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Catalysis Today 96 (2004) 21–30

CATALYSIS TODAY

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Further evidence of multiple NO_x sorption sites on NO_x storage/reduction catalysts

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Abstract

NO_x storage/reduction (NSR) catalysts are a potential solution for meeting the upcoming, diesel engine exhaust emissions regulations. A single-site adsorption kinetic mechanism for NO_x storage on NSRs is commonly accepted in the literature; however, there is growing evidence that more than one type of active site or reaction pathway is involved. Bench reactor data described in this work using a model $Pt/Ba/Al_2O_3$ NSR catalyst provide additional evidence in support of a more complex kinetic model of NO_x storage. This issue has direct practical significance for optimization of the NSR catalyst operation, and for controlled design of more efficient NSR catalyst formulations. First, the impacts of CO_2 and H_2O on NO_x adsorption were investigated, since these species are believed to be competing for the same adsorption sites as NO_x. These two components were found to strongly influence the NO_x adsorption process, although in very different manners and to different extents depending on the operating conditions. The resulting phenomenological picture is complex and cannot be described using a single type of adsorption site. Additional, NO_x speciation experiments showed that the commonly accepted NO_2 disproportionation mechanism clearly dominates at the later stages of the adsorption process, such that a satisfactory N-balance can be obtained using this mechanism alone. However, at the early stages of adsorption the stoichiometric relationships for this mechanism are not observed. Experimental evidence strongly suggests that this is due to presence of two distinct types of storage sites, most likely based on the proximity of Ba and Pt components.

Keywords: NO_x trap; NO_x storage/reduction; $Pt/Ba/Al_2O_3$; Diesel emissions

1. Introduction

Most gasoline-burning engines are run with a stoichiometric mixture of air and gasoline so that the exhaust gas contains little or no O_2. Three-way catalytic (TWC) converters are used in these conditions to meet the NO_x, CO and hydrocarbon emissions regulations. Lean-burn engines, where diesel engines are a common example, can result in improved fuel economy and reduced CO_2 emissions in comparison to engines run in the stoichiometric regime. As there has been increased focus on these two qualities, lean-burn engine use has recently received more attention. Upcoming legislation, again due to increasing environmental concerns, also sets emissions limits on NO_x, particulate, hydrocarbon and CO emissions from diesel engines [1]. The inherent problem in reducing the NO_x emissions from lean-burn engines is the need to reduce ppm levels of NO_x to N_2 in the presence of percentage levels of O_2. Current TWC technology has not practically led to the necessary emissions reductions from lean-burn engines with this excess O_2. This is not unexpected since these catalysts were designed to operate with little or no O_2 present in the exhaust gas.

NO_x storage/reduction (NSR) catalysts, which are also sometimes referred to as NO_x adsorption catalysts and lean NO_x traps, have been developed as a promising alternative to meet the upcoming regulations. These catalysts operate in a cyclic manner where during the lean period of operation, the catalyst stores or "traps" NO_x as nitrate species. A periodic and short rich pulse is introduced so that the trapped NO_x is released and reduced to N_2 and the catalyst is regenerated.

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doi:10.1016/j.cattod.2004.05.004

Therefore, lean-burn engines or their exhaust will have to be adapted to supply this periodic pulse of rich gas which unfortunately also results in an associated fuel penalty.

The NSR reaction sequence can be separated into five general reactions and these are:

1. NO oxidation to NO_2,
2. NO_x storage on the catalyst surface,
3. reductant evolution,
4. NO_x release from the trapping site,
5. NO_x reduction to N_2.

Although this sequence of reactions is generally agreed upon, each step consists of multiple reactions resulting in a more complex reaction scheme and some of the steps listed above may also be coupled.

These catalysts are typically composed of a Pt-group metal component and an alkali or alkaline-earth component, supported on a high surface area oxide support, e.g. γ-Al_2O_3. Such catalyst formulations are typically further supported on honeycomb substrates which offer the mechanical and flow properties required for engine exhaust applications. The Pt-group component is believed to play a key role in the red-ox processes involved in all five steps of NSR catalyst operation; the alkali or alkaline-earth component provides NO_x storage capacity. To date, most of the research surrounding these catalysts has been directed at step 2, and indeed this study is as well. A mechanistic understanding is warranted since increasing the trapping ability of the catalyst can result in improved performance and understanding this step is necessary for controls and diagnostic development.

In many cases, single-site sorption models have been used to explain the observed chemistry or trends in data. A comprehensive kinetic model of NO_x adsorption on NSR catalysts has been developed at Chalmers University, which is based on a single type of NO_x storage site [2]. Under the specific conditions of the tests performed [2], the model performed well. However, multiple types of sites for sorption have been proposed and these vary in their literature description. For example, a geometric proximity effect has been proposed where sites near Pt versus those further away differ in reactivity [3–5]. Different sorption precursor species have also been observed and include hydroxide, carbonate and oxide sites [6,7]. Furthermore, data have been explained by invoking bulk versus surface sorption sites and the effects of diffusion on their reactivities [8–10]. Throughout the remainder of this paper, “site” will refer to chemically or energetically distinct sorption sites, or sites that can be differentiated by the mechanism of adsorption that leads to the final product, $Ba(NO_3)_2$.

In this study, two experimental approaches were used in an attempt to identify the presence of and to differentiate between these proposed sites. The effects of H_2O and CO_2 on the sorption performance were evaluated and used to develop a better understanding of the reaction process. Also, NO_x speciation during sorption was monitored, while adding NO_2 as the NO_x source, and the results will be discussed in terms of the mechanisms that might be involved at the surface during sorption.

2. Experimental

$Pt/Ba/Al_2O_3$ is the standard formulation for an NSR catalyst in literature studies and this same formulation was used in the current study. First, the Ba/Al_2O_3 washcoat was prepared by mixing a high surface area γ-Al_2O_3 (160 m^2/g) with Ba acetate in an aqueous solution. The resulting Ba content of the Ba/Al_2O_3 mixture, on a dry basis, was 8.3 wt.%. The cordierite honeycomb monolith core samples were dipped into the slurry, removed and drained. The sample was dried and calcined at 500 °C. The Pt was then added by dipping the core samples into an aqueous solution containing an amine-based Pt precursor. The target catalyst Pt content level was 50 or 100 g Pt/ft^3 of monolith sample.

These cores were then wrapped in fiber glass insulation tape or matting and inserted into the reactor tube. The tape or matting eliminates gas bypass around the sample during the tests. The reactor tube was positioned in a furnace such that the catalyst core was located towards the outlet end of the reactor tube. Furthermore, all entering gas lines were preheated in an attempt to maintain a uniform catalyst temperature. The gas mixture was introduced using mass-flow controllers, except for H_2O which was introduced into a heated zone using a high-precision liquid metering pump. The reactor is equipped with a bypass line so that both the entering and exiting gases can be analyzed. The inlet gas was periodically analyzed to ensure the target concentrations were being met. Gas analysis included NO_x, CO, CO_2 and O_2 concentration measurements using California Analytical Instruments analyzers. H_2O was removed prior to gas analysis with a membrane dryer. Also, during the NO_x speciation experiments each test was performed twice, once while allowing the NO_x analyzer to monitor NO only and once to measure total NO_x, so that NO/NO_2 speciation could be performed. The NO_2 concentration was calculated from the analyzer readings using: (total NO_x signal − NO only signal)/converter efficiency factor. This conversion efficiency factor was close to 85% for the instrument used and was measured before and after the testing using calibrated gas mixtures.

In order to gain a better understanding of the phenomena occurring during the sorption phase, a consistently regenerated catalyst needs to be used. To achieve consistent initial surface conditions, excess reductant and regeneration time were always used during the rich phase of the cycle. The data associated with the effects of CO_2 and H_2O were obtained after at least three lean/rich cycles had elapsed. In each case, enough cycles were run so that the data presented are no different than the data obtained in the prior cycle. In the experiments where the effects of H_2O and CO_2 were evaluated, the lean phase of the cycle contained 250 ppm NO, 8% O_2, 0 or 8% H_2O, 0 or 8% CO_2 and a balance of N_2. The rich phase consisted of 1500 ppm H_2, 0 or 8% H_2O, 0 or 8% CO_2 and a balance of N_2. The NO/NO_2 speciation experiments described in the second part of the paper were performed at a relatively low temperature (200 °C). In order to ensure complete regeneration at the end of each test, the catalyst was cycled in lean/rich environments at 325 °C but with no NO_x in the lean phase. The catalyst was then cooled to 200 °C and exposed for 10 min to 1500 ppm H_2, 8% H_2O, 10% CO_2 and a balance of N_2. Under the conditions of these NO_x speciation tests, the deep regeneration phases resulted in a complete removal of NO_x from the catalyst surface. Although not shown, this was verified through multiple experiment repetitions.

3. Results and discussion

A typical NO_x breakthrough profile from a NSR catalyst is shown in Fig. 1. This profile can be broken into three areas for descriptive purposes. For some period of time, complete uptake of the entering NO_x can be attained. This is one of the primary attractions of NSR technology for NO_x emission control applications. After breakthrough or slip begins, there is still a period of time where a rapid uptake of NO_x is occurring. However, as the trapping sites slowly fill, the rate of trapping decreases, but does not quickly reach zero. At the latest stages of adsorption, for some period of time, which can extend as long as 3–10 h depending on test conditions, a slow but measurable uptake of NO_x may occur. This is not due to selective catalytic reduction of NO_x (lean-NO_x catalysis) as no reductant is being added to the inlet gas stream and no reductant formation should occur from the entering gas components.

The initial part of the sorption process, where NO_x uptake occurs with a very high rate, is the acceptable operating range for most applications. Once the NSR catalyst begins to saturate, the amount of NO_x slipping through the catalyst quickly exceeds the normally strict application limits. However, it is very difficult to characterize the behavior of the catalyst based solely on the region where complete uptake is occurring. In this study, longer sorption times were therefore used in an attempt to resolve and characterize the reaction pathways. Unfortunately, due to the integral nature of operation of this catalyst, kinetic studies using differential analysis are not possible in this type of test.

3.1. *The effects of H_2O and CO_2 on sorption*

In the first set of experiments, the impacts of H_2O and CO_2 on the sorption chemistry of a 50 g/ft^3 $Pt/Ba/Al_2O_3$ catalyst were evaluated. It was expected that these two gases will have an effect on the catalyst surface and therefore on the reaction chemistry. The presence of CO_2 and H_2O should lead to the formation of Ba carbonate and hydroxide species, respectively. Indeed, calculations and experimental evidence have shown that both of these exist on an NSR catalyst surface [6,7,11]. Since the stability of these species, relative to each other, differs depending on reaction or operating conditions, nitrate formation from these precursor species will vary as well. The NO_x breakthrough data during sorption with and without CO_2 and/or H_2O at a catalyst inlet temperature of 200 °C are shown in Fig. 2. When the sorption inlet gas contains no CO_2 nor H_2O, but only NO, O_2 and N_2, the catalyst does not allow NO_x slip until approximately 105 s has elapsed. With the addition of both CO_2 and H_2O, the time before the observed slip drops to approximately 40 s. Actually, the addition of either CO_2 or H_2O individually decreases this time. However, it is apparent that these two components have different effects on the breakthrough profile and therefore the sorption chemistry. Their individ-

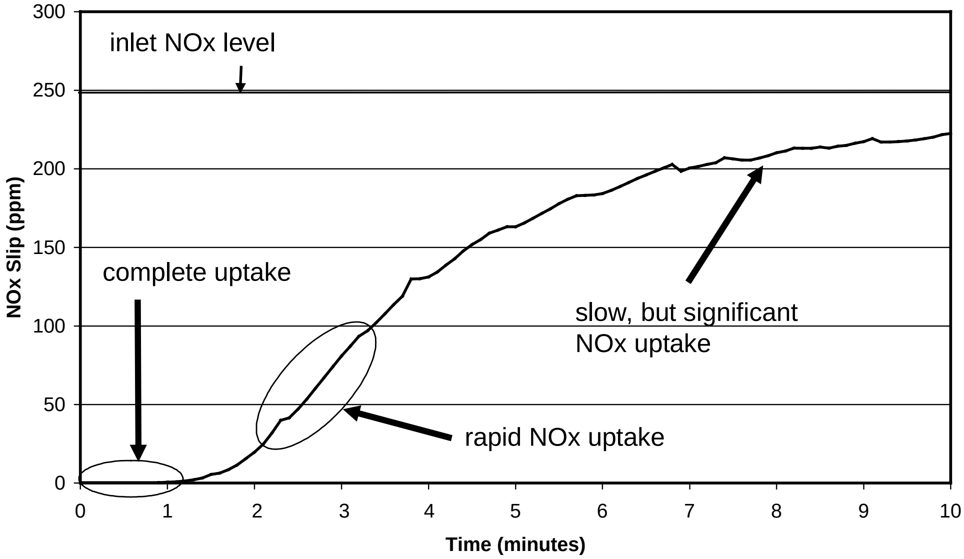

Fig. 1. A typical NO_x breakthrough profile. The data were obtained at 200 °C and an SV of 25,000 h^{-1}, with an inlet gas composition of 250 ppm NO, 8% H_2O, 8% CO_2, 8% O_2 and a balance of N_2. The catalyst was cleaned or regenerated prior to this run with 1500 ppm H_2, 8% H_2O, 8% CO_2 and a balance of N_2 for 5 min.

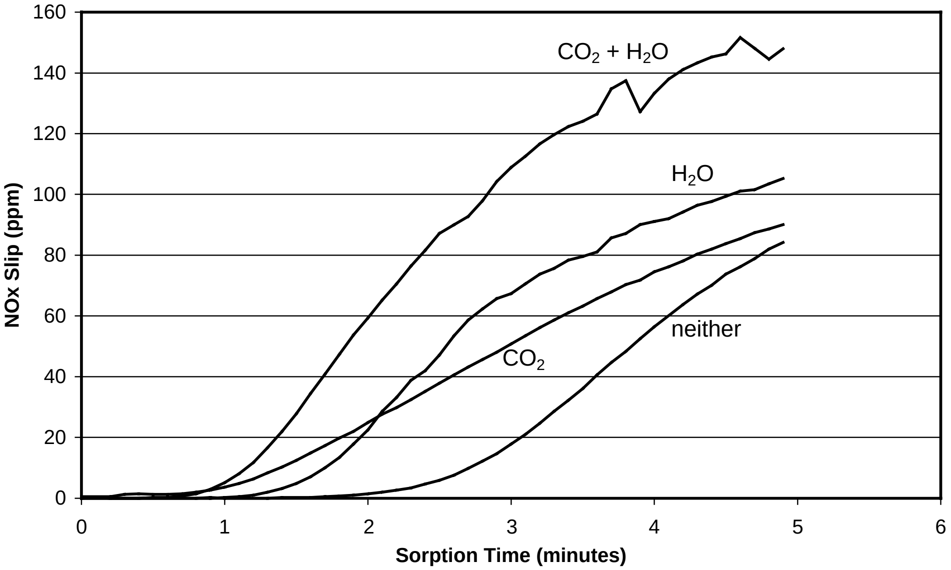

Fig. 2. The effects of CO_2 and H_2O on NO_x sorption performance. The data were obtained at 200 °C and an SV of 25,000 h^{-1}, with an inlet gas composition of 250 ppm NO, 0 or 8% H_2O, 0 or 8% CO_2, 8% O_2 and a balance of N_2. The catalyst was cleaned or regenerated prior to this run with 1500 ppm H_2, 0 or 8% H_2O, 0 or 8% CO_2 and a balance of N_2 for 5 min.

ual effects are not the same nor are their effects additive. The presence of CO_2 has a greater impact on the time for complete capture than does H_2O. And although the effect of H_2O in the complete uptake portion of the breakthrough profile is less in comparison to CO_2, once breakthrough or slip does begin, H_2O has a stronger negative impact. At the end of 5 min, the NO_x slip is greater due to the presence of H_2O in comparison to CO_2 and their combined effect exceeds those of the two individually.

The data obtained under identical conditions, but at a catalyst inlet temperature of 400 °C and for a longer sorption time, are shown in Fig. 3. These data again demonstrate that H_2O and CO_2 have different impacts on the NO_x sorption performance and chemistry. H_2O shows a very similar effect both quantitatively and qualitatively at 400 °C as it does at 200 °C indicating that its mechanism of change or influence is not necessarily a function of the temperature. These data also indicate that at these elevated temperatures, when both CO_2 and H_2O are present, CO_2 has a greater influence and basically minimizes the observed influence of the H_2O. The combined effect of CO_2 and H_2O was very similar to the impact of CO_2 alone and in this case was less than the sum of the individual components. This could be caused by the carbonate species ability to displace hydroxide species on the

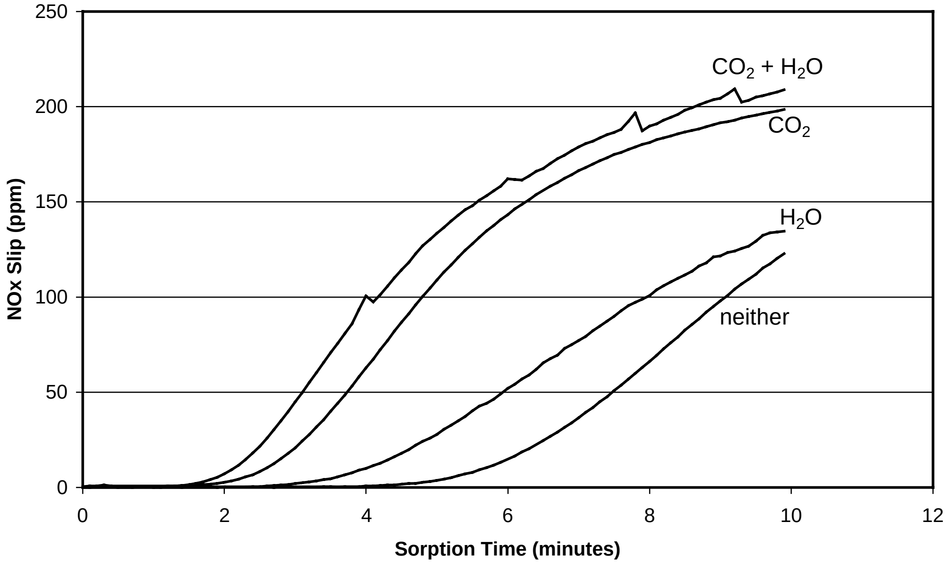

Fig. 3. The effects of CO_2 and H_2O on NO_x sorption performance. The data were obtained at 400 °C and an SV of 25,000 h^{-1}, with an inlet gas composition of 250 ppm NO, 0 or 8% H_2O, 0 or 8% CO_2, 8% O_2 and a balance of N_2. The catalyst was cleaned or regenerated prior to this run with 1500 ppm H_2, 0 or 8% H_2O, 0 or 8% CO_2 and a balance of N_2 for 10 min.

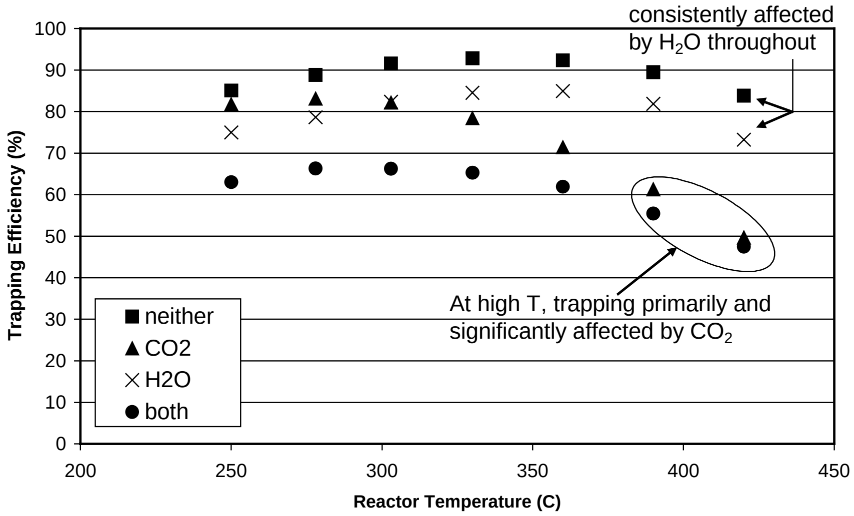

Fig. 4. Integral trapping efficiencies of a 50 g/ft^3 Pt/Ba/Al_2O_3 NSR catalyst as a function of temperature. The inlet gas compositions are identical to those listed in Fig. 3.

Ba sorber component when both CO_2 and H_2O are present, which would minimize the H_2O effects on $Ba(NO_3)_2$ formation. This possibility is further discussed below.

The results of a number of analogous experiments performed at different temperature points are summarized in Fig. 4 in the form of integrated adsorption efficiencies over a 10 min period. Remarkably, the presence of H_2O reduced the adsorption efficiency by virtually a constant margin across the entire studied temperature range. Given the roughly similar overall shapes of the two NO_x breakthrough curves (Figs. 2 and 3), with H_2O and without both H_2O and CO_2, the same relationship is retained even if the NO_x adsorption efficiency is integrated over a shorter sorption time. If the NO_x adsorption sites were homogeneous, the presence of H_2O may have impacted the NO_x storage efficiency in two major ways: by reducing the total number of sites available for adsorption, e.g. based on the thermodynamic equilibrium between the respective surface nitrates and hydroxides, or by reducing the overall reaction rates. It is difficult to imagine that either of the above possibilities may result in such a constant reduction of the NO_x adsorption efficiency across such a broad range of temperatures. Rather, this observation would be consistent with the hypothesis that several types of storage sites exist, one of which essentially becomes unavailable for NO_x adsorption in the presence of H_2O. This formalism allows us to explain the lack of a temperature dependence, since the number of these different, unavailable, sites would be constant.

It should be noted that a somewhat different effect of water vapor on NO_x adsorption on NSR catalysts has previously been reported [6]. At 300 and 400 °C, the presence of merely 1% H_2O negatively impacted the sorption characteristics of a Pt/Ba/Al_2O_3 catalyst [6], which is consistent with the data collected for this work. However, at 200 °C, the presence of 1% H_2O was shown to positively influence the sorption of NO_x [6]. It is not clear if such different behavior at 200 °C was specific to the lower concentration of water, or was due to some other reasons, as this phenomenon was not explained.

Unlike H_2O, the impact of CO_2 noticeably increased with increasing temperature (Fig. 4). In a mixture containing both CO_2 and H_2O, the former eventually completely overrides the effect of the latter. This is consistent with computational and experimental results reported in the literature, regarding the relative stability of the respective alkali or alkaline-earth hydroxide and carbonate species [5,6,10]. For example, when Ba carbonates, hydroxides and oxides co-exist on a NSR catalyst, the order of decomposition to form the nitrate is oxide then hydroxide then carbonate [5,6] and thermodynamic calculations support this trend if bulk attributes are assumed [10].

To summarize the above observations, H_2O appears to have a fixed impact on NO_x storage, while the effect of CO_2 is consistent with an increasing relative stability of surface Ba carbonates compared to Ba nitrates, or hydroxides, with temperature, based on thermodynamic equilibrium considerations. We would like to propose the following reasoning to describe the experimental phenomenology discussed above:

- In the presence of H_2O, adsorption of NO_x on γ-Al_2O_3 becomes significantly less or even essentially impossible due to the formation of respective hydroxyl groups. Recent in situ IR data [12] provide an unambiguous, independent confirmation of this effect. Under the conditions examined in the IR study, the addition of H_2O to the reactant stream reduced the amount of Al nitrates formed by 90%. At the same time, the hydroxyl groups associated with the alkali- or alkali-earth adsorption sites, are known to be much less stable than respective surface nitrates. Thus, the presence of H_2O probably has less effect on the ability of the catalyst to store NO_x on these sites. The combination of these two factors would explain why the presence of

H_2O renders a certain fixed number of sites inaccessible for NO_x storage regardless of the temperature (the sites associated with γ-Al_2O_3), while the remaining majority of sites, associated with the alkali- or alkaline-earth component, are not significantly or substantially affected.
- Surface carbonates formed on the alkali-or alkaline-earth component in the presence of CO_2, have a much higher stability than the respective hydroxyl groups. Also, their stability compared to the respective nitrates increases with temperature. This explains why the impact of CO_2 increases with temperature. At the same time, based on IR data [12], CO_2 had essentially no impact on NO_x storage on γ-Al_2O_3.

While not exhaustive, this analysis is consistent with the entire set of experimental observations. The above data support that different adsorption sites for NO_x exist, associated with the different components of the catalyst. However, they do not allow us to determine if multiple adsorption sites associated with the alkali/alkaline-earth component exist.

From the experimental perspective, one of the major implications of this work in combination with previously reported data [12,13] is that NO_x adsorption experiments on NSR catalysts, performed in the absence of H_2O and CO_2, should lead to an overestimated NO_x storage capacity via different mechanisms. H_2O and CO_2 are always present in substantial amounts in real diesel exhaust gas (at least several percent) and these data show that they need to be accounted for in any model or mechanistic development. Also, this information has some implications for the practical application of NSR catalysts. For example, high temperature points in the operation of diesel engines are typically associated with high concentrations of CO_2 (and H_2O), due to a high fuel consumption rate. High levels of CO_2 at high temperatures hinder storage and may aggravate the existing high-temperature NO_x capacity problems.

3.2. NO_2 adsorption experiments

An additional series of experiments was undertaken with the objective of further investigating the nature of the adsorption sites but more specifically those associated with the alkali/alkaline-earth component of the catalyst:

- In this series, H_2O was always present in the reaction gas mixture, in order to minimize NO_x storage on the sites associated with γ-Al_2O_3.
- CO_2 was also present in all the experiments, since it represents an inevitable component of the exhaust gas and, as found above, has a strong effect on the NO_x storage.
- NO_x was introduced in the form of NO_2, in an attempt to decouple the NO_x storage process from the NO oxidation reaction. In order to illustrate the extent of limitations imposed by the $NO \rightarrow NO_2$ oxidation process on NO_x storage, adsorption curves for inlet gas mixtures containing NO_2 or NO (the reactant gas mixture being otherwise identical) are presented in Fig. 5. As one can see, $NO \rightarrow NO_2$ oxidation limitations can significantly reduce performance at 200 °C on a 100 g/ft^3 Pt/Ba/Al_2O_3 catalyst. It is difficult to directly measure $NO \rightarrow NO_2$ oxidation on Pt/Ba/alumina since oxidation and storage effects are coupled. The literature indicates that under similar conditions, NO oxidation on Pt/Al_2O_3 achieves less than 20% efficiency at 200 °C [14–16]. Addition of Ba to such a catalyst to produce a Pt/Ba/Al_2O_3 NSR catalyst similar to the one used in this study, reduced the red-ox efficiency of Pt ~15 times [16]. Thus, for NO produced by disproportionation, we expect re-oxidation to be significantly limited.

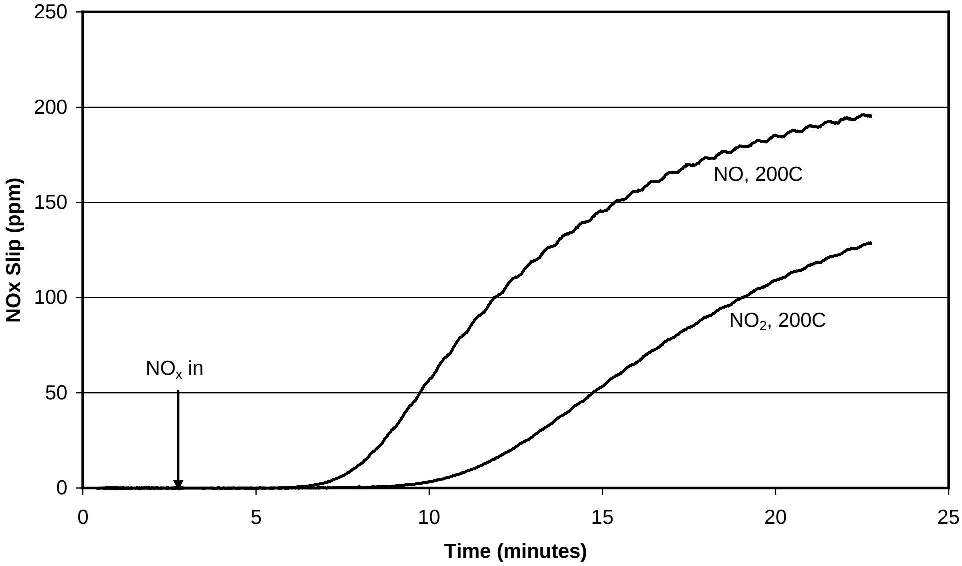

Fig. 5. Comparing the effect of NO vs. NO_2 as the NO_x source on sorption performance. The data were obtained at 200 °C and an SV of 15,000 h^{-1}, with an inlet gas composition of 250 ppm NO or NO_2, 8% H_2O, 10% CO_2, 8% O_2 and a balance of N_2. The catalyst was cleaned or regenerated prior to this run with 1500 ppm H_2, 8% H_2O, 10% CO_2 and a balance of N_2 for 10 min.

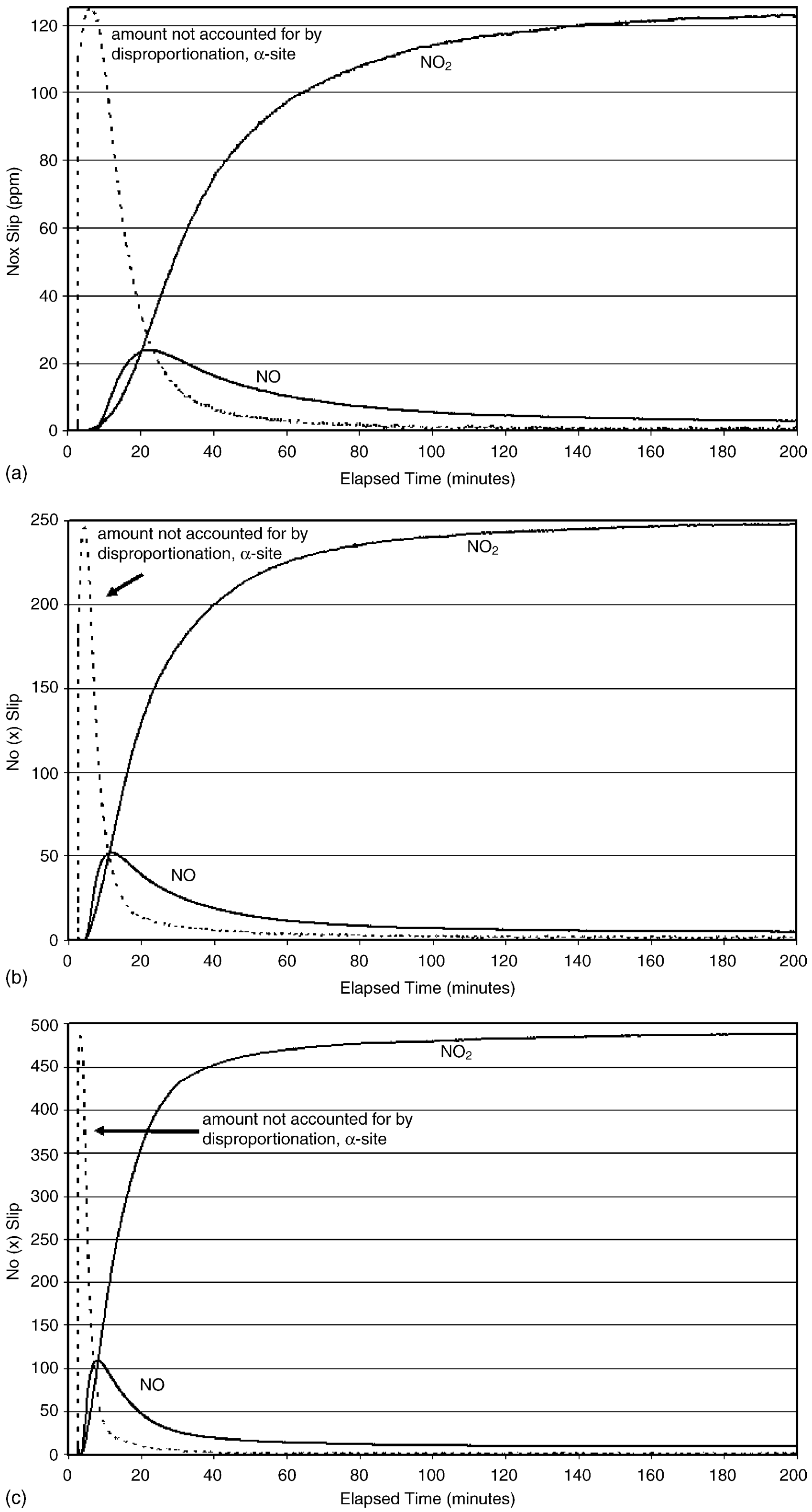

Fig. 6. The evolution of NO and NO_2 during a sorption run, with NO_2 as the NO_x source. The data were obtained at 200 °C and an SV of 15,000 h^{-1}, with an inlet gas composition of: (a) 125 ppm NO_2, (b) 250 ppm NO_2, or (c) 500 ppm NO_2, 8% H_2O, 10% CO_2, 8% O_2 and a balance of N_2. The catalyst was cleaned or regenerated prior to this run with 1500 ppm H_2, 8% H_2O, 10% CO_2 and a balance of N_2 for 10 min. The N "imbalance" curve is the discrepancy in attempting a mass balance solely based on using the entering and exiting NO_x levels with the disproportionation mechanism. This is referred to as α-site in the text.

NO_x storage in the form of nitrate requires further oxidation of NO_2 to the respective nitrate species. The oxygen atom required for this oxidation may be provided by either of the two oxidants present in the gas stream: O_2 or NO_2. The O atom subsequently takes place in the reaction via one or another mechanism, e.g. involving the product of the dissociative adsorption of O_2 on Pt or formation of barium peroxides [2]. If the oxidation of a NO_2 molecule to a nitrate species occurs with the participation of another NO_2 molecule, disproportionation stoichiometry should be observed; $3NO_2 + BaO \rightarrow Ba(NO_3)_2 + NO$ [17,18]. This stoichiometry implies that for every two molecules of NO_x stored on the surface, one molecule is released in the form of NO. The tests described below were all performed in such a way to validate the presence of the disproportionation reaction and to determine if other mechanisms exist. The experiments were done at lower temperatures, around 200 °C, to minimize the re-distribution of NO and NO_2 in the products of the reaction. Although at such low temperatures NO_2 is thermodynamically favored over NO, the process of establishing the $NO \leftrightarrow NO_2$ equilibrium is kinetically slow. For example, as will be shown below, at 200 °C the concentration of NO in the NSR catalyst outflow can substantially exceed the equilibrium values for this temperature and partial pressure of O_2. At 325 °C the ratio of NO and NO_2 in the catalyst outflow is consistently close to the equilibrium values and therefore results at these higher temperatures were not used in this evaluation and are not shown.

The data shown in Fig. 6 depict the NO and NO_2 slip through a 100 g/ft^3 Pt/Ba/Al_2O_3 sample at 200 °C during a lean phase of a cycle. Three different inlet NO_2 concentrations, with all other parameters constant, were used in the tests. The disproportionation mechanism was applied to these results as follows. The amount of NO_x stored on the catalyst was assumed to be two times the amount of NO released. The dashed lines in Fig. 6 reflect the difference between the inlet NO_x concentration and the sum of the instantaneous amount of NO_x being trapped as accounted for by the disproportionation mechanism and the measured NO_x slip (dashed line = inlet NO_x concentration − NO_x slip − 2 × NO_x slip).

As shown in Fig. 6b, for example, there is a significant amount of time before breakthrough is observed under the conditions of this test and once breakthrough begins, at ~7 min after NO_2 is introduced, both NO and NO_2 are detected. NO evolution reaches a maximum value after 16 min of sorption and then the amount of NO evolving begins to decrease. Importantly, the concentration of NO during this period of time substantially exceeds the thermodynamic equilibrium value (3 ppm) for this temperature and oxygen concentration. The concentration of NO_2 detected continuously increases throughout the test. The amount of nitrogen not accounted for by disproportionation approaches zero after approximately 80 min. For the remaining ~120 min of the experiment, the nitrogen balance could be closed solely based on the disproportionation mechanism. Similar experiments performed at different inlet concentrations of NO_2 are reported in Fig. 6a and c. The maximum of the respective ordinate scales represent the inlet NO_2 concentrations for the given experiment. As the inlet NO_x concentration or flux increases, the disproportionation mechanism can account for the N balance at earlier sorption times. Several possible explanations of this behavior are given below.

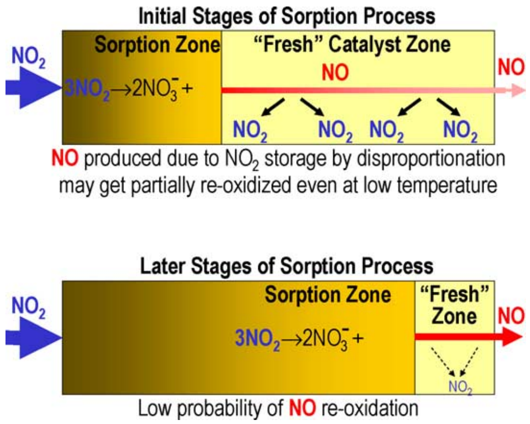

Fig. 7. A possible representation of a series of reactions occurring during sorption. This possibility also dictates that decoupling NO oxidation and NO_x sorption would not be possible. This was first presented at the 18th Meeting of the North American Catalysts Society, June 2003.

First of all, it should be noted that deviation from the disproportionation stoichiometry does not necessarily imply the dominance of a different reaction pathway at the early stages of adsorption. A reaction schematic reflecting a theoretical possibility explaining the entire adsorption process using the disproportionation mechanism only, but invoking the integral nature of this device, is shown in Fig. 7. According to this logic, at early stages of the sorption period, NO_x is being sorbed via disproportionation on the front section of the NSR catalyst. This allows a higher probability of the released NO to oxidize to NO_2 downstream. As the trapping sites begin to fill, the adsorption zone moves closer to the catalyst outlet. Now, there is less opportunity for the NO to oxidize to NO_2 and the mass balance using just the disproportionation mechanism can be closed. This proposed scheme implies that essentially all of the NO molecules released during the initial several minutes of adsorption, when no NO_x is slipping through the catalyst, are re-oxidized to NO_2 and scavenged by the catalyst. Realistically, however, we expect very limited conversion of NO to NO_2 at 200 °C since as mentioned above at this temperature the NO oxidation efficiency of the catalyst is poor and such complete conversion of released NO to NO_2, leading to zero slip of NO_x is very unlikely.

Another possible explanation involves a different type of Ba site that does not obey disproportionation stoichiometry, and which dominates at the early stages of adsorption. In this case, the amount of nitrogen not accounted for by the disproportionation mechanism should be related to this different type of site (hereafter referred to as α-sites). A

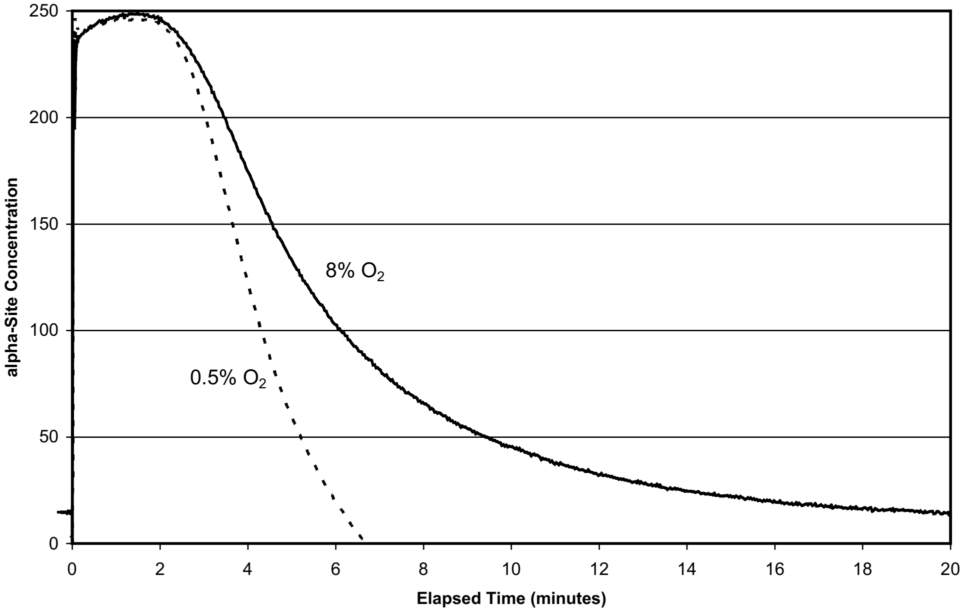

Fig. 8. The N “imbalance” curve is the discrepancy in attempting a mass balance solely based on using the entering and exiting NO_x levels with the disproportionation mechanism. This is referred to as α-site in the text. These two sets of data were obtained at 200 °C and an SV of 15,000 h^{-1}, with an inlet gas composition of 250 ppm NO_2, 8% H_2O, 8% CO_2, 0.5 or 8% O_2 and a balance of N_2. The catalyst was cleaned or regenerated prior to this run with 1500 ppm H_2, 8% H_2O, 8% CO_2 and a balance of N_2 for 10 min.

fixed number of such α-sites should translate into a fixed amount of NO_x stored on these sites regardless of the experimental details. Remarkably, integration of the instantaneous NO_x imbalance or α-site curves in Fig. 6a–c for the three different NO_2 concentrations indeed produced nearly identical values of NO_x stored on this different type of site (Table 1). The amount of NO_x stored on these α-sites represents about one third of the total NO_x storage capacity of this catalyst.

Within the scope of this approach, all the characteristics of these α-sites are consistent with the hypothesis that their distinction is based on a close proximity to Pt, as follows. NO_x adsorption on the α-sites does not obey the disproportionation stoichiometry. Dissociative adsorption of O_2 on Pt, instead of NO_2, could provide the proximal, α-sites with a ready source of oxygen atoms for the reaction process. Therefore, O_2 serves as a source of oxygen atoms for the final oxidation step to nitrate (NO_3^-), and the more potent oxidant, NO_2, appears to have no advantage over O_2 at sites that involve Pt chemistry. For the other sites not located in the immediate proximity of Pt, NO_2 molecules provide a much more preferable source of oxygen, i.e. would lead to the disproportionation pathway. There is no doubt that some Ba atoms on the surface exist in close contact with Pt atoms, since substantial modification of the Pt catalytic properties has been observed for such catalysts. For example, previous research has shown a substantial reduction in red-ox efficiency of Pt/Al_2O_3 catalysts with the addition of Ba [16,19]. The logical implication of this proposed explanation is that substantially lower oxygen concentrations should reduce the amount of NO_x stored on these α-sites. An additional experiment was performed, for verification, with a low O_2 concentration (0.5% compared to 8% used above) and as expected, the amount sorbed on these α-sites was much lower in this case (Fig. 8). The exact pathway of NO_2 storage on these proximal sites with the participation of O_2 however cannot be directly determined from the above data, only what reactants are participating. Overall, these data are consistent with a previously proposed model, based on in situ FT-IR evidence [6,20], where nitrites formed at the early stages of NO_2 adsorption processes and were progressively oxidized as the sorption time elapsed. The current data set suggests that the nitrites formed at “proximal” sites are oxidized to nitrates with the participation of oxygen atoms, available via dissociation of O_2 on the adjacent Pt sites.

Table 1
Amount of NO_x stored on α sites during each experiment

Inlet NO_2 concentration (ppm)	Amount of NO_x not accounted for by the disproportionation reaction (μmol)
125	0.560
250	0.545
500	0.577

4. Conclusions

The resolution of several different aspects of NO_x adsorption on NSR catalysts and a proposed way to de-convolute different types of NO_x storage sites via two types of experiments are reported in this work. The first distinction was observed in the experiments with and without H_2O and CO_2. The results suggested that in the absence of H_2O, NO_x can effectively adsorb on γ-Al_2O_3 and Ba sites. The presence of H_2O essentially eliminated NO_x adsorption on the sites associated with γ-Al_2O_3. This is consistent with the recent in situ FT-IR work by Toops et al. [12]. Therefore, the storage of NO_x on γ-Al_2O_3 has limited relevance to the practical application of NSR catalysts, since the presence of H_2O in diesel combustion exhaust gas is inevitable. The presence of CO_2, which is another inevitable component of diesel exhaust, also had a strong, although different effect on the NO_x storage capacity and chemistry of NSR catalysts, resulting in a progressive loss of NO_x storage capacity with increasing temperature. Overall, due to pronounced and complex effects of H_2O and CO_2 on NO_x storage, which appear to be not only quantitative but also qualitative (different types of sites involved), experimental studies performed in the absence of H_2O and CO_2 should have limited relevance to the practical applications.

The second part of this work provided some insight into a possible distinction between different types of Ba sites. The experimental conditions were adjusted to minimize the impact of several factors confounding NO_x storage on Ba sites, such as NO oxidation on Pt sites and NO_x storage on γ-Al_2O_3, and to preserve the distribution of NO_x species produced by the storage process. Under these conditions, the presence of a disproportionation mechanism was clearly demonstrated. At later stages of adsorption, an instantaneous nitrogen balance was achieved using the disproportionation stoichiometry alone. However, at the early stages of adsorption, this stoichiometry did not result in a closed N-balance. Explanations of this effect due to integral nature of NSR catalyst were essentially ruled out based on indirect experimental evidence. The integral amount of NO_x stored without regards to disproportionation stoichiometry was found to be constant even with a four-fold variation of NO_2 concentration in the inlet gas. The experimental results strongly suggest the presence of two types of Ba sites, which differ based on their proximity to Pt, such that the proximal Ba sites store NO_2 with participation of O_2 as an oxidant, while the remote Ba sites rely on the disproportionation mechanism. While the reported evidence is not sufficient to irrefutably confirm this hypothesis, it explains different aspects of the entire set of experimental results, and is consistent with recent literature findings.

Acknowledgements

The authors would like to thank Jim Lucas and Heather Eadler for help in the data collection process. Also, this work was done with partial support from the US Department of Energy under the Heavy Duty Diesel Program.

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