 as the inlet NO_X source would lead to less. This however, just as with the trends in trapping, does not explain the differences observed at higher temperatures, as above 300 °C, nitrites are rapidly oxidized to nitrates during the lean phase [4, 7, 19]. Another possibility is that NO is released as the decomposition product when NO is used and NO_2 is released when NO_2 is used, for example from $Ba(NO_3)_2$ decomposition, which is more prevalent with NO_2 as the NO_X source. And in the absence of gas-phase O_2, NO_2 still has some affinity for downstream adsorption, whether it be on Pt or Ba [14]. Therefore, if NO_2 can indeed re-adsorb to downstream sites during the regeneration phase, it will have more opportunity for reduction as the reductant propagates along the catalyst length. Again, however, this should only be expected at low temperature where nitrites might still exist with the switch to the regeneration phase.

A last consideration was the associated temperature rise with the switch from the trapping to regeneration phase. This is caused by reaction of the entering reductant with surface oxygen species, nitrate reduction and possibly mixing phenomena between the two phases. Measured temperature rises at the very inlet and outlet of the sample were on the order of 5 °C during all tests. These are significantly smaller than those observed with a commercial sample [37], due to the lack of a purposefully added oxygen storage component, such as ceria, in the sample used in this study. This small temperature increase, and it being observed at both the front and back of the sample, suggests that temperature change is not a significant factor for the trends seen. Furthermore, previous work with $Pt/Ba/Al_2O_3$ model samples at 350 °C has also indicated that with little or no temperature rise at the onset of regeneration,

regeneration is associated with a surface-catalyzed reaction, as mentioned above, and not via thermal decomposition of nitrate species [45]. Again, however, at higher temperatures thermal decomposition of the nitrates is expected and therefore this effect distinguishing NO from NO_2 less significant.

Overall, of the possibilities proposed, only the integral nature of the NSR catalyst can explain the observations at all temperatures and amounts of NO_X trapped used in this study. The different surface species and their relative rates of decomposition can contribute to the observations at low temperature, but not to the differences still observed at 400 and 500 °C. At low temperature, NO_2 is readily trapped at the very inlet, while NO is oxidized and then trapped. At higher temperature, NO_2 will decompose to establish NO/NO_2 equilibrium, but this still leaves higher NO_2 amounts at the very inlet. Therefore, with NO, there is a distribution of trapped NO_X as a function of axial position along the catalyst length during cycling that has a maximum, rather than a monotonic decrease as with NO_2 as the NO_X source. This leads to the better performance consistently observed with NO_2 as the NO_X source and when upstream oxidation catalysts are used.

5 Conclusions

In this study, the performance of a model monolith-supported NSR catalyst when using NO or NO_2 as the inlet NO_X source at temperatures between 200 and 500 °C was investigated. The evaluation was based on two different types of experiments; one with the same lean cycle times and the other with same amount of NO_X trapped. The results clearly demonstrated that performance was better when using NO_2 at all operating temperatures. At 300 °C, similar performance between the two was observed, due to high NO oxidation activity, rapid trapping of formed NO_2 and therefore no inhibition effect on NO oxidation, but differences were becoming apparent at the end of the lean phase.

The improved performance with NO_2 relative to NO at the other temperatures can be explained by NO_2 being more reactive towards trapping than NO, or even being an intermediate in the trapping process. This NO_2 dependency leads to more NO_X trapped at the catalyst inlet when NO_2 was used, while with NO there was less since oxidation to NO_2 prior to trapping is required or leads to more appreciable trapping. A distribution of stored NO_X along the length of catalyst forms, where with NO_2 it monotonically decreases and with NO there is a maximum downstream of the very inlet. Thus more NO_X is stored with NO_2 as the NO_X source since the very front of the catalyst can be used and there are no NO_2/reactant concentration limitations. Also, less released NO_X during regeneration was observed when NO_2 was used. Again, if with NO_2 more is trapped at the very inlet, upon switching from lean to rich, the reductant is used to simultaneously reduce both surface oxygen and stored NO_X. While in the case of NO, the reductant will be consumed first to deplete the surface oxygen and lesser quantities of stored NO_X at the catalyst inlet, resulting in less reductant available to reduce NO_X at downstream positions where it is being released in higher concentrations. Analysis of byproduct N_2O and NH_3 formation during the regeneration phase support this conclusion, as more N_2O was observed with NO as the inlet NO_X source, and more NH_3 with NO_2. Possible contributions to improved performance with NO_2 at lower temperatures were also discussed, and included nitrate versus nitrite stability and trapping at sites near or far from the Pt sites.

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