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Ammonia is a hydrogen carrier in the regeneration of $Pt/BaO/Al_2O_3$ NOx traps with H_2

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Abstract

We report that the regeneration of a $Pt/BaO/Al_2O_3$ NOx trap in H_2 occurs through the formation of NH_3 as an intermediate. When NH_3 is used instead of H_2, the reduction process is equivalent and equally effective to using H_2, thus confirming our hypothesis. The regeneration is localized, occurring at the plug flow front and is limited by mass transfer of the gas phase reductant to the catalyst. The process is consistent with the release of NOx from the trapping material, followed by its reduction over Pt. The high selectivity of $Pt/BaO/Al_2O_3$ in forming mostly N_2 during regeneration is achieved by the release of NOx only in the presence of H_2 which guarantees the formation of N_2 and NH_3 and only small amounts of N_2O. An oxygen source on the catalyst support, usually the stored NOx, is necessary for the oxidation of NH_3 to N_2.

Keywords: Mechanism of reduction of NOx traps; $Pt/BaO/Al_2O_3$ NOx traps; Ammonia as a NOx reduction intermediate

1. Introduction

The NOx storage/reduction (NSR) process is one of the technologies in development to abate the NOx ($NO + NO_2$) in the exhaust emitted from combustion engines. This system works by the Pt catalyst transforming the NO in the exhaust to NO_2, which then reacts with a barium or potassium component to form a stable compound, which is periodically reduced to release most of the nitrogen as N_2 [1]. This cycle of oxidation, trapping, release and reduction is performed, for example, with a 60 s capture (oxidation and trapping) followed by a four second regeneration (release and reduction). On a commercial system, the efficiency in transforming the emitted NOx to N_2 is over 95%. This is remarkable, as the Pt itself is selective for the formation of N_2 from NO and H_2 only in a narrow range of NO to H_2 ratio, as reported in the literature [2,3] and as we will show below. A more detailed account of this technology can be found in a recent review [4].

A few studies have been devoted to the analysis of the regeneration or the reduction phase. Burch and Millington [5] proposed a mechanism in which NO is decomposed on reduced Pt sites, and the role of the reductant is to reduce the oxidized Pt to Pt^0, which is capable of reducing NO to N_2. On the other hand, direct reaction between released NOx species and the reductant molecules on the precious metal has also been proposed [6]. Here the debate on the possible mechanism governing NOx release remains open. Kabin et al. [7] proposed that the NOx is released as a result of the heat generated by the exothermic reactions upon switching to the regenerating gases (thermal release), while others have proposed a decrease in the equilibrium stability of the stored nitrates due to either the decrease in the partial pressure of oxygen [8,9] or the establishment of a net reducing environment [9,10]. In addition, Liu and Anderson [9] have proposed a different mechanism of NOx release in which the reductant molecule (or its activated form spilled over from Pt) may interact directly with the stored NOx on the storage component where the nitrates are reduced to nitrites which then release NO and gaseous oxygen. Recently, Nova et al. [11] reported a similar mechanism that involves the activation of H_2 on Pt sites, followed by spillover on the alumina support toward

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nitrate adspecies that decompose to gaseous NOx, which is then reduced on Pt or is directly reduced by spilled over hydrogen. They also included the possibility of a mechanism involving surface diffusion of NOx adspecies toward reduced Pt sites, which reduce the NOx to N_2.

The objective of this contribution is to gain further insight into the mechanism governing the reduction of stored NOx species and provide a model of how the reduction process occurs, including why it is so selective to N_2. We will show that the reduction process can be explained by the release of NO or NO_2 which is then optimally reduced to N_2 or over-reduced to NH_3 on the Pt clusters. If N_2O is formed, most of it continues to react with hydrogen on the Pt surface to form N_2 or NH_3. Most importantly, we will show that the NH_3 formed is as effective as H_2 in the reduction/regeneration process and is eventually transformed to N_2.

2. Experimental methods

The Pt/Al_2O_3 and $Pt/BaO/Al_2O_3$ catalysts used in this study were supplied by EmeraChem in monolithic form. Both monoliths had a cell density of 200 channels per in^2. The Pt loading for both samples was ca. 50 g ft^{-3} of monolith. The Ba loading in the $Pt/BaO/Al_2O_3$ sample was 20 wt%. The Pt/Al_2O_3 sample was cut into a 1-inch long core weighing about 3 g and having a cross-section of 60 channels. The total gas flow rate over this sample was 6.6 L min^{-1} (space velocity of 80,500 h^{-1}). The percentage of metal exposed (PME) or metal dispersion of this catalyst, defined as the ratio of the number of surface Pt atoms to the total number of Pt atoms, was measured by H_2–O_2 titration [12] and was 42%. The $Pt/BaO/Al_2O_3$ catalyst was cut into a 3-inch long core with a cross section of 60 cells. The total flow rate over this sample was 7.0 L min^{-1} corresponding to a gas hourly space velocity of 30,000 h^{-1}. The PME of Pt in this sample was 60%. This gives an exposed Pt content of 6.2 and 8.2 μmol g^{-1} for the Pt/Al_2O_3 and $Pt/BaO/Al_2O_3$ samples, respectively.

The experimental apparatus used for this study is described in detail elsewhere [13] and briefly here. All the experiments reported here were run at 300 °C, except where specified. The NO, NO_2, N_2O, NH_3 and H_2O concentrations in the outlet gas stream were detected with an FTIR gas analyzer (MKS MultiGas™ Analyzer, Model 2030), while the N_2 concentration was detected with a quadrupole mass spectrometer (SRS RGA 200). The mass spectrometer was calibrated to measure N_2 concentrations in the 0–6500 ppm range either by the injection of pulses of known volumes of N_2 or by sampling calibrated N_2/Ar mixtures. Argon was used as the carrier gas to allow for the measurement of the released N_2. Mass flow controllers were used to control all the gas flows except for the experiments where high concentrations (>1000 ppm) of NH_3 and NO were utilized. These flows were controlled through needle valves. The system was automated to switch 3-way valves between lean-rich cycles. Thermocouples were placed 6 mm before and after the catalyst sample to verify inlet and outlet gas temperatures.

3. Results and discussion

Fig. 1 shows a comparison of the evolution of the outlet gas concentrations from a $Pt/BaO/Al_2O_3$ catalyst after the switch to regeneration gases containing either H_2 or NH_3. The solid lines indicate regeneration with 0.75% H_2/Ar and the dashed lines indicate regeneration with 0.53% NH_3/Ar. The number of hydrogen atoms per unit of time flowing over the sample in the regenerating gas mixture was kept nearly identical in both cases to illustrate the effectiveness of H_2 and NH_3 for regeneration. The regeneration phase (ca. 3 min long) was preceded by a 7 min long trapping (lean) phase that contained 350 ppm NO and 10% O_2, balance Ar, and a 5 s purge with Ar. To obtain reproducible results, it was necessary to run 4–5 lean-rich cycles. The nitrogen balance between capture and regeneration phases was found to close within experimental error. After regeneration for 3 min with H_2 or NH_3, the same amount of NOx was stored (0.54 mmol) during the subsequent 7-min capture phase, and the N_2 selectivities for both reductants were similar.

As seen in Fig. 1A, the N_2 and H_2O traces for both regenerating mixtures increase rapidly to a constant value until the end when they sharply decrease. This rectangular wave shape indicates a “plug flow” type of mechanism implying a complete

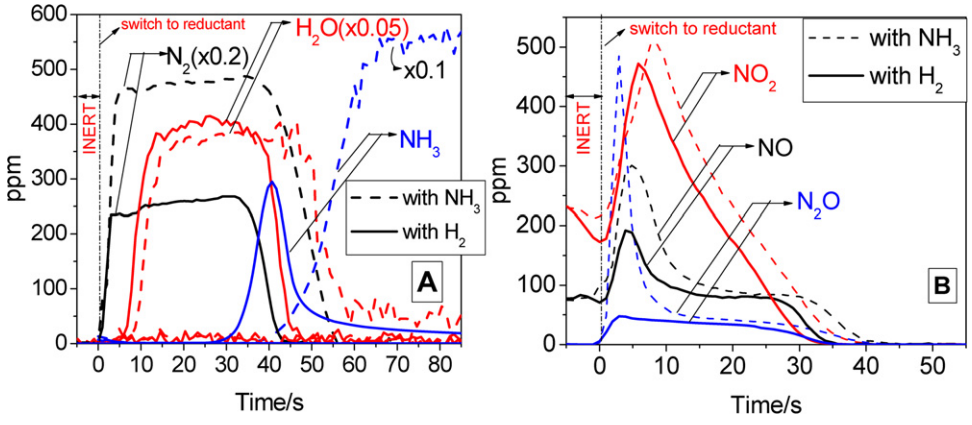

Fig. 1. Evolution of the species after the switch to the regeneration phase following a 7 min trapping period with 350 ppm NO/10%O_2/Ar at 300 °C over a $Pt/BaO/Al_2O_3$ monolith. The solid lines represent regeneration with 0.75% H_2/Ar and the dashed lines represent regeneration with 0.53% NH_3/Ar. The space velocity over the catalyst is 30,000 h^{-1}. (A) N_2, H_2O and NH_3 traces, (B) NO_2, NO and N_2O traces.

reaction between the reductant and the NOx to produce N_2 and H_2O. Since the reductant is the limiting reagent, this implies that the time for regeneration should be inversely proportional to the amount fed per unit time, as we verified experimentally. Note, however, that the data do not provide a mechanism for how the NOx is released from the trapping sites. Fig. 1A also shows that the H_2O and N_2 traces in the case of NH_3 as the reductant continue at constant levels for a 15% longer duration before starting to decrease, when compared to the case with H_2 as the reductant. This difference is caused by the uncertainty in the reproducibility of the total flow rate. The H_2O trace for NH_3 as a reductant did not return to zero because the NH_3/Ar mixture contained H_2O as an impurity. Accounting for this H_2O impurity, the area under the H_2O traces of Fig. 1A for the two reductants are the same within error (ca. 1.39 and 1.31 mmol). The N_2 level is higher when NH_3 is used as the reductant (0.74 mmol vs 0.22 mmol) since in addition to the nitrogen species in the stored NOx, NH_3 also contributes (through oxidation of NH_3 by the NOx) to the total N_2 formed. This makes the calculation of N_2 selectivity less precise.

Since the NH_3 and H_2 (H_2 data not shown since only non-quantifiably small H_2 amounts were observed in the mass spectrometer before breakthrough, and the H_2 concentration measurement was not precise) traces evolve close to the end of the cycle, the reductants are proposed to be limiting in the regeneration phase. As seen in Fig. 1A, NH_3 appears in the effluent (slips) only after 30–35 s into the regeneration cycle. The NH_3 (or H_2) is consumed below detection level until this point and starts to slip only when the stored NOx starts to deplete toward the end of the catalyst bed. Thus, the shape of the NH_3 evolution curves for the H_2 and NH_3 cases are consistent with our plug flow model. In the case of regeneration by H_2, the NH_3 evolution curve is the result of the competition between the generation (by NOx–H_2 reaction) and consumption (discussed below) of NH_3 at the end of the catalyst bed. In the case of regeneration by NH_3, the NH_3 evolution curve has the characteristic "S" shape of strong gas adsorption seen, for example, during adsorption of NO_2 on BaO. Examining the NH_3 curves, we propose that the reason why NH_3 is seen only toward the end of the cycle must be due to the fact that the NH_3 front moves along the length of the catalyst bed in a plug flow manner while getting consumed in reducing NOx to N_2 (thereby regenerating the catalyst). When the NH_3 front reaches the end of the catalyst bed, it begins to break through due to the absence of NOx to oxidize the NH_3 to N_2 and H_2O. This breakthrough is similar to the model presented by Epling et al. [14] for NOx storage, where the NOx sorption zone propagates down the catalyst bed in a plug flow manner and begins to breakthrough after reaching the end of the catalyst bed.

Experiments performed by varying the H_2 concentration in the regenerating phase over the range of 1.0–2.5% at the same total flow on the Pt/BaO/Al_2O_3 catalyst (that has stored a similar NOx amount during the preceding capture phase) have shown that the time required for regeneration is inversely proportional to H_2 concentration. The selectivity to N_2 was maintained at 80–85%. In all cases, the evolution of H_2 (observed in the mass spectrometer) was delayed, indicating that the reductant was completely consumed during the initial stages of the regeneration phase. The time delay in evolution of H_2 decreased proportionally with increasing H_2 concentration as should be the case if the reductant is the limiting species in this reaction. We also observed that lowering the temperature for the tests to 242 °C made no difference on the reduction profiles, except that the amount of N_2O produced was about twice as high. This insensitivity to temperature suggests that the regeneration is limited by transport of reactants and not by kinetics.

The sharp rise in the N_2 trace, as seen in Fig. 1A, implies that the H_2O trace, the other product of the reduction reaction, should follow a similar profile. Although the curve shapes are similar, a delay is seen in the H_2O trace, relative to N_2, for both reductants. We investigated this phenomenon by including H_2O (ca. 7.5%) in both the capture and regeneration phases. Interestingly, the usual NOx spike that arises immediately after the switch to the regeneration phase decreased by a factor of two compared to the dry feed conditions, and the H_2O trace had a sharp rise similar to the N_2 trace (i.e., no delay) when H_2O was included in the feed. In light of this data, we propose the following. It is well known that H_2O decreases the NOx storage capacity of the NSR catalysts [4] and hence H_2O could be competing for some of the NOx sites. In the absence of H_2O in the trapping or lean-phase, the sites that generally favor the adsorption of H_2O over NOx are occupied by NOx. However, when H_2O is formed during the regeneration phase due to the reductant coming into contact with either residual O_2 or stored NOx, it first adsorbs on those sites that favor H_2O adsorption over NOx, causing the delay in H_2O evolution, while displacing the NOx that were stored on those sites, resulting in a larger NOx spike. When H_2O is added to the feed during the trapping phase, it is preferentially adsorbed on some of the sites during the capture phase (decreasing NOx storage) and this prevents the adsorption of the H_2O that is formed during the regeneration phase, resulting in the sharp rise (no delay) in the H_2O trace and a decreased NOx spike. However, a small NOx spike (about 5% of total NOx stored) is still observed at the beginning of the regeneration phase even in the presence of H_2O in the trapping phase. We hypothesize that this is due to the combination of desorption (explained below) and a few highly reactive sites that release NOx as a result of the low concentration of H_2 or NH_3 that contacts these sites in the initial phase of regeneration.

The NO and N_2O traces in Fig. 1B are similar for both the reductants except for a higher initial spike with NH_3. The concentration of NO and N_2O (after the spike) is approximately constant with time. We propose that their shape is a result of depletion of H_2 at the end of the moving reduction front, and the reactions that take place in the non-reducing environment encountered there. In particular, we have observed that the reaction between NO and reduced Pt in the absence of adsorbed hydrogen will produce N_2O until the surface is titrated to Pt–O and the reaction stops. Fig. 1B also shows that the NO_2 decrease (after the initial rise) is linear with time in both cases. We propose that this is simply due to the desorption of NO_2 arising from the shift in equilibrium between the surface and the gas phase that is accompanied with the switch to the re-

generating gases [9]. As the catalyst bed is reduced in a plug flow type mechanism, the amount of NO_2 available for desorption ahead of the front decreases linearly with time, resulting in a linear decrease in NO_2 evolution with time. To reinforce the hypothesis of NO_2 desorption, we performed experiments with an inert substitute (Ar only with no reductant) in the regeneration phase spanning the same regeneration time period (ca. 3 min) as with H_2. After a 7 min trapping phase containing 350 ppm of NO, 10% of O_2, balance Ar, we observed 12% of the stored NOx desorbing as NO_2 and 6% as NO under the inert flow conditions during the 3 min regeneration period compared to 7% as NO_2, 3% as NO under H_2 rich conditions.

To summarize the findings, NH_3 or H_2 are capable of regenerating the trap in a similar way. We will investigate next the reaction of NH_3 or H_2 with NO over a Pt/Al_2O_3 catalyst (without the trapping component) as a way to simulate the reduction steps (Figs. 2A and 2B). Most of the experiments were carried out under nearly isothermal conditions (300 °C). However, in experiments where a significant amount of NH_3 was formed, the outlet gas temperature was 30–40 °C higher than that of the inlet. For this reason we carried out experiments at 200 °C to make sure the selectivity was not due to a hot spot. We observed similar product selectivity to that at 300 °C. The Pt/Al_2O_3 monolith catalyst was first exposed to NO/Ar mixture for 2 min and then H_2 (or NH_3) was added to the NO flow at varying NO/reductant ratios for 6 min (the reactions reached steady state in less than 1 min). The data reported here was obtained by averaging the concentrations after 2 min of reaction. The NO/reductant (H_2 or NH_3) ratio was varied to simulate the different NOx/reductant environments that occur along the NSR trap.

As seen in Fig. 2 when all the reduction chemistry occurs on Pt, then the steady state selectivity to N_2 is a strong function of the NO/reductant ratio. The H_2 conversions noted in Fig. 2A were calculated based on the amounts of N_2, NH_3 and N_2O formed and the appropriate reaction stoichiometry, since the H_2 concentration was not measured precisely. The selectivity to N_2 is defined as the ratio of two times the total amount of N_2 formed to the total amount of nitrogen species in the product (NO_2, N_2O, NH_3, and N_2) formed during the reaction on an atomic N basis. Fig. 2A shows that as the NO/H_2 ratio increases from 0.4 (excess H_2) to 4.6 (excess NO) the product selectivity changes from mostly NH_3 at low NO/H_2 ratios to N_2O at high NO/H_2 ratios. The highest N_2 selectivity was observed for a stoichiometric ratio (1:1) of NO/H_2. The formation of mostly NH_3 under low NO/H_2 ratios (reducing conditions) has previously been observed by Shelef et al. [15]. The product selectivities we have obtained for the NO/H_2 reaction over the Pt/Al_2O_3 sample are similar to that reported by Kosaki et al. [2] for their Pt/Al_2O_3 powdered catalyst. Similarly, as the NO/NH_3 ratio is varied from 0.67 (excess NH_3) to 5 (excess NO), Fig. 2B, the product selectivity changes from mostly N_2 at low NO/NH_3 ratios to N_2O at high NO/NH_3 ratios. Otto et al. [16] have previously shown that NH_3 is an effective reductant in the removal of NO from waste effluents over supported Pt. Although similar experiments with $NO_2 + H_2$ or NH_3 were not performed, we expect similar results with respect to the product selectivity as with the experiments with NO described above, with the possibility of NO_2 being more reactive. We have also carried out experiments involving N_2O and H_2 at 300 °C over the Pt/Al_2O_3 catalyst. In this case, with ca. 50 ppm N_2O and ca. 1% H_2 at 300 °C, the N_2O was reduced to N_2 and H_2O at a total conversion of 90%. These results for reduction with H_2 or NH_3 show that selectivity to N_2 is high only in specific ranges of oxidant/reductant ratios. This information is important to the formulation of our regeneration model.

Fig. 3 shows a schematic of the proposed regeneration mechanism for a single monolith channel of a $Pt/BaO/Al_2O_3$ NSR catalyst. The figure illustrates the propagation of the reductant front along the catalyst bed with complete regeneration of the trapping sites. A zoomed-in version of the chemistry occurring within the reductant front is also illustrated in Fig. 3. It shows that as the NOx ($NO + NO_2$) is released from the trapping sites (the exact mechanism of release is not known), it reacts with H_2 over Pt to form NH_3, N_2 and N_2O as the N-containing species. The selectivity of the individual species will depend on the local NOx/H_2 concentration ratios as shown in Fig. 2A. In regions where the H_2 level is high compared to the NOx, the reaction with the released NOx over Pt will form mostly NH_3 and some N_2. The NH_3 formed will further react with more NOx to

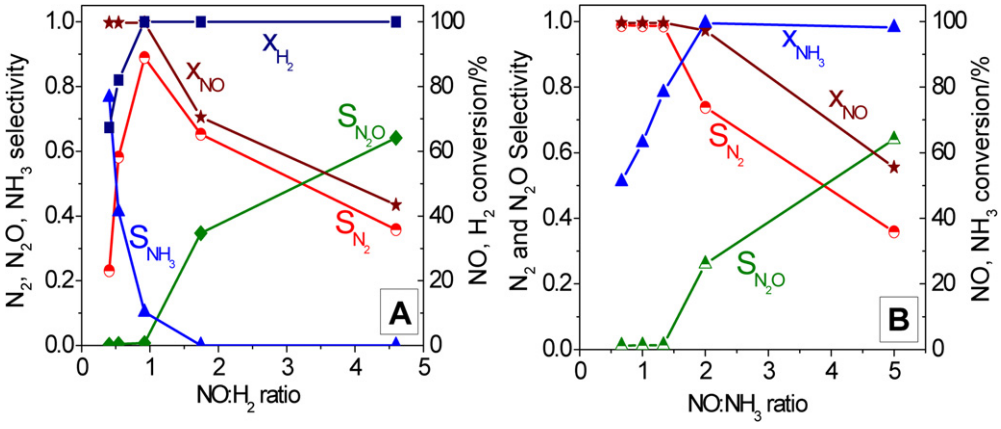

Fig. 2. Steady-state product selectivity and reactant conversion at 300 °C as a function of NO: reductant ratio for the reaction of (A) $NO + H_2$ and (B) $NO + NH_3$ over a Pt/Al_2O_3 monolith.

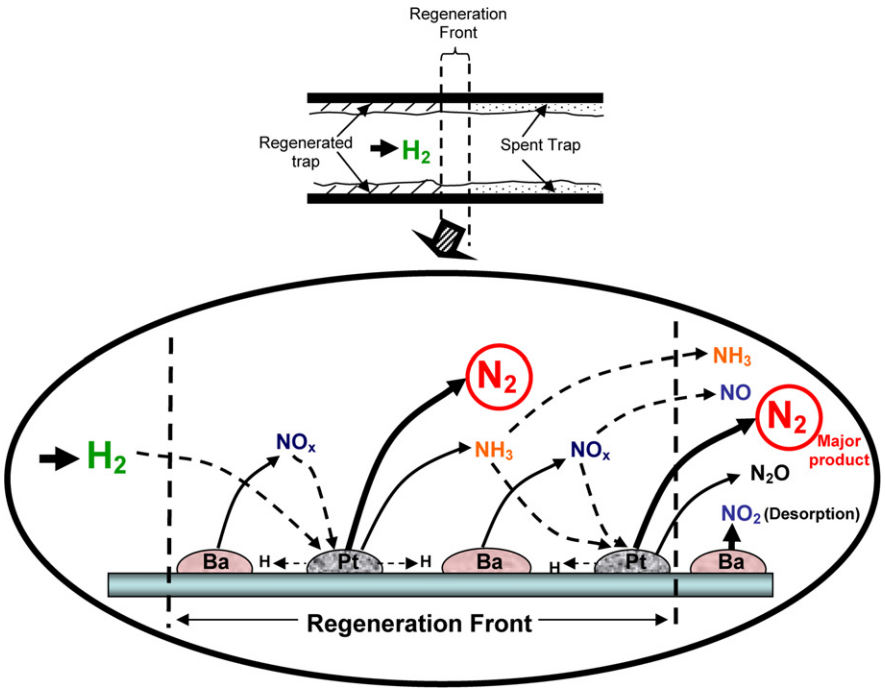

Fig. 3. Schematic of the reduction mechanism for a Pt/BaO/Al_2O_3 monolith regenerated with H_2. Bottom panel illustrates a zoomed-in picture of the reaction front.

give either N_2 or N_2O. If the N_2O is formed behind the front, it will be reduced to N_2 by H_2/NH_3. As the front approaches the end of the catalyst, the supply of NOx starts to deplete and will be insufficient to react with the NH_3 formed upstream, leading to the NH_3 breakthrough seen in Fig. 1A. Before the reaction front reaches the end of the bed, most of the non-selective products formed by the reaction of H_2 with NOx over Pt, such as N_2O and NH_3, will further react to form N_2 and maintain the high N_2 selectivity of the overall NSR catalyst. Using this rationale, and by reference to Fig. 2A, one might expect that as the concentration of H_2 is depleted at the end of the front, N_2O should become a major product. This is not observed experimentally. We believe the reason is that there is a self-adjusting mechanism. As the concentration of H_2 is lowered, the amount of released NO is also lowered thus keeping the local overall ratio unfavorable to the formation of N_2O. The N_2O is formed in a stoichiometric reaction between Pt and NO to form N_2O and Pt–O and is confined to the leading edge of the reaction front.

The reduction model proposed indicates that the trapping phase of the NSR cycle should not extend up to the full capacity of the trap since in that case the NOx released during regeneration would not be captured downstream. Furthermore, we propose that having an oxygen storage capacity (OSC) substrate such as ceria would allow the oxidation of NH_3 to N_2 when there are no more nitrates to oxidize it, and, hence, the OSC would decrease the NH_3 slip in the NSR catalysts.

4. Conclusion

We have proposed a model for reduction by H_2 where NH_3 is the hydrogen carrier. In this model, derived from the results presented here, NO and NO_2 are first released into the gas phase and then reduced over Pt. It is not necessary to invoke a mechanism of surface diffusion of NO-containing species that are reduced on Pt. We propose a localized reaction front which travels through the bed with complete regeneration of the trapping sites as it propagates down the catalyst bed. This chemistry seems to be fast enough to make the process mass transfer limited and does not depend on whether the reactant is H_2 or NH_3. Thus, the reaction kinetics and associated rate constants are not necessary to model the quantitative behavior of this system. The efficiency of the NSR catalyst in converting NOx to mostly N_2 is achieved because the other products that form over Pt, such as N_2O and NH_3, are either not favored (N_2O) or can further react to produce N_2. The low observed amounts of NO and N_2O are explained by a self-limiting NO production rate as the H_2 concentration is depleted at the leading edge of the front. The hydrogen on the surface of Pt will react first to reduce NO and N_2O before it will spillover to release more NO. As the hydrogen on the surface is depleted, the NO in the gas phase will adsorb and react on Pt to produce N_2O until the surface is oxidized and the remaining NO will escape. The NO_2 profile is due to simple desorption. The NH_3 profile measured at the end of the cycle when using H_2 as a reductant is a result of insufficient NOx left in the bed to consume the NH_3 formed as the front reaches breakthrough.

Acknowledgments

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