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Spatially resolved in situ measurements of transient species breakthrough during cyclic, low-temperature regeneration of a monolithic Pt/K/Al₂O₃ NO_x storage-reduction catalyst

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Abstract

We employed a new experimental technique known as spatially resolved capillary-inlet mass spectrometry (SpaciMS) to observe the evolution of multiple species inside the channels of a monolithic NO_x storage-reduction (NSR) catalyst. The NSR material consisted of a Pt/K/ Al₂O₃ washcoat deposited inside cordierite monolith channels. Spatially and temporally resolved measurements were made over the monolith length in a bench flow reactor during fast cycling between synthetic lean and rich environments at 200 and 300 °C. Regeneration was found to be very efficient at 300 °C regardless of whether pure H₂, pure CO, or mixtures of H₂ and CO were employed. At 200 °C, CO was noticeably less effective than H₂. We conjecture that at 200 °C CO may be inhibiting the regeneration process through its strong adsorption on Pt. Generation of H₂ by water-gas shift was seen at 300 °C but not at 200 °C.

Keywords: NO_x storage-reduction; Lean NO_x trap; Pt/K/Al₂O₃; Monolith; Regeneration; Spatially resolved speciation; SpaciMS; Water-gas shift reaction

1. Introduction

Lean-burn engines (such as diesels and gasoline direct injection engines) are generally more fuel-efficient than stoichiometric gasoline engines and emit less carbon dioxide. Thus there are both economic and environmental incentives to equip vehicles with lean-burn engines. However, lean-burn engines still require supplemental exhaust aftertreatment to meet planned emission standards [1]. Conventional three-way catalysts are highly effective for control of NO_x, CO, and hydrocarbons (HCs) from stoichiometric exhaust [2,3], but the technology for removal of nitrogen oxides (NO_x) from lean exhaust is still not fully developed. Specifically, the excess oxygen present in lean exhaust competes with NO_x for available reductants (CO, HCs), and significantly decreases

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 NO_x reduction efficiency of conventional three-way catalysts.

Several technologies have been proposed for lean NO_x removal, and one of these, the NO_x storage-reduction (NSR) catalyst, is now considered a promising candidate [4]. Also known as lean NO_x traps (LNTs) or NO_x adsorber catalysts (NACs), NSR catalysts combine NO_x storage components (in general, alkali- or alkaline-earth metal) with more conventional-supported precious metals [5,6]. Under typical lean exhaust conditions, NSR catalysts reversibly store NO_x as nitrates or nitrites (storage step). During short periodic excursions to rich conditions the stored NO_x is released and reduced (regeneration step). Current literature [5–9] suggests that the main scenario for NO_x storage and regeneration can be summarized as follows:

- Under lean conditions, NO is oxidized on precious metal sites to NO₂.
- Acidic NO₂ transports to and reacts with the basic alkali-/ alkaline-earth components to form stable surface nitrates.

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- During rich conditions, stored nitrates are decomposed to NO_x by interaction with reductant molecules and this process is catalyzed by precious metal.
- "Released" NO_x is reduced to N₂ on precious metal sites consuming available reductants.

Despite this general understanding, the mechanistic details are not fully understood, especially with respect to regeneration.

In practice, the intermittent rich conditions for NSR catalyst regeneration are typically created by injecting additional fuel in the engine while decreasing the intake air flow [10]. An important technical challenge is to maximize regeneration efficiency in order to minimize the resulting fuel consumption penalty. In this context, it is critical to acquire fundamental knowledge about the chemistry involved in NSR catalyst regeneration. Indeed, detailed information about the nature and relative reductive "power" of different reductants generated during rich engine operation, the specific catalytic reactions involved, and the global regeneration mechanisms will help to build a reliable kinetic model of NSR catalysis. A good model will, in turn, not only permit fuel-efficient control of NSR catalyst operation but also facilitate the design and engineering of better catalyst.

In catalysis research, it is often useful to study the evolution of the reaction mixture composition as a function of reaction time to understand the underlying reaction kinetics and mechanisms [11,12]. In the case of steady-state reactors, the composition of reaction effluents is usually analyzed at different space velocities to obtain data about composition versus reaction time or residence time (inverse of space velocity). In practice, the space velocity can be changed either by changing the total flow rate of the reactant stream at a given catalyst volume, or by changing the catalyst volume while maintaining a constant total flow rate. However, reaction rate measurements are especially challenging with NSR catalysts because they inherently function only in transient modes. In particular, spatiotemporal effects that depend on initial conditions, space velocity, and monolith channel length are of central importance. Therefore, it is important to understand the dynamic chemistry along the monolith channels as it develops over space and time.

Researchers in the Fuels, Engines, and Emissions Research Center (FEERC) at Oak Ridge National Laboratory (ORNL) have developed a new measurement technique referred to as spatially resolved capillary-inlet mass spectrometry (SpaciMS) to study the dynamic chemistry of NSR catalysts [10,13]. "SpaciMS" employs fused-silica capillary tubes that are inserted axially into monolith channels for minimally invasive sampling of reaction mixtures at different locations. Extracted gas samples are analyzed with a mass spectrometer to provide highly timeresolved species concentration measurements. The technique is minimally invasive both in terms of its sampling rate, ca. 10 μ L/min, and probe size, ca. 185 μ m. The capillary sampling probes can be positioned at multiple axial and/or radial locations to build up a detailed spatio-temporal picture of the reaction and breakthrough fronts.

In the present work, SpaciMS was applied in a bench flow reactor to study the chemistry and kinetics involved in regeneration of a monolithic Pt/K/Al₂O₃ NSR catalyst. During transient operations alternating between simulated lean and rich environments, the gas composition was analyzed in situ by SpaciMS. Special attention was given to the intra-channel evolution of different species, in an effort to understand the nature and sequence of reactions involved. H₂, CO, and mixtures of both gases were injected as reductants and the resulting NO_x release and reduction behavior was compared. H₂ and CO were selected for this study because they are frequently the dominant reducing species produced during rich operation of lean-burn engines [10].

The temperature range of 200-300 °C was selected for this study, based on previous observations that this same type of Pt/K/Al₂O₃ catalyst showed very different performance over this range [14]. This is also a temperature range of particular relevance to certain lean exhaust engines and for most engines during cold start. Other studies have previously found that K-containing NSR catalysts also have reduced low-temperature performance compared to Ba-based catalysts [15,16]. Thus we expected that SpaciMS might be useful for understanding these known performance transitions.

2. Experimental

A Pt/K/Al₂O₃/cordierite catalyst was prepared and provided by a catalyst manufacturer (EmeraChem). The substrate was 31 cells per cm² Rauschert cordierite monolith. The monolith was dipped into an aqueous slurry containing a high surface area ($160 \text{ m}^2 \text{ g}^{-1}$) alumina. Excess solution was drained, the sample was allowed to dry, and then was calcined for 1 h in ambient air. The platinum and potassium components were then added by incipient wetness methods. First, a proprietary platinum salt dissolved in water was impregnated onto a coated monolith and calcined in ambient air. Potassium was subsequently deposited by using aqueous carbonate solution and the sample was dried in ambient air. For the bench reactor study, a sample was removed from the monolith block by boring out a 1.9 cmdiameter and 9.2 cm-long core.

All measurements were made with the NSR monolith core inserted in a bench flow reactor. The catalyst core was wrapped in glass fiber insulation tap before its insertion into the reactor tube. The bench flow reactor consisted of a 2.2 cm-i.d. quartz tube enclosed in an electric furnace, which stabilized the reactor at specified isothermal conditions. Simulated exhaust gas was mixed from cylinders, metered through mass flow controllers, and pre-heated before entering the quartz tube. Water was vaporized and added to the simulated exhaust mixture, but CO_2 was not included in the inlet gas in these experiments so that CO could be indirectly observed by the CO_2 it formed.

A rapid switching valve system was provided to alternate between the lean and rich gas mixtures (with mixed flows already fully established) so that the lean/rich/lean transitions in these experiments were almost instantaneous. Before every series of measurements, the catalyst sample was pre-treated in flowing 2% H₂/N₂ at 300 °C to establish a consistent initial surface condition. Possible catalyst deactivation was checked for by performing standardized NO_x storage runs at regular intervals after H₂ pre-treatment. No significant deactivation was observed during this study. For cyclic operation of the NSR catalyst, the fully regenerated catalyst was exposed to alternating lean (56 s) and rich (4 s) mixtures at a given temperature. Table 1 lists the conditions of the storage and regeneration steps. The gas mixture composition was identical for all experimental runs, except the nature of reductant used in the regeneration step (H_2, CO) or equimolar mixture of H_2 and CO).

Under the cycling conditions described above, the observed catalyst breakthrough profiles stabilized to a fixed limit cycle in about 1–2 h. We were then able to characterize the spatial performance in terms of the 'stationary' concentration cycles observed at different locations with SpaciMS. Total NO_x concentration was also measured with conventional heated chemiluminescent detectors (California Analytical Instruments, 400-HCLD) at both the inlet and the outlet of the reactor.

The mass spectrometer, employed in this study had a magnetic-sector mass filter, which allows quantitative measurement of H₂ [17] as well as total NO_x, O₂, and CO₂. The high temporal resolution of the SpaciMS was sufficient to resolve the fast species transients inherent to NSR catalyst operations. A minimally invasive capillary-inlet system was employed to transport time-varying species pools to the mass spectrometer for analysis. A capillary probe was introduced from the reactor inlet and positioned at one of the five reactor locations along the 9.2 cm-long core (catalyst-inlet, 1/4 length, 1/2 length, 3/4 length, catalyst-outlet). The 1/4-, 1/2-, and 3/4-length locations were inside a single channel of the core monolith positioned near the catalyst center.

 Table 1

 Conditions of the storage and regeneration steps

	Storage (lean)	Regeneration (rich)
Duration (s)	56	4
Space velocity (h^{-1})	25000	25000
NO (ppm)	300	0
$O_2(\%)$	12	0
Reductant ^a (%)	0	0.5
H ₂ O (%)	5	5
N ₂	Balance	Balance

^a H₂, CO or equimolar mixture of H₂ and CO.

3. Results

SpaciMS measurements of NO_x, O₂, H₂, and CO₂ were made for three different reductant mixtures during regeneration (0.5% H₂, 0.5% CO, and 0.25% H₂ + 0.25% CO). In addition, two different nominal operating temperatures (200 and 300 °C) were studied. The evolution of H_2 and total NO_x (NO + NO₂) was followed by monitoring the m/z 2 and 30 signals, respectively. The m/z 30 signal provides a quantitative total NO_x measurement [13]. It was not possible to follow CO dynamics directly by monitoring m/z 28, because the N₂ balance gas produces an abundant interference at m/z 28. Therefore, CO₂, i.e. oxidized CO, was monitored at m/z 44 to understand the chemistry involving CO. There is potential for N2O interference (also at m/z 44) of the CO₂ measurement, but our preliminary study showed that the amount of N2O formed under these conditions was very small compared to CO_2 concentration. Therefore, the large disparity between the maximum possible N2O and CO2 concentrations in our work makes the potential impact of N₂O interference on CO₂ measurements negligible. To establish the timing of lean-to-rich and rich-to-lean transitions, O2 concentration changes (12% for lean/0% for rich) were monitored at m/z = 32.

3.1. NSR catalyst performance with 0.5% H_2 as reductant for the regeneration step

Fig. 1a-c summarizes the transient NO_x , O_2 , and H_2 breakthrough profiles obtained by SpaciMS, at different catalyst locations for the 300 °C experiment with 0.5% H₂ reductant. Regeneration inception was marked by a step decrease in NO_x and O₂ concentrations (Fig. 1a and Fig. 1b, respectively) and a step increase in H₂ concentration (Fig. 1c) at the catalyst-inlet. Inside the catalyst, a sharp NO_x peak was observed early in the regeneration phase. Fig. 1a clearly shows that regeneration was not complete during the steady-state cyclic operation of the NSR catalyst because of the non-zero NO_x breakthrough at the beginning of each storage phase. This incomplete regeneration resulted in an overall NO_x conversion of about 50%, but it provided sufficient NO_x breakthrough to clearly delineate the NO_x front as it traversed the intra-catalyst sampling locations during storage.

Taking into account the amount of reductant introduced during the 4 s regeneration step (ca. 2% s) and the total amount of NO introduced during 56 s storage step (ca. 1.68% s), the ratio of the H₂ consumed to the NO_x removed was estimated to be of about 2.4. This value is in good agreement with previously reported data [18,19]. A large portion of the reductant was consumed within the first 1/4 of catalyst, and the reductant was fully depleted by the 1/2 catalyst position (Fig. 1c). This is consistent with the corresponding NO_x profiles which show little evolution beyond the 1/2 catalyst position (Fig. 1a). And this is further



Fig. 1. Spatially resolved in situ breakthrough profiles of (a) NO_x, (b) O₂, and (c) H₂ during cyclic operation of a monolithic Pt/K/Al₂O₃ NSR catalyst at 300 °C with 0.5% H₂ reductant.

evident in the evolution of cycle-averaged conversion over the five sample locations as shown for NO_x and H_2 in Fig. 2a.

The overall NO_x removal efficiency at 200 °C was almost identical to that at 300 °C, and nearly 50% NO_x conversion was obtained at the catalyst-outlet (Fig. 2b). However, intra-channel monitoring indicated that a broader portion of the catalyst was used (i.e., there was deeper penetration of the reductant fronts) at 200 °C compared to that at 300 °C. Indeed, H₂ was still available at the 1/2 catalyst position and further consumed between 1/2 and 3/4 catalyst positions (Fig. 2b). Accordingly, catalyst regeneration and NO_x storage extended deeper into the catalyst at 200 °C.

3.2. NSR catalyst performance with 0.5% CO as reductant for the regeneration step

Fig. 3 summarizes the NO_x and CO₂ breakthrough profiles for regeneration with 0.5% CO reductant at 300 °C. Carbon monoxide consumption was almost complete at the 1/4 catalyst position, as deduced from CO₂ profiles (Fig. 3b). Accordingly, little change in the NO_x profile was observed beyond the 1/4 catalyst position (Fig. 3a). A sharp NO_x peak was observed early in the regeneration step, its maximum increased slightly from 1/4 to 1/2 positions and then stabilized (Fig. 3a). The overall NO_x conversion approached 50%, indicating a ratio of the CO consumed to the NO_x removed of about 2.4.



Fig. 2. NO_x and H₂ conversion at different axial locations during cyclic operation of a monolithic Pt/K/Al₂O₃ NSR catalyst at (a) 300 °C and (b) 200 °C with 0.5% H₂ reductant.



Fig. 3. Spatially resolved in situ breakthrough profiles of (a) NO_x and (b) CO₂ during cyclic operation of a monolithic $Pt/K/Al_2O_3$ NSR catalyst at 300 °C with 0.5% CO reductant.



Fig. 4. NO_x and CO conversion at different axial locations during cyclic operation of a monolithic $Pt/K/Al_2O_3$ NSR catalyst at (a) 300 °C and (b) 200 °C with 0.5% CO reductant.

In Fig. 4a, the cycle-averaged CO conversion at 300 °C is based on the amount of CO₂ produced during the entire storage/regeneration cycle compared to the nominal total amount of CO introduced during regeneration. Even though the maximum CO conversion deduced from CO₂ production was about 80%, we believe that the actual CO conversion was almost 100% even at 1/4 catalyst position, as little change occurred beyond this position. Indeed, the cycleintegrated CO₂ values were constant within ca. 5% over the back three quarters of the reactor indicating complete CO consumption over this spatial reactor region and an independent NDIR (Non-Dispersive IR) measurement of CO concentration indicated no significant CO slip at the reactor outlet (result not shown here). As explained later in this section, CO_2 evolution from the catalyst surface continued well beyond the rich phase and very long CO_2 desorption was observed during the lean phase (Fig. 3b). The 100 ppm level of this long CO_2 tail was near the detection limit associated with the setup used and made accurate determination of the integrated CO conversion difficult.

Very low NO_x conversion (less than 7%) was observed with CO at 200 °C (Fig. 4b). The effect of temperature on NO_x conversion was even more significant than would be inferred from catalyst-outlet measurements alone. This is demonstrated by the fact that a conversion of nearly 50% was achieved inside the first 1/4 of catalyst at 300 °C (Fig. 4a), while the conversion of 7% at 200 °C was obtained over the entire catalyst length (Fig. 4b). The CO



Fig. 5. Comparison of breakthrough profiles at different axial locations just before, during, and just after catalyst regeneration at 300 °C with 0.5% CO reductant: (a) O_2 , and CO_2 ; (b) O_2 and NO_x .



Fig. 5. (Continued).

consumption also decreased, but the amount of CO_2 produced (therefore that of CO consumed) was significantly higher than the amount necessary for the 7% NO_x reduction considering the ratio CO/NO_x of 2.4.

Figs. 5 and 6 compare CO₂, O₂, and NO_x breakthrough profiles at the five catalyst locations at 300 and 200 °C, respectively, to better understand the chemistry involved during NSR catalyst regeneration with CO. The O₂ profiles establish the timing of lean-to-rich and rich-to-lean switching. Only the range from 49 to 60 s (of a 60 s cycle) is shown in Figs. 5 and 6 to detail the regeneration step. As previously shown in Fig. 4, Fig. 5a indicates that CO₂ formation at 300 °C occurred immediately with regeneration inception, and CO conversion was nearly complete by the 1/4 catalyst location. Corresponding NO_x profiles also show little change beyond the 1/4 location except some minor increase in initial NO_x peak (Fig. 5b). Apparently, a constant level of CO consumption was maintained during the entire regeneration phase. An interesting point is that the CO₂ concentration decreased from the 1/4 catalyst location through the catalystoutlet during the early regeneration times (Fig. 5a). Moreover, CO₂ evolution did not stop immediately at the end of the regeneration phase as did O₂, rather CO₂ concentration decreased slowly and continually into the early lean phase times as we mentioned above. It indicates that some CO₂ was stored on catalyst surface during regeneration and released during the subsequent storage phase. Recently, Toops et al. have confirmed, by quantitative DRIFTS analysis, carbonates formation on Pt/K/Al₂O₃ catalyst in the presence of CO_2 [20].

Very different CO_2 profiles were obtained at 200 °C (Fig. 6a), as compared to the 300 °C results (Fig. 5a). The most obvious difference is the two distinct peaks at 200 °C which appear to correspond in time to the lean-to-rich and rich-to-lean transitions. This indicates that some CO conversion occurred at the leading edge of the regeneration phase, but CO conversion (CO₂ production) was continually and substantially slowed down during the body of the regeneration phase. At the regeneration phase trailing

edge, CO_2 production again sharply increased producing the second peak of greater intensity than the first. Overall, CO conversion was much slower and more progressive along the catalyst length at 200 °C, compared to the behavior at 300 °C. Very low regeneration performance at 200 °C is also obvious from the corresponding NO_x profiles (Fig. 6b).

3.3. NSR catalyst performance with a mixture of 0.25% H_2 and 0.25% CO as reductant for the regeneration step

The overall (cycle-average) NO_x conversion at 300 $^{\circ}$ C with an equimolar mixture of H₂ and CO peaked at near 50%



Fig. 6. Comparison of breakthrough profiles at different axial locations just before, during, and just after catalyst regeneration at 200 $^{\circ}$ C with 0.5% CO reductant: (a) O₂, and CO₂; (b) O₂ and NO_x.



Fig. 6. (Continued).

by the 1/2 catalyst position (Fig. 7a). As expected, H₂ and CO consumption was also rapid, and major reductant depletion occurred within the first 1/4 of the catalyst (Fig. 7a). In fact, CO consumption appears to have been faster than H₂ consumption. Specifically, a finite amount of H₂ remained available at the 1/4 catalyst position, whereas CO was apparently fully depleted by the 1/4 catalyst position as indicated by the invariant CO_2 pulse area at the 1/4 catalyst position and beyond.

The NO_x conversion at 200 $^{\circ}$ C with an equimolar mixture of H₂ and CO decreased significantly compared to that at 300 °C (Fig. 7b). Based on the catalyst-out measurements, the cycle-averaged NO_x conversion was about 50% at 300 °C (Fig. 7a) and about 30% at 200 °C (Fig. 7b); i.e., ca. 40% decrease at the lower temperature. However, the incremental difference in NOx conversion at the two operating temperatures was much more dramatic as demonstrated by intra-catalyst assessments. Based on the 1/4 catalyst location, the cycle-averaged NO_x conversion was 33% (Fig. 7a) and 2% (Fig. 7b) at 300 and 200 $^\circ$ C, respectively; i.e., ca. 94% decrease at 200 °C. Hydrogen consumption was fairly uniformly distributed along the catalyst length, with a small amount (ca. 15% of the inlet concentration) remaining available at the catalyst-outlet (Fig. 7b). The global CO consumption trend generally followed that of H₂ (Fig. 7b). However, the detailed dynamics of CO consumption was significantly different as discussed below.



Fig. 7. NO_x, H₂, and CO conversion at different axial locations during cyclic operation of a monolithic Pt/K/Al₂O₃ NSR catalyst at (a) 300 °C and (b) 200 °C with mixed reductant (0.25% H₂ + 0.25% CO).

Figs. 8 and 9 compare H₂, CO₂, O₂, and NO_x profiles at the five catalyst locations at 300 and 200 °C, respectively. As previously shown, both H₂ and CO consumption occur much faster (i.e. earlier along the catalyst length) at 300 °C (Fig. 8a) compared to 200 °C (Fig. 9a). Accordingly, catalyst regeneration was more efficient at 300 °C (Fig. 8b) than at 200 °C (Fig. 9b). It is noteworthy that the initial NO_x peak was almost absent during the regeneration at 200 °C (Fig. 9b) contrary to at 300 °C (Fig. 8b), suggesting a better balance between NO_x release rate and reduction rate of released NO_x at 200 °C. However, the integrated NO_x peak area even at 300 °C is very small compared to the amount of stored NO_x and therefore does not contribute significantly to overall catalyst performance.

The net CO_2 generated (i.e., area under the CO_2 profile) during regeneration at 300 °C peaked at the 1/4 location and monotonically decreased through the catalyst-outlet location, and a long CO_2 tail was apparent during the early lean phase times (Fig. 8a).

The CO₂ profiles reveal profound differences at 200 °C (Fig. 9a) compared to 300 °C (Fig. 8a). One especially notable feature is the bimodal nature of the CO₂ profile, with the trailing peak growing larger relative to the first as the gas travels downstream. At a given catalyst location, CO conversion began immediately with regeneration inception, but decreased rather quickly as regeneration continued (the early CO₂ peak in Fig. 9a). At the end of regeneration, a sharp second CO_2 peak appeared indicating considerable CO consumption during the subsequent storage step. The detailed H₂ behavior also differed at 200 °C compared to 300 °C in addition to its differences in overall conversion. Indeed, the H₂ conversion level was greater late in time at 300 °C (see Fig. 8a and the asymmetric H_2 profile at the 1/4 position). Conversely, the H₂ conversion level was greater early in time at 200 °C (see Fig. 9a and the H₂ asymmetric profile at 1/4 location). This difference in H₂ breakthrough at the different temperatures was even more apparent at locations deeper into the catalyst.

3.4. Evaluation of water-gas shift performance of the studied monolithic $Pt/K/Al_2O_3$ catalyst during the cyclic operation

To assess the possible contribution of the water-gas shift (WGS) reaction in the presence of CO, the reactor was cycled without NO and O₂ feed during the nominal storage step. Instead, only 5% H₂O + N₂ were added for 56 s and then 0.5% CO, 5% H₂O, and N₂ added for 4 s. Fig. 10a and Fig. 10b show H₂ profiles at different catalyst locations measured by SpaciMS at 300 and 200 °C, respectively. At 300 °C, hydrogen production via WGS reaction was progressive along the catalyst length (Fig. 10a). On the other hand, no WGS reaction could be discerned over the entire catalyst length at 200 °C (Fig. 10b).

4. Discussion

4.1. Comparison of regeneration efficiency among H_2 , H_2/CO , and CO at 300 °C

Overall, very similar NO_x conversion was obtained with the three candidate reductants, H₂, CO, and H₂/CO, at 300 °C. Indeed, both the catalyst-outlet NO_x conversion (ca. 50%) and reductant consumption (ca. 100%) were relatively constant regardless of the reductant used for regeneration (Figs. 2a, 4a, and 7a). In addition, intra-channel NO_x and reductant conversion trends also seem to show no significant dependence on reductant type. This suggests that NO_x release and reduction are similarly effective for all H₂/CO combinations at 300 °C. This also seems to imply that the Pt/ K/Al₂O₃ catalyst studied here behaves consistently with many other NSR catalysts in responding to H₂ and CO at temperatures greater than 250 °C [4–6,18,21].

Detailed consideration of the breakthrough profiles indicates that any differences are probably slight between CO and H_2 at 300 °C. Possible indications of such a slight difference can be seen in the relative breakthroughs of CO

and H₂ at the 1/4 catalyst location, where CO conversion appeared to be a little greater than H₂ conversion (Figs. 2a and 4a). Furthermore, CO conversion also appeared to be greater than H₂ conversion in the case of the equimolar H₂/ CO mixture (Fig. 7a). The cycle-averaged NO_x conversion at the 1/4 catalyst position was slightly greater with CO reductant compared to H₂, and these were both greater than that obtained with the H₂/CO reductant. Li et al. have reported that CO is a more effective reductant than a H₂/CO mixture or C₃H₆ at 300 °C [22]. However, the differences observed in this study were relatively small and it would be difficult to assert that there are major global efficiency differences for CO and H₂ at 300 °C. One potentially important question at this point is whether or not the observed similarity between H₂ and CO at 300 °C might be attributable to the WGS reaction (that is, H₂ could be produced from CO + H₂O and the H₂ product could then act as reductant). In fact, even though no H₂ production was observed during NSR catalyst regeneration, one could suspect intermediate H₂ formation. In the absence of NO_x and O₂ (thus no possibility of consumption of H₂ produced via WGS), Pt/K/Al₂O₃ catalyst did show WGS activity reaching over 60% conversion at catalyst-outlet (Fig. 10a). However, intra-channel monitoring of H₂ production reveals that H₂ conversion at the 1/4 catalyst location was less than 10% (less than 500 ppm H₂ per second) (Fig. 10a). This



Fig. 8. Comparison of breakthrough profiles at different axial locations just before, during, and just after catalyst regeneration at 300 °C with mixed reductant (0.25% H₂ + 0.25% CO): (a) O_2 , H₂, and CO_2 ; (b) O_2 and NO_x .





Fig. 8. (Continued).

conversion level at 1/4 location is expected to be even lower in the presence of NO_x and/or O₂, since WGS reaction should compete with CO + NO_x and CO + O₂ reactions for the limited amount of CO and also possibly catalytic sites. Considering that at 300 °C the 1/4-location CO conversion was near 100% during NSR operation (Fig. 4a), we consider it very probable that CO acted directly as a reductant with a regeneration efficacy comparable to H₂.

Although the impact of WGS reaction on Pt/K/Al₂O₃ NSR catalyst regeneration at 300 $^{\circ}$ C seems negligible, WGS reaction could be beneficial in other circumstances like desulfation, which is a slower process and requires much higher temperatures than denitration. At elevated temperatures, the WGS reaction might be fast enough to provide H₂

for desulfation in a timely manner. Hydrogen is well known for its high desulfation performance compared to CO, and researchers at Ford have reported beneficial effects due to the WGS reaction in desulfation [23,24].

4.2. Comparison of regeneration efficiency among H_2 , H_2/CO , and CO at 200 °C

Several previous studies have concluded that H₂ is a more effective NSR reductant than CO at or below 200 °C [4,21–25]. Our SpaciMS observations of the Pt/K/Al₂O₃ catalyst at 200 °C are consistent with this trend. Specifically, NO_x conversion decreased as the reductant was varied from H₂ > H₂ + CO > CO (Figs. 2b, 4b, and 7b). Also, NO_x

conversion decreased for all three reductants at 200 °C compared to 300 °C. However, the performance decrease for CO was much greater than for H_2 .

For H₂ regeneration, the intra-channel evolution of NO_x and H₂ depletion at 200 °C was more progressive than at 300 °C, but still very efficient [9] reaching a similar level of conversion by the monolith midpoint (Fig. 2b). Regeneration with CO at 200 °C produced very low NO_x conversion efficiency as shown in Fig. 4b (<7% at the monolith exit).

The bi-modal CO₂ breakthrough profile observed with CO regeneration at 200 °C (Fig. 6a) suggests that some process begins to inhibit CO oxidation after the onset of reducing conditions, and then this inhibition process appears

to be reversed as oxidizing conditions return. To explain this bi-modal profile, we conjecture that CO might be poisoning the precious metal pathway for reductant to reach the surface (e.g., by strong adsorption on the precious metal). When oxidizing conditions return, direct oxidation of this CO could reverse the poisoning effect. Our conjecture is further supported by the fact that the cycle-averaged NO_x conversion was much lower than CO conversion estimated from CO₂ production (Fig. 4b): suggesting that a portion of the observed CO₂ was produced by CO + O₂ instead of CO + NO_x.

If the CO inhibition scenario described above is correct, the different behavior at 200 and 300 $^{\circ}$ C might be a result of



Fig. 9. Comparison of breakthrough profiles at different axial locations just before, during, and just after catalyst regeneration at 200 °C with mixed reductant (0.25% H₂ + 0.25% CO): (a) O_2 , H₂, and CO_2 ; (b) O_2 and NO_x .





Fig. 9. (Continued).

the transition between the so-called "high reaction rate branch" and "low reaction rate branch" of the $CO + O_2$ reaction on Pt/Al₂O₃ that has been previously reported [26,27]. If CO oxidation follows the Langmuir–Hinshelwood mechanism, the reaction is known to proceed through interaction between adsorbed CO and oxygen species on the Pt surface [28]. The high reaction rate branch dominates when there is a high level of O on the surface (which would be expected during the lean period), while the low reaction rate branch dominates under conditions favoring a high level of CO coverage (which would occur during the rich period) [26,27]. The low reaction rate branch is also called "CO self-poisoned" [27], since a dense layer of adsorbed CO on the surface prevents O_2 adsorption and thus inhibits oxidation. Low-temperatures and/or low concentrations of oxygen relative to CO favor the low reaction rate branch [26,27].

Mixtures of $H_2 + CO$ (Fig. 7b) exhibited NO_x conversion activity intermediate to the pure H_2 and pure CO. Overall (monolith-out) NO_x conversion with $H_2 + CO$ was 30%, as compared to 50% for H_2 only and 7% for CO only. The internal breakthrough profiles for the mixed reductant better revealed the relative activities of CO and H_2 , however. Specifically, the CO oxidation rate spiked, dropped, and spiked again (Fig. 9a) as in the case of pure CO (Fig. 6a). The peak concentration of the second CO₂ peak (ca. 0.4%) in



Fig. 10. Water-gas shift production of H₂ in the catalyst at (a) 300 °C and (b) 200 °C during 0.5% CO injection.

Fig. 9a was greater than the nominal inlet CO concentration (0.25%), which further suggests that the second CO₂ peak was produced from surface scavenging of CO by O₂ at the front end of the oxidation wave (the subsequent storage step).

If CO poisoning does occur at 200 °C, it is interesting that H_2 continues to show NO_x removal activity (Figs. 7b and 9). This suggests that the highly mobile H_2 may still find available Pt surface sites in spite of high CO coverage. However, even NO_x conversion with H_2 seems to have been reduced, to some extent, by adsorbed CO. In fact, we can resolve that H_2 conversion, at a given catalyst location, was higher at early stages of regeneration and then deteriorated, possibly as the result of increasing CO surface masking (Fig. 9a). As a result, some portion of H_2 exited the catalyst unreacted.

4.3. Hypothesized reaction networks involved in NSR catalyst regeneration

As mentioned in the Introduction section, Miyoshi et al. proposed a simple regeneration mechanism for NSR catalysts based on two global steps: (1) decomposition of stored nitrates into NO_x by activated reductants (i.e., activated on precious metal sites); (2) reduction of "released" NO_x to N_2 on precious metal sites [5,6]. The importance of reductant for step 1 is supported by the fact that little NO_x is released when reductant is absent (for example in He flow), while active NO_x release and reduction occur in the presence of reductants during regeneration [6].

The importance of precious metals in NSR catalyst regeneration was also discussed by Fridell et al. in their study on Pt-Rh/BaO/Al₂O₃ using reactor test, FT-IR, and TPD [7]. More recently, Liu and Anderson reported further supporting evidence for these two steps, but they also suggest that significant NO_x release can be caused by direct interaction of stored NO_x with reductant without activation on Pt [29]. Liu and Anderson also considered other

less-significant mechanisms that may contribute to NO_x release [29]:

- (i) Destabilization of stored NO_x resulting from lower O₂ concentration [30].
- (ii) Displacement of nitrates (of alkali- or alkaline-earth metal) by formation of hydroxides or carbonates in the presence of CO₂ [30,31].
- (iii) Displacement of NO_x from the storage sites to Pt sites in response to removal of NO_2 from Pt sites by reductants [32].

Contrary to the mechanism (ii), Nova et al. have reported little effect of gas phase CO_2 on the regeneration of Pt/Ba/ Al₂O₃ at 300 °C with C₃H₆ reductant [33]. This discrepancy seems to come from temperature differences. Indeed, the papers proposing the mechanism (ii) deal with reaction temperatures much higher than 300 °C [30,31], where the stored nitrates would be less stable.

The transient profiles described in Sections 4.1 and 4.2 seem to confirm the key role played by Pt sites in release and reduction of stored NO_x . For example, CO_2 -induced and/or thermally induced NO_x releases appears to be negligible under the conditions used in this study. Indeed, hardly any change could be observed in NO_x profiles at 300 °C beyond 1/2 position (Fig. 3a), even though a considerable amount of gas-phase CO_2 was present during rich phase as a result of CO consumption at the front portion of the catalyst (Fig. 3b). In addition, the loss of activity at 200 °C might be explained as the result of Pt site poisoning by CO.

Fig. 11 summarizes the CO₂ and NO_x breakthrough profiles at the 1/2 axial position for the 200 °C experiment with CO reductant, illustrating the correspondence between these two species during the regeneration event. At this catalyst position, the cycle-averaged NO_x conversion was less than 2%. At regeneration inception however, NO_x release was immediate and the initial CO₂ peak indicated CO consumption (Figs. 7b and 11). The 2% conversion was



Fig. 11. NO_x and CO₂ breakthrough profiles at the 1/2 axial location during catalyst regeneration with 0.5% CO at 200 $^{\circ}$ C.

probably achieved early in the regeneration event, before inhibition of Pt sites during the subsequent circled period in Fig. 11. Inhibition of H_2 consumption in the presence of CO co-reductant further supports the critical role of Pt (Fig. 9a).

These observations indicate that the non-Pt-dependent mechanisms are of little importance for our catalyst at these temperatures. One obvious missing element in the results reported here is the impact of the large CO_2 concentrations that typically occur in engine exhaust. This would clearly be an area that needs to be addressed in future work.

5. Conclusions

Spatially resolved capillary-inlet mass spectrometry has been applied to study spatio-temporal species profiles inside individual channels of a monolithic NO_x storage-reduction catalyst based on Pt/K/Al₂O₃. These measurements have revealed new information regarding the relative regeneration activity of H₂ and CO for NSR catalysts of this type. Key findings were:

- At 300 °C, NO_x removal and conversion was similarly high for pure H₂, pure CO, and an equimolar mixture of H₂ and CO. Some slightly higher efficiency may have been achieved with CO. For all three reductants combinations, the molar ratio of reductant consumed to NO removed was about 2.4.
- The regeneration performance of our NSR catalyst was significantly lower at 200 °C than at 300 °C for all three reductant combinations. At the lower temperature, H₂ was a significantly better reductant than CO.
- The water-gas shift reaction appeared to have little impact for this catalyst at these temperatures.
- We conjecture that the degradation of CO regeneration efficiency at 200 °C is the result of Pt poisoning by strongly adsorbed CO.

- The detrimental effects of CO at lower temperature also appeared to reduce the efficiency of H₂ when the two reductants are used in combination.
- More studies are needed to refine the details of the regeneration mechanism and the role of precious metals in NSR catalysts.

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