

NO_x storage/reduction catalyst performance with oxygen in the regeneration phase

William S. Epling*, Darren Kisinger, Chris Everest

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Abstract

NO_x storage/reduction (NSR) catalysts operate over a cycle where the catalyst is periodically regenerated with a reductant-rich gas mixture. In this study, the effects of including O₂ during this regeneration phase on the performance, NO_x reduction to N₂, of a model NSR catalyst and a commercial NSR catalyst were investigated. The increased temperature associated with reductant oxidation when oxygen was available resulted in improved performance at temperatures below 375 °C for the model sample, but resulted in decreased performance at higher test temperatures. The improved performance primarily originated from increased trapping in the subsequent lean phase but was also improved by decreased byproduct formation during the rich phase under some conditions. The improved performance measure is based on an increase in the lean-phase time before a regeneration phase would need to be triggered, with the increase on the order of 10 s for 288 and 375 °C operating temperatures. The decreased trapping performance at higher temperatures is due to decreased nitrate stability, while the increased trapping performance at lower temperature is due to improved oxidation kinetics. Similar effects were observed with the commercial sample, although the presence of surface oxygen storage resulted in an already significant temperature increase with no O₂ added in the regeneration gas composition. The results demonstrate that the time between regenerations can be increased significantly by tuning or optimizing the amount of reductant and oxygen added during the regeneration phase.

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1. Introduction

There has been significant research in reducing NO_x emissions from lean-burn vehicles, of which diesel is one, over the last several years. One reason for this research intensity is the prediction that more diesel or lean-burn engines will be available in the near future due to their better fuel efficiency and lower CO₂ emissions in comparison to today's gasoline engines. A second reason is of course government regulations. One technology that has emerged as a possible solution is NO_x storage/reduction (NSR) catalysis [1,2].

NSR relies on the ability of a catalyst to trap or store NO_x during normal engine operating conditions. Once the catalyst nears saturation or some unacceptable amount of NO_x slip occurs, the catalyst is regenerated via exposure to a reductant-rich exhaust gas composition. During this reductant-rich exposure, the stored NO_x species, usually present on the

catalyst surface as nitrates, decompose and the resulting decomposition products are reduced to N₂ [3]. The lean phase lasts on the order of 1–3 min and the rich phase lasts on the order of 1–5 s. The rich or regeneration phase gas composition varies depending on how it is produced; either by injecting raw fuel upstream of the NSR catalyst [4–6], reforming fuel upstream of the NSR catalyst [7], or the gas mixture is derived from running the engine with excess reductant (fuel) relative to oxygen [8–11]. Most published studies have used one of the latter two methods, which have proven better than directly injecting fuel into the exhaust/onto the NSR catalyst [7]. Reasons for the improved performance are the availability and reactivity of smaller reductant molecules, including H₂ and CO, and the ability to remove most or all of the oxygen from the gas prior to the NO_x reduction catalyst system.

Previous research has demonstrated that the presence of O₂ stabilizes nitrates and therefore inhibits NO_x release [12]. NO_x was still released but the temperatures required were higher than in the absence of O₂. The experiments leading to these conclusions were performed in the absence of any reductant. Previous work has also shown that reductant oxidation on the

* Corresponding author.

E-mail address: wepling@uwaterloo.ca (W.S. Epling).

catalyst surface during the regeneration phase results in increased catalyst surface temperatures [13]. Under some conditions the measured temperature rises exceeded 30 °C, as a significant amount of oxygen storage capacity (OSC) existed on the sample evaluated. Since nitrate stability decreases with increasing temperature, the exotherms generated during regeneration would result in larger NO_x release amounts. And although the discussed temperature rise was associated with the reaction occurring in the regeneration phase of the cycle, temperature changes were still being observed later in the subsequent trapping phase due to slower heat conduction along the monolith. This later temperature increase affected the trapping performance of the catalyst under the test conditions used, again because of decreased nitrate stability with increasing temperature. Therefore, the presence of O₂ in the regeneration, when reductant is present, can stabilize the nitrates via equilibrium (where equilibrium is based on gas and surface phase concentrations, e.g. BaO(s) + 2NO(g/s) + 3/2O₂(g/s) → Ba(NO₃)₂) or decrease their stability via exothermic oxidation of the reductant and a surface temperature increase. Which would be more significant depends on the operating conditions.

Although most studies leave out O₂ in the regeneration phase, it is possible that some would be present, either from incomplete removal during reforming or residual O₂ as a result of incomplete combustion. Overall, there should not be a large amount of O₂ left, relative to the reductant, if the process is “tuned” appropriately [10,14]. NSR catalysts however, typically contain at least one precious metal component and therefore when reductant and oxygen are coincidentally present, oxidation would occur at the very front of the catalyst, if the surface temperature is higher than the light-off temperature [15]. As most studies suggest appreciable NSR operation only above 200 °C, being above the light-off temperature for at least the H₂ and CO reductant components seems reasonable. With available H₂ or CO, little if any O₂ will be present to stabilize the nitrates along the monolith channel, beyond a small zone at the front of the catalyst where oxidation is occurring. This leaves only the exotherm having an impact.

As was mentioned above, nitrate stability decreases with increasing temperature. However, consistently data have shown that overall NSR performance increases with increasing temperature until an operating temperature range of 350–400 °C is reached [16–23]. This improved performance has been attributed to increased NO oxidation, trapping and diffusion rates and better regeneration during the rich phase of the cycle allowing better trapping in the subsequent lean phase. In this study, the effect of different amounts of O₂ in the reductant-rich phase was evaluated. The hypothesis was that an exotherm at lower operating temperatures would increase the average catalyst temperature and result in improved performance. The effects evaluated include; trapping performance, NO_x and byproduct release, and temperature changes in the monolith. Both a model Pt/Ba/Al₂O₃ sample and a manufacturer-supplied catalyst were tested, the latter to verify that the effects observed translate to a production sample.

2. Experimental

The samples, 7/8" in diameter, were cut from 9" diameter, 6" long monoliths. The model sample was Pt/Ba/Al₂O₃ supported on the monolith, with the deposited amounts being 2.0 g/in.³ Al₂O₃ and 1.45% Pt and 20 wt.% BaO relative to the Al₂O₃. The second sample was catalyst vendor-supplied and details of its composition were not given. The core samples were cut to 3" in length and then inserted into a quartz tube. Insulating material was wrapped around the samples so that no gas bypass around the core could occur.

Gas mixtures were made using Bronkhorst mass flow controllers from gas cylinders supplied by PraxAir. Water was introduced downstream of the mass flow controllers after the gas had been heated above 100 °C. The mixture was then preheated to the target temperature prior to entering the furnace that held the quartz tube with the catalyst sample. The reactor furnace simply maintained the target temperature. The lean and rich gas mixtures were made in separate manifolds and a pneumatically driven, fast-acting, four-way valve directed one mixture to the reactor and the other to a vented exhaust. The lean-phase gas composition consisted of 330 ppm NO, 5% CO₂, 5% H₂O, 10% O₂ and a balance of N₂. The rich-phase gas composition consisted of 5% H₂O, 5% CO₂, a 3:5 mixture of 1–3.8% H₂:CO as the reductant, 0–1.4% O₂ and a balance of N₂. The percentages of reductant and oxygen were varied as part of this study. All flow rates were set for a 30,000 h⁻¹ space velocity.

The outlet gas composition was monitored using an MKS MultiGas 2030 FTIR analyzer. NO, NO₂, N₂O, NH₃, CO, CO₂, and H₂O were quantitatively measured at a rate of ~2 Hz. Data described below as NO_x are a summation of NO + NO₂. H₂O was not removed prior to analysis. The gas lines running to the analyzer were maintained at 195 °C to ensure no H₂O condensation and NH₃ losses. Four K-type thermocouples were used to measure temperatures in the quartz tube section. Two were used to measure temperatures just upstream and downstream of the sample. The thermocouple upstream of the sample was used to set the target temperature. Two other thermocouples were set just inside the upstream and downstream faces of the sample, inside a radially-centered channel.

The model sample was degreened at 625 °C for several hours in the reactor; which consisted of cycling the gas mixture between lean and rich compositions with 60 s lean and 5 s rich. This was found to give consistently reproducible results at any test temperature below 500 °C. Previous experience has demonstrated that degreening the samples at temperatures lower than ~625 °C did not result in reproducible performance at lower operating temperatures before and after cleaning procedures. Between experiments, each sample was heated to >500 °C and exposed to 5% H₂O, 5% CO₂, 1% H₂ and a balance of N₂ for 15 min to clean the sample of residual nitrates. Previous research has shown that nitrate decomposition, at least from Pt/Ba/Al₂O₃ samples, occurs from 225 to 500 °C [24], indicating that 500 °C with H₂ present should be sufficient to clean these samples. The commercial sample

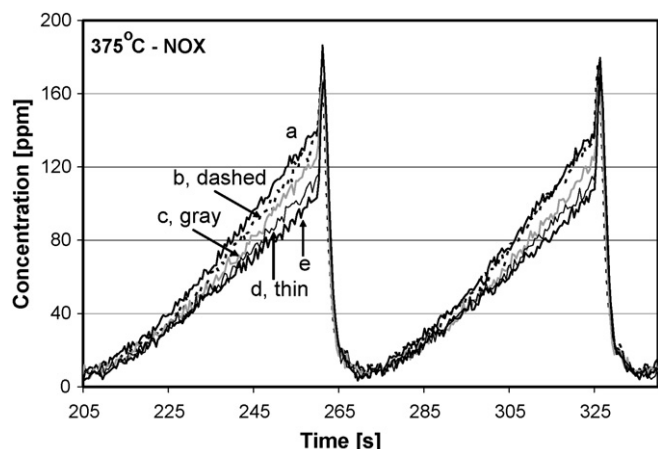


Fig. 1. NO_x concentration obtained using the model catalyst at an upstream temperature of 375 °C with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 1.2% and 0%, (c) 1.8% and 0.3%, (d) 2.8% and 0.9% and (e) 3.8% and 1.4%, respectively.

underwent a similar degradation protocol and was also cleaned at 500 °C between each experiment.

3. Results and discussion

The data shown in Fig. 1 were obtained at an inlet temperature of 375 °C using the model Pt/Ba/Al₂O₃ sample that had been aged at 625 °C. These data, and all the others following, occur after a steady cycle-to-cycle performance had been attained. As shown, there is only a brief period of 0 ppm NO_x breakthrough for any of the test conditions, lasting approximately 3–5 s. Prior to the aging, the breakthrough NO_x amount was less than 10 ppm after 60 s of trapping under similar test conditions. With 1% reductant (0.675% CO and

0.325% H₂), the outlet NO_x level reached 138 ppm after 60 s, just prior to the regeneration phase. 161 μmol of the 200 μmol of NO_x were trapped during the cycle, which corresponds to 82.5% trapped. The amount released during the regeneration phase was 5.8 μmol and the total NO_x conversion across one cycle was therefore 79.6%. Table 1 contains a summary of similar results attained with this catalyst at the three temperatures and the different reductant-to-oxygen ratios evaluated.

As shown in Fig. 1 and Table 1, at 375 °C, the addition of 20% extra reductant had little effect on the trapping ability, but possibly a small effect on the amount released during the regeneration phase. Increasing the reductant level to 1.8% had no further effect on either trapping or release. These amounts of reductant are lower than those used in some studies due to a lack of OSC component on this catalyst. The absence of an effect during trapping indicates that the sites being used during trapping are being cleaned sufficiently with the 1% reductant addition and higher amounts are unnecessary. The lack of an observed effect on NO_x release during the rich phase is due to the already small magnitude of the release. There is however a significant effect on the amounts of byproduct NH₃ and N₂O released. For NH₃, the amount released increased from 64.3 to 97.1 μmol with the increase from 1.0 to 1.8% reductant. The N₂O formed also increased, but the amount released was significantly lower, increasing from 0.063 to 0.98 μmol. The NH₃ trends were expected based on previous work that has focused on byproduct formation [25–27].

The addition of 0.3% O₂ with the 1.8% reductant results in the same stoichiometric amount of “excess” reductant as the experiment with 1.2% reductant and 0% O₂ added. The data show that this addition of O₂ caused an increase in the amount of NO_x trapped, and little if any change in the amount released.

Table 1
Pt/Ba/Al₂O₃ sample performance as a function of temperature and reductant-to-oxygen ratio during the regeneration phase

Reductant concentrations (%)	Oxygen concentrations (%)	NO _x trapped (μmol)	% Trapped	NO _x released (μmol)	Total conversion (%)	NH ₃ released (μmol)	Selectivity (% NO converted to N ₂ , N ₂ O or NH ₃)
288 °C							
1	0	90	46.2	10.5	40.8	50.4	40.8
1.2	0	91	46.3	11.5	40.4	55.7	40.4
1.8	0	91	46.3	13.8	39.2	59.2	39.1
1.8	0.3	96	49.1	10.6	43.7	59.9	43.7
2.8	0.9	106	54.0	8.26	49.8	63.6	49.8
3.8	1.4	113	57.8	8.21	53.6	77.7	53.6
3.8	0.9	105	53.9	11.5	48	75.7	48.0
375 °C							
1	0	161	82.5	5.67	79.6	64.3	79.6
1.2	0	162	83.0	5.04	80.4	72.9	80.4
1.8	0	162	82.6	4.78	80.2	97.1	80.2
1.8	0.3	166	84.9	4.96	82.4	76.2	82.4
2.8	0.9	167	85.5	5.36	82.8	57.7	82.8
3.8	1.4	168	86.1	5.18	83.4	55.9	83.4
463 °C							
1	0	125	63.8	16.1	55.5	40.2	55.5
2.8	0.9	123	63.1	15.6	55.1	44.4	55.1
3.8	1.4	120	61.4	15.2	53.5	38.2	53.5

Similarly, the addition of 0.9% O₂ to a 2.8% reductant-containing mixture gave improved performance for trapping in comparison to the 1% reductant-containing regeneration, both of which would contain the same amount of reductant after the added oxygen was consumed. The addition of more O₂, while keeping the resulting excess reductant amount consistent at 1%, resulted in further improvement.

In terms of NH₃ or N₂O measured, approximately 72.9 μmol of NH₃ were observed with 1.2% reductant and 0% O₂. This amount did not change with 1.8% reductant and 0.3% O₂. The amount observed in the experiment with 1.0% reductant, as mentioned above, was less than with 1.2% reductant, 64.3 μmol. When 2.8% reductant and 0.9% O₂ was used, the same in excess reductant as 1% reductant and no O₂, the NH₃ observed was only slightly less, 57.7 μmol. Again, the N₂O amounts observed were negligible in all experiments at 375 °C.

Temperatures inside of a channel of the monolith were measured in two locations, one approximately 1 cm from the upstream face (inside of the channel, therefore 1 cm inside of the monolith), and one approximately 1 cm inside the monolith from the downstream face; these will be called inlet and outlet, respectively. With the addition of no oxygen, the temperature at the inlet increased by approximately 2 °C at the onset of the regeneration phase as shown in Fig. 2. This could be due to nitrate or Pt oxide reduction or reaction on the catalyst between O₂ in the lean phase and reductant in the rich phase that mix upstream as the “front” travels to and along the sample. Another small increase was observed with the switch back to the lean phase, and is of the same intensity as that observed with the switch to the rich phase. Again, this could have been caused by the mixing between the lean and rich phases, but could also be due to residual NH₃ oxidation. Within 8 s of the switch back to the lean phase, the temperature dropped below 376 °C. The data obtained from the thermocouple placed inside the monolith at the outlet position are shown in Fig. 3. With no O₂ addition, a temperature rise was observed at the outlet, on

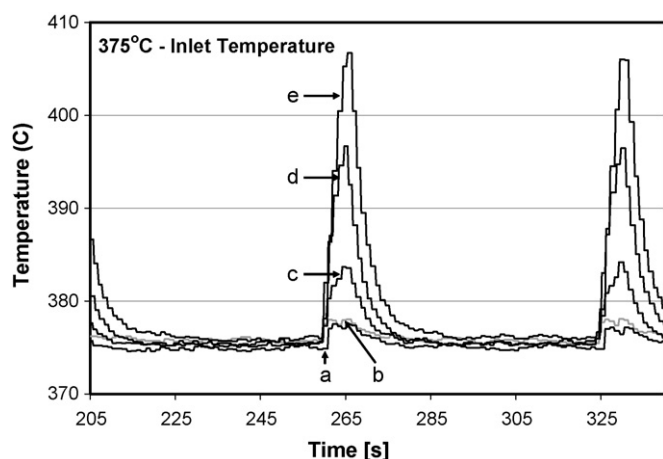


Fig. 2. Temperature data obtained from the thermocouple set just inside the inlet face of the model catalyst with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 1.2% and 0%, (c) 1.8% and 0.3%, (d) 2.8% and 0.9% and (e) 3.8% and 1.4%, respectively. These were obtained simultaneously to the data shown in Fig. 1.

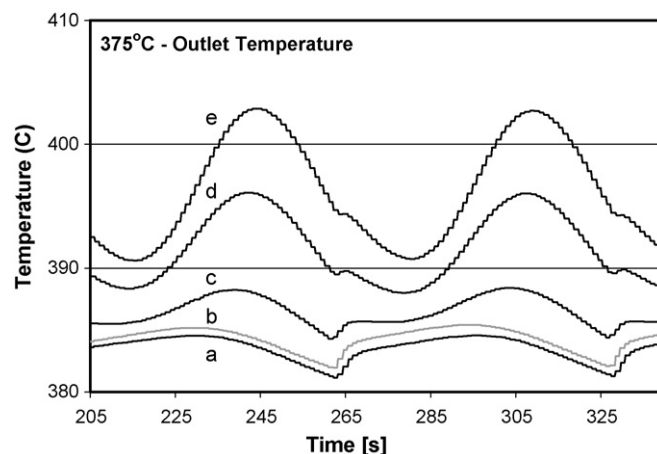


Fig. 3. Temperature data obtained from the thermocouple set just inside the outlet face of the model catalyst with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 1.2% and 0%, (c) 1.8% and 0.3%, (d) 2.8% and 0.9% and (e) 3.8% and 1.4%, respectively. These were obtained simultaneously to the data shown in Fig. 1.

the order of 3–4 °C. Note that the lowest temperature observed at the outlet was higher than 375 °C. Prior to the experiments beginning, the temperature was 375 °C, but with each cycle the temperature minimum increased slightly until steady cycle-to-cycle conversions and performance were obtained. At this point, the temperatures from cycle-to-cycle were also consistent, and those are plotted in Fig. 3. The heat associated with this temperature rise did not dissipate as quickly as that observed at the inlet. A maximum in temperature was reached 30 s after the switch back to the lean phase. Similar temperature patterns have been observed on a commercial catalyst, with coincident effects on the lean-phase trapping profiles [13]. This temperature evolution toward the catalyst outlet is associated with heat conduction along the monolith from earlier upstream exothermic reactions. As conduction progresses down a monolith, there will of course be heat loss to the gas phase. In these experiments, the gas moved through the catalyst at a high rate, with a residence time less than 0.1 s. This reduces the observed temperature downstream, beyond this short time period, if there are not other reactions occurring that are exothermic. During the trapping phase, there are no reactions occurring that result in any significant heat evolution. Since the temperature rise observed at the outlet was larger than that at the inlet and the maximum occurred well after the rich phase ended, Fig. 2, there must have been a larger temperature rise just downstream of the inlet thermocouple during regeneration. Recent results obtained with IR thermography (data not shown) demonstrate that with no O₂ addition in the regeneration phase and with NO as the NO_x source during the trapping phase, the highest temperature observed during regeneration is indeed not at the very inlet, but at positions just downstream.

As shown in Fig. 2, adding O₂ to the regeneration gas composition resulted in increased temperatures observed at the inlet. With 1.4% O₂ addition, the thermocouple reading at the inlet reached 407 °C at its maximum. The inlet temperature began decreasing as soon as the switch to the lean phase occurred. The maximum temperature at the outlet position

shifted further into the lean-phase relative to the temperatures observed when no O₂ was added, and the temperatures observed were also higher, Fig. 3. The temperature data do not reflect the true surface temperature during these reactions. If the gas composition was unchanging and no reaction occurs, then the gas temperature and surface temperature could be assumed the same. However, as recent research has shown, calculated temperatures at the trapping site during hydrocarbon oxidation at a precious metal site can be 50 °C higher than a measured temperature [28,29]. These data indicate that the overall temperature at the surface of the catalyst was higher than that targeted, due to the temperature rise caused by the exothermic reactions, coming from nitrate reduction, mixing between the rich and lean gas phases and from the addition of O₂ into the rich gas mixture. The improved performance observed with the addition of O₂ into the rich gas composition mixture, discussed above, is caused by the associated extra temperature rise.

The addition of 0.3% O₂ to the 1.8% reductant-containing experiment resulted in improved performance compared to the experiment run with just 1.8% reductant and no O₂. This indicates that although some reductant was lost via oxidation with the gas-phase O₂ as the reactant source, there was still enough to regenerate the surface. Based on the data shown in Fig. 1, reductant beyond 1–1.2% was in excess, agreeing with this conclusion. The addition of the O₂ resulted in oxidation of some reductant, therefore an increased average catalyst temperature and improved performance.

Similar experiments were performed at a catalyst inlet temperature of 288 °C with some of the results shown in Fig. 4 and Table 1. Again, no changes in performance were evident with an increase in the reductant amount beyond 1%. And again, the addition of a small amount of O₂ to the regeneration gas mixture resulted in improved performance. Further O₂ additions resulted in further improvements, to the extent that with 1.4% O₂ and 3.8% reductant, which is equivalent in excess reductant amount to 1% reductant with no O₂, a 13% overall conversion improvement was observed. As further proof that the effect

relies on the O₂, with 3.8% reductant, the amount of O₂ was dropped from 1.4 to 0.9% and decreases in overall conversion and trapping percentage were observed, as shown in Table 1. The addition of O₂, but keeping the amount of excess reductant consistent, resulted in increased NH₃ measured at the catalyst outlet. With 0% O₂ and 1.0% reductant the amount observed was 50.4 μmol, with 0.9% O₂ and 2.8% reductant it was 63.6 μmol, and with 1.4% O₂ and 3.8% reductant it was 77.7 μmol. Again, little N₂O was observed. The increase in NH₃ measured with O₂ addition is in contrast to the observations at 375 °C, indicating that the increased catalyst temperature associated with the O₂ addition resulted in more NH₃, but that any increases beyond 375 °C would not have this effect.

Some of the inlet and outlet temperature data for the 288 °C experiments are plotted in Figs. 5 and 6, respectively. Again, without O₂ in the regeneration gas mixture, little temperature difference was observed between the 1 and 1.8% reductant-containing experiments at the inlet or outlet. The outlet temperatures measured after a steady cycle-to-cycle performance had been obtained are also again higher than the inlet but admittedly in this case the temperature measured at the outlet prior to the experiment start was slightly higher than 288 °C, approximately 291 °C. However, the minimum temperature reached during the cycle was 294 °C after steady performance, slightly higher due to heat build-up with slower dissipation along the monolith; similar to the trend observed during the 375 °C test. With the addition of O₂ during the regeneration, higher temperatures were observed, as expected. It should be noted that the temperatures observed with 3.8% reductant/0.9% O₂ and 2.8% reductant/0.9% O₂ were identical; Figs. 5 and 6 plots d and e. And, the amounts trapped were also identical. Differences in the amounts of NO_x released were observed, as some of the NO_x was further reduced to NH₃ with the higher reductant amount, 63.6 μmol with 2.8% reductant vs. 75.7 μmol produced with 3.8% reductant.

Even though nitrate stability decreases with increasing temperature, at lower temperatures this negative impact is

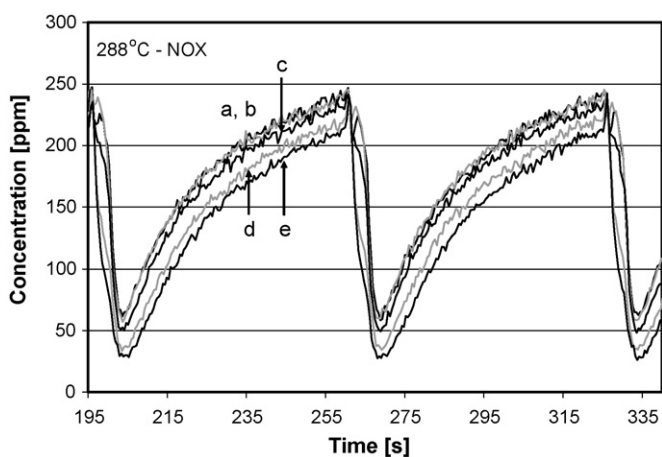


Fig. 4. NO_x concentration obtained using the model catalyst at an upstream temperature of 288 °C with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 1.2% and 0%, (c) 1.8% and 0.3%, (d) 2.8% and 0.9% and (e) 3.8% and 1.4%, respectively.

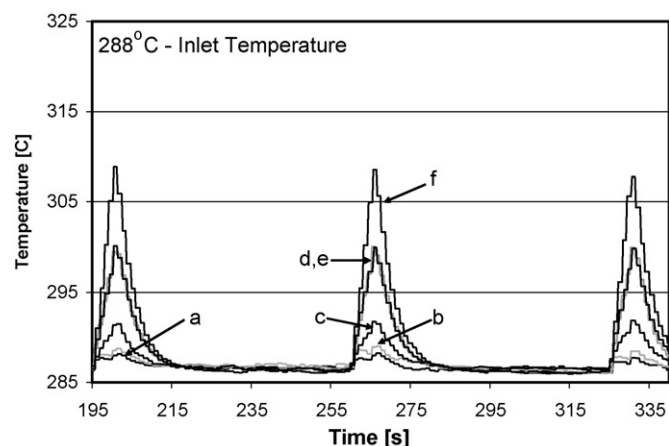


Fig. 5. Temperature data obtained from the thermocouple set just inside the inlet face of the model catalyst with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 1.2% and 0%, (c) 1.8% and 0.3%, (d) 2.8% and 0.9% and (e) 3.8% and 1.4%, respectively. These were obtained simultaneously to the data shown in Fig. 4.

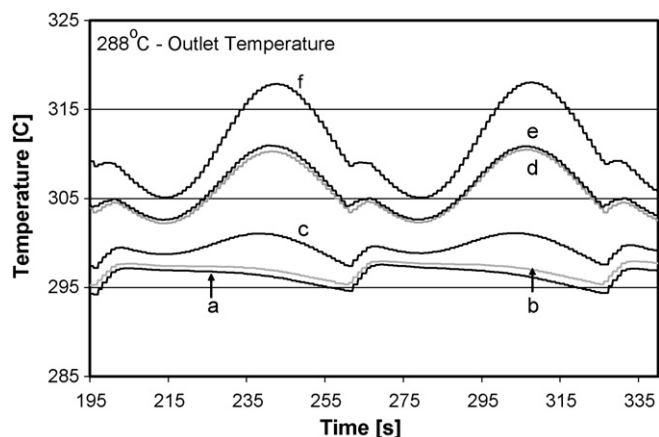


Fig. 6. Temperature data obtained from the thermocouple set just inside the outlet face of the model catalyst with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 1.2% and 0%, (c) 1.8% and 0.3%, (d) 2.8% and 0.9% and (e) 3.8% and 1.4%, respectively. These were obtained simultaneously to the data shown in Fig. 4.

offset by improved NO oxidation, nitrate formation and improved regeneration of the surface for the subsequent trapping phase. Therefore, NSR catalyst performance typically improves with increasing temperature until it reaches somewhere between 300 and 400 °C [16–23,30]. Above this range, nitrate instability and NO oxidation thermodynamic limitations become more significant, and decreased performance is observed, primarily through a lack of catalyst trapping capacity. To further verify that the effects observed and discussed above were from an increase in the average catalyst temperature, the same set of experiments was run at a nominal inlet temperature of 463 °C, above the range where an increase in temperature should improve performance. The performance data obtained are presented in Fig. 7. The released amounts during regeneration for each test were identical, and therefore the range of the y-axis has been stopped at 300 ppm to better show differences in the trapping phase. At the beginning of the trapping phase, the performance was indeed better when no O₂ was added to the regeneration gas mixture. At approximately

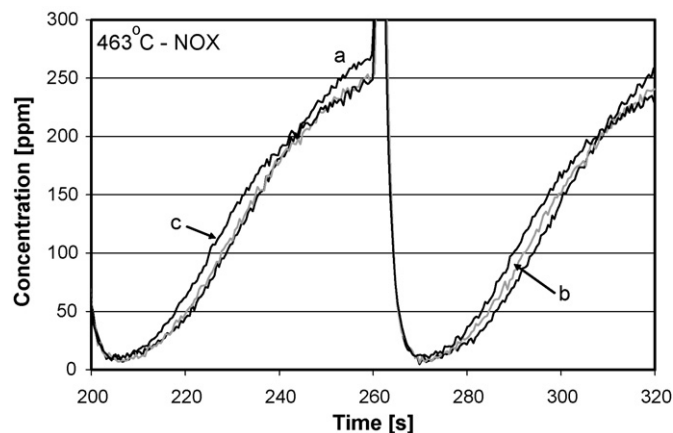


Fig. 7. NO_x concentration obtained using the model catalyst at an upstream temperature of 463 °C with reductant and O₂ concentrations in the regeneration phase of (a) 1% and 0%, (b) 2.8% and 0.9% and (c) 3.8% and 1.4%, respectively.

40 s after trapping began however, the outlet NO_x concentration in the experiment with no O₂ in the regeneration phase began to exceed that of the experiments with O₂. This was also the time where the outlet temperature had just passed through its maximum in the experiments with O₂. As the sample which had been exposed to O₂ during regeneration cooled, nitrate stability increased and therefore more NO_x could be trapped. Overall however, as the data listed in Table 1 show, with the addition of O₂ into the regeneration gas-phase mixture, there was a decrease in trapping performance during the 60-s lean phase, caused by an increase in the average catalyst temperature. There was little change in the observed NH₃, ranging from 38.2 to 44.4 μmol measured.

The significance of the effects presented above becomes more evident when describing the difference in times needed prior to a regeneration trigger. For the 288 and 463 °C tests, an arbitrary trigger to demonstrate the effect was set at 100 ppm and the resulting times to begin a regeneration event are plotted in Fig. 8. For the 375 °C test, an 80 ppm trigger was chosen. As an example of how this corresponds to performance, these triggers correspond to 69, 90 and 93% of the incoming amount of NO_x trapped for the 288, 375 and 463 °C tests with no O₂ during regeneration, respectively. The chosen trigger values are higher than those targeted in engine applications, but this is a model sample and as will be shown below, similar trends were observed with a commercial catalyst that has higher trapping capacity and overall conversion efficiency. At 288 °C, the time prior to 100 ppm breakthrough increased from 7 to 16 s with the addition of 1.4% O₂ but maintaining an excess reductant amount of 1.0%. At 375 °C, the effect was less significant, with an increase from 41 to 49 s. At 463 °C, the time prior to 100 ppm breakthrough decreased from 22 to 18 s with the same addition of O₂ and reductant. These trends match the discussion above and are related to the temperature increases that occur with O₂ addition into the regeneration gas mixture. These data also indicate that the positive effect will be more significant at lower operating temperatures, as is expected.

Commercial NSR catalysts will likely include an OSC component, especially if applied to lean-burn gasoline engines

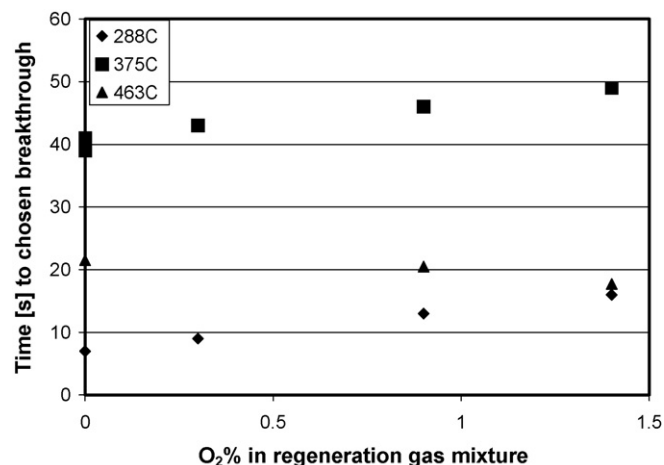


Fig. 8. Trapping time when 100 ppm for the 288 and 463 °C experiments and 80 ppm for the 375 °C experiment was reached.

where some operating conditions rely on three-way catalysis and not solely NO_x storage/reduction chemistry. With OSC, introduction of the reductant during the regeneration phase will result in heat generated due to the oxidation of the reductant with the oxygen associated with that OSC component. Even with no O_2 purposefully added during the regeneration phase, temperature increases of $>30^\circ\text{C}$ at the outlet of a commercial NSR catalyst have been observed [13].

Experiments were performed at 248°C with a manufacturer-supplied sample and the inlet and outlet thermocouple temperature data obtained during this experiment are plotted in Fig. 9. Note, the cycle time was changed, from 60/5 s lean and rich in the experiments above, to 240/5 s lean and rich for this experiment. This was done so that changes in performance could be observed; using the shorter trapping time resulted in 0 or near-0 ppm breakthrough during the lean phase. Also, the amount of reductant was increased to 4% without any O_2 added, in order to compensate for the amount of OSC. This was not done quantitatively to match the experiments above. As shown, with no O_2 added during the regeneration phase the inlet temperature rose 8°C and began decreasing as soon as the reactor gas mixture was switched back to the lean-phase composition. A 28°C temperature rise was observed at the outlet. There was a small shift in where the maximum was reached as a function of time between the two, with the outlet maximum reached after the inlet of course. Unlike the temperature patterns observed with the model sample, the maximum at the outlet was reached very shortly after that at the inlet. This is due to the heat generated from the reaction between the OSC and reductant rather than solely a conduction effect. The OSC is present throughout the length of the sample, so heat was being generated with the presence of the reductant “front” passing through/along the monolith channel. There was still evidence of conduction or heat being retained by the monolith, and was evident at the end of the first lean phase, plotted between 50 and 200 s in Fig. 9.

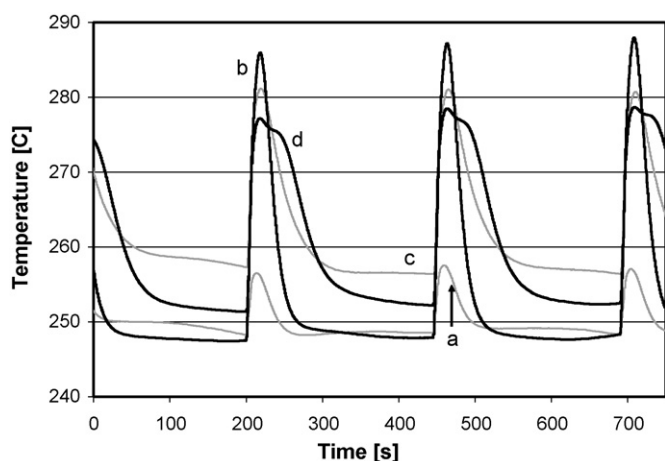


Fig. 9. Temperature data obtained from the thermocouples set just inside the inlet and outlet faces of the commercial catalyst with reductant and O_2 concentrations in the regeneration phase of (a-inlet) and (b-outlet) 4% and 0%, (c-inlet) and (d-outlet) 6% and 2% respectively. These were obtained simultaneously to the data shown in Fig. 10.

The thermocouple data obtained when 1% O_2 was added to 6% reductant, and therefore comparable to 4% reductant and 0% O_2 , are also plotted in Fig. 9. Again, temperature increases were observed at both the inlet and outlet with the switch to the regeneration gas mixture due to the reaction between reductant and the OSC component. There was a larger increase at the inlet than was observed when no O_2 was added, due again to reductant oxidation, but now there is a ready/continuous source of O_2 beyond the surface-stored oxygen from the previous lean phase. Once the reactor gas mixture was switched back to the lean mixture, the temperatures at both locations began to decrease. The inlet decreased monotonically, reaching 250°C 50 s after the switch. The outlet decreased regularly for approximately 30 s, but then a second temperature increase feature became evident. This is associated with the conduction from the inlet positions, where oxidation was occurring with gas-phase O_2 as the reactant during the regeneration phase. These data demonstrate that there was an overall increase in the catalyst temperature during the lean phase when O_2 was added during the regeneration phase. This increase translates to an increased average catalyst temperature during a complete lean/rich cycle.

The coincident NO_x breakthrough data are shown in Fig. 10. The addition of O_2 and proportionally increasing the reductant amount again resulted in improved performance. Choosing, arbitrarily, 80 ppm as a breakthrough regeneration trigger, the O_2 addition increased the time between regeneration events by 27 s. Furthermore, as the lean-phase progressed, the difference in the outlet NO_x concentration values decreased, suggesting that as the temperatures converged, similar trapping rates were occurring.

These results demonstrate that although there is already a significant temperature rise during regeneration of a commercial catalyst due to the presence of surface-stored oxygen, additional O_2 in the regeneration phase can still have a positive effect on trapping. This improved observed performance for both the model and commercial samples admittedly comes at the price of additional reductant to compensate for the additional O_2 . However, if there is already residual O_2 in the regeneration gas mixture, incompletely removed from whatever

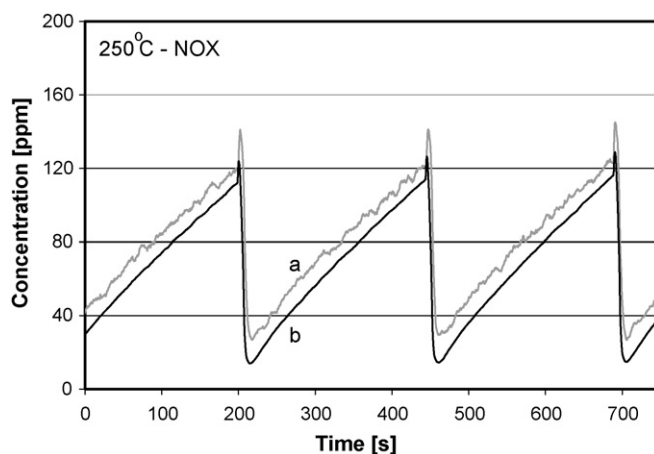


Fig. 10. NO_x concentration obtained using the commercial catalyst at an upstream temperature of 248°C with reductant and O_2 concentrations in the regeneration phase of (a) 4% and 0% and (b) 6% and 2%, respectively.

upstream process is generating the reductant gases, this may not have a negative effect on performance, if the operating temperature is low enough. Furthermore, this alternative can be pursued for engine performance and fuel use optimization for catalyst warm-up strategies. Rather than using the engine to warm-up the exhaust gas for improving catalyst performance, residual O₂ might be used to do the same. Which is preferable will of course depend on the extent of temperature change needed, while at the same time not adding too much O₂ so that rich conditions cannot be met. Therefore, in tuning the upstream reductant-generating process, trade-offs between amounts of residual O₂, NO_x reduction efficiency and amount of reductant generated should be evaluated. Fuel efficiency and engine performance optimization consideration should be additionally based on the exhaust/catalyst temperature, and not solely target complete removal of any O₂. Sacrificing efficiency or extra fuel to completely remove O₂ from the regeneration gas composition is not warranted at low catalyst temperatures.

4. Conclusions

In this study, the effects of including O₂ during the regeneration phase using a model NSR catalyst and a commercial NSR catalyst were investigated. With the model sample, improved performance at temperatures below 375 °C was observed when O₂ was added and while keeping excess reductant available for NO_x reduction consistent. The performance increase was attributed to increased catalyst temperature associated with reductant oxidation when oxygen was available. The increased performance was evident in both the subsequent lean phase with increased trapping and decreased byproduct, NH₃ specifically, concentrations measured during the rich phase under some conditions. Decreased performance was observed at higher temperatures when O₂ was added to the regeneration mixture due to a more dominant effect of decreased nitrate stability. Similar trends were observed with a commercial sample, although the presence of oxygen storage from an added OSC component resulted in an unavoidable temperature increase with no O₂ added in the regeneration gas composition.

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References

- [1] L. Campbell, R. Danzinger, E. Guth, S. Padron, U.S. Patent 5,451,558, 1994.
- [2] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, *Catal. Today* 27 (1996) 63.
- [3] W. Epling, L. Campbell, A. Yezerets, N. Currier, J. Parks, *Catal. Rev.* 46 (2004) 163.
- [4] J. Parks, A. Watson, G. Campbell, B. Epling, SAE Technical Paper Series 2002-01-2880.
- [5] J. Stang, D. Koerberlein, M. Ruth, SAE Technical Paper Series 2001-01-2065.
- [6] C. Webb, P. Weber, M. Thornton, SAE Technical Paper Series 2004-01-0585.
- [7] Y. Kong, S. Crane, P. Patel, B. Taylor, SAE Technical Paper Series 2004-01-0582.
- [8] D. Tomazic, M. Tatur, M. Thornton, SAE Technical Paper Series 2004-01-0581.
- [9] K. Makatani, S. Hirota, S. Takeshima, K. Itoh, T. Tanaka, SAE Technical Paper Series 2002-01-0957.
- [10] B. West, S. Huff, J. Parks, S. Lewis, J.S. Choi, W. Partridge, J. Storey, SAE Technical Paper Series 2004-01-3023.
- [11] S. Huff, B. West, J. Parks, M. Swartz, J. Green, R. Graves, SAE Technical Paper Series 2006-01-1416.
- [12] A. Amberntsson, H. Persson, P. Engstrom, B. Kasemo, *Appl. Catal. B: Environ.* 31 (2001) 27.
- [13] W. Epling, A. Yezerets, N. Currier, *Catal. Lett.* 110 (2006) 143.
- [14] J. Parks, S. Huff, J. Pihl, J.S. Choi, B. West, SAE Technical Paper Series 2005-01-3876.
- [15] A. Jaree, H. Budman, R. Hudgins, P. Silveston, V. Yakhnin, M. Menzinger, *Catal. Today* 69 (2001) 137.
- [16] M. Brogan, J. Brisley, J. Moore, A. Clark, SAE Technical Paper Series 962045.
- [17] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson, G. Smedler, *J. Catal.* 183 (1999) 196.
- [18] L. Lietti, P. Forzatti, I. Nova, E. Tronconi, *J. Catal.* 204 (2001) 175.
- [19] Y. Li, S. Roth, J. Dettling, T. Beutel, *Top. Catal.* 16/17 (2001) 139.
- [20] C. Schenk, J. McDonald, B. Olson, SAE Technical Paper Series 2001-01-1351.
- [21] P. Blakeman, P. Andersen, H. Chen, J. Jonsson, P. Phillips, M. Twigg, SAE Technical Paper Series 2003-01-0045.
- [22] M. Takeuchi, S. Matsumoto, *Top. Catal.* 28 (2004) 151.
- [23] L. Gill, P. Blakeman, M. Twigg, A. Walker, *Top. Catal.* 28 (2004) 157.
- [24] D. James, E. Fourre, M. Ishii, M. Bowker, *Appl. Catal. B: Environ.* 45 (2003) 147.
- [25] H. Abdulhamid, E. Fridell, M. Skoglundh, *Top. Catal.* 30/31 (2004) 161.
- [26] J. Pihl, J. Parks, S. Daw, T. Root, SAE Technical Paper Series 2006-01-3441.
- [27] L. Cumarantunge, S. Mulla, A. Yezerets, N. Currier, W. Delgass, F. Ribeiro, *J. Catal.* 246 (2007) 29.
- [28] J. Theis, E. Gulari, *Appl. Catal. B: Environ.* 74 (2007) 40.
- [29] J. Theis, E. Gulari, *Appl. Catal. B: Environ.* 75 (2007) 39.
- [30] R. Muncrief, P. Khanna, K. Kabin, M. Harold, *Catal. Today* 98 (2004) 393.