The effects of CO_2 and H_2O on the NO_x destruction performance of a model NO_x storage/reduction catalyst

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The effects of CO_2 and H_2O on the NO_x storage and reduction characteristics of a $Pt/Ba/Al_2O_3$ catalyst were investigated. The presence of CO_2 and H_2O, individually or together, affect the performance and therefore the chemistry that occurs at the catalyst surface. The effects of CO_2 were observed in both the trapping and reduction phases of the experiments, whereas the effect of H_2O seems limited to the trapping phase. The data also indicate that multiple types of sorption sites (or mechanisms for sorption) exist on the catalyst. One mechanism is characterized by a rapid and complete uptake of NO_x. A second mechanism is characterized by a slower rate of NO_x uptake, but this mechanism is active for a longer time period. As the temperature is increased, the effect of H_2O decreases compared to that of CO_2. At the highest temperatures examined, the elimination of H_2O when CO_2 is present did not affect the performance.

KEY WORDS: lean NO_x trap; NO_x storage/reduction catalyst; NO_x sorber; $Pt/Ba/Al_2O_3$; emission control.

1. Introduction

Economic and environmental concerns have led to increased demands for vehicles with better fuel economies and reduced NO_x, CO, hydrocarbon and CO_2 emissions. Lean-burn engines, of which diesel engines are an example, are more fuel-efficient than current, stoichiometric, gasoline-burning engines, and therefore result in lower overall CO_2 emissions. Although both of these characteristics are desired, diesel engines produce significant amounts of NO_x and particulate. In order to meet EPA's upcoming tiered emission standards for diesel engines, a reduction in these emissions is required.

Three-way catalytic converters that reduce NO_x, CO and hydrocarbon emissions have been optimized for use in engine exhaust gases that do not contain oxygen or with an engine that fluctuates around stoichiometric operation (e.g. today's gasoline-burning car). Using three-way catalyst technology for NO_x emission control in lean-burn engine exhaust has not succeeded in meeting the necessary NO_x emission reductions. The catalyst was not designed for, and is not very efficient under, these conditions. A different technology is therefore needed to appreciably reduce the NO_x emissions from lean-burn engines. One such technology being developed is NO_x storage/reduction (NSR) catalysts, also referred to as lean NO_x traps (LNT) or sorbers.

Owing to the potential impact and importance of NSR catalysts in emission control, a complete understanding of this complex catalytic system is ongoing [1–7]. The present study addresses the effects of two of the primary exhaust gas components, H_2O and CO_2, on the performance of a model NSR catalyst. There is already preliminary evidence in the literature that suggests that CO_2 affects catalyst performance. For example, CO_2 influences the release of NO_x from an NSR catalyst [8,9]. Although demonstrated, the significance and underlying reasons of the observed effects are not clear. Furthermore, the effects of CO_2 may not be limited to the regeneration/reduction step. For example, during the sorption (lean) mode, do CO_2 and NO_x compete for the same sites? With a reductant present, would CO_2 still accelerate release? What is the effect of H_2O during regeneration? Water may also play a role as competitor for sorption sites (formation of hydroxyls) and/or could influence the oxidation of NO to NO_2. Is there competition between the nitrate and hydroxyl and carbonate formation during lean operation and is this competition a function of the operating temperature? These hypotheses and questions are not meant to suggest that NSR catalysts should be operated in isothermal, dry, CO_2-free environments. But instead, can meaningful, fundamental studies be accomplished or models developed and verified without H_2O and CO_2 in the contact stream? The purpose of this phenomenological study is to address some of these questions by examining the influence of these two exhaust gas constituents on the performance of a typical, model NSR catalyst under "clean" exhaust gas conditions (no S, particulate matter or other possible poisons or masking agents).

2. Experimental description

2.1. Catalyst preparation

A $Pt/BaO/Al_2O_3$/cordierite sample was prepared for this study. The support was a 200 cell per square inch (cpsi) Rauschert cordierite monolith. A sample was

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removed from the monolith block by boring out a 0.625″ diameter core. The core sample was dipped into an aqueous slurry containing a high surface area (160 m^2/g) Al_2O_3. The excess solution was then drained, the core was allowed to dry and was finally calcined at 500 °C. The Ba and Pt components were added by incipient wetness methods. The Ba was added by preparing a Ba acetate solution in which the Al_2O_3-washcoated core was dipped. The core was then dried and calcined in air at 500 °C for one hour. A calculated BaO loading of 20 wt% relative to the Al_2O_3 washcoat was attained. The Pt was added as an organometallic precursor, again using an aqueous solution. Finally, the core was dried and calcined at 500 °C for one hour.

2.2. *Reactor experiments*

A bench-top, vertical-flow reactor was used in this study. A manifold system is attached that allows precision mixing of N_2, O_2, H_2O, CO, H_2, CO_2 and NO. N_2 was used as the balance gas in all experiments. Each gas except H_2O was introduced via a calibrated mass flow controller. The water was introduced just downstream of the gases, into a heated zone, using a syringe pump. The mixture entering the reactor was preheated to 150 °C. Table 1 lists the typical constituents of the gases introduced during the sorption and regeneration phases (lean versus rich). Although the concentrations listed in table 1 may not precisely mimic those present in diesel engine exhaust over the range of its operation, they are representative. The only component that may not be considered at this time to be representative is H_2. However, H_2 appears to be the best regeneration candidate and may be produced on the catalyst from CO via the water-gas-shift reaction or from hydrocarbon reductants via reforming. Also, the focus of this study is directed more at the effects of CO_2, H_2O and temperature, and a consistently clean surface is desired for the experiments. Therefore, H_2 was used instead of other potential reductant candidates.

The core sample was wrapped in high-temperature insulation material and placed into a steel reactor tube. The insulation material prevents any gas bypass around the catalyst during the experiments. The reactor tube was in turn placed inside a 3-zone tube furnace. Thermocouples were placed at the top and bottom of the core sample to verify inlet and outlet gas temperatures. In an effort to decouple the effects of H_2O, CO_2 and temperature on the trapping and reduction chemistry of the catalyst, four separate groups of experiments were accomplished. In these four sets, multiple temperatures were examined and the reactant gas stream included

1. all exhaust gas constituents listed in table 1 or,
2. all exhaust gas constituents listed in table 1 except H_2O or,
3. all exhaust gas constituents listed in table 1 except CO_2 or,
4. all exhaust gas constituents listed in table 1 except H_2O and CO_2.

The reactor system contains a bypass loop that allows the gas mixture to bypass the catalyst. The bypass was used at the beginning and end of each experiment to verify the nominal inlet concentrations. No divergence was observed between the concentrations desired and those observed with the analyzers. O_2, CO_2, CO and NO_x concentrations were measured using California Analytical Instrument's analyzers. NO_x speciation was not accomplished as part of this study.

Ten catalyst operating temperatures ranging from 175 to 420 °C were tested via furnace setpoint control. At each temperature, the catalyst was put through a minimum of three sorption/regeneration cycles to ensure catalyst performance stability. No differences in the data were observed between the second and third cycles at each temperature. The sorption cycle lasted 5 or 10 min and an identical time was used for the regeneration cycle. This cyclic process is representative of an end-use catalyst process [10,11]. At the beginning of each experiment set, the catalyst was pretreated in order to obtain a consistent initial surface for the 175 °C cycles.

Table 1
Details of the sorption and regeneration cycles

Bench-flow conditions	Sorption (lean)	Regeneration (rich)
Space velocity	25 000/h	25 000/h
NO	250 ppm	0 ppm
CO	150 ppm	150 ppm
O_2	8%	0%
H_2O	0 or 8%	0 or 8%
CO_2	0 or 8%	0 or 8%
H_2	0	1500 ppm
N_2	Balance	Balance

3. Results and discussion

3.1. *Effects of temperature*

Performance data were collected at reactor temperatures ranging from 175 to 420 °C. The flow conditions are described in table 1. In this first experiment, both H_2O and CO_2 were present during sorption and regeneration. The NO_x breakthrough data obtained at reactor temperatures of 175, 278 and 420 °C are shown in figure 1. The breakthrough profiles obtained at temperatures between 175 to 278 °C and 278 to 420 °C transitions between those in figure 1 (the optimum trapping performance occurs at 278 °C).

As indicated by the data shown in figure 1, under these experimental conditions, the catalyst removes all of the entering NO_x (no breakthrough observed) for at least 0.5 min at all of the temperatures examined. As the

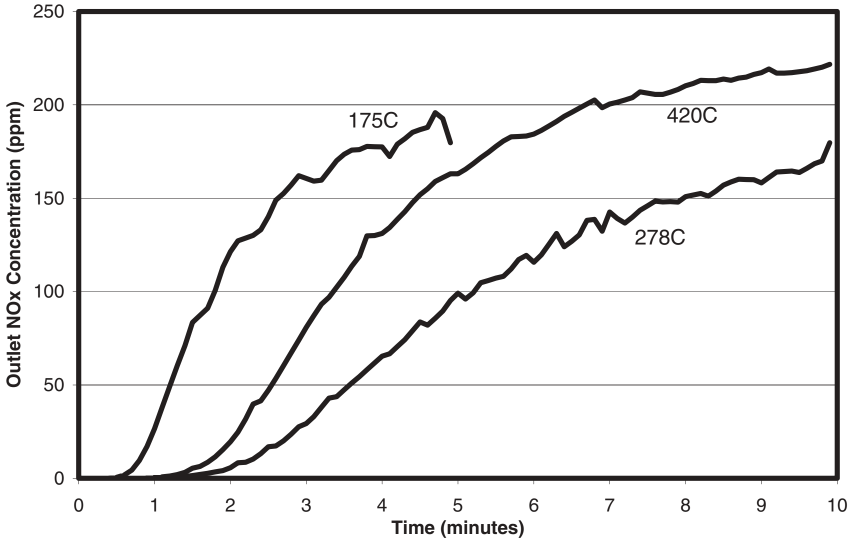

Figure 1. NO_x breakthrough profiles during sorption at 175, 275 and 400 °C. Sorption gas contains H_2O, CO_2, O_2, 150 ppm CO and 250 ppm NO in a balance of N_2.

operating temperature is increased to 278 °C, the amount of time that the catalyst traps *all* of the entering NO_x increases to 1.4 min. This is one characteristic of NSR catalysts that makes them such promising candidates for NO_x emission control. For some amount of time, complete NO_x removal from an oxygen-containing exhaust stream is obtained. By regulating the sorption time, very high NO_x conversions can be obtained. For example, if the sorption time is kept short, less than 1–2 min in this experiment, > 99% trapping is achieved at most temperatures and if the sorption time is limited to 30 s, > 99% trapping is achieved at all the temperatures examined in this study. High conversion of NO_x to N_2 requires this high trapping efficiency, but also a high reduction efficiency of trapped NO_x during the regeneration phase. Regeneration and reduction will be discussed below. After this initial period of complete capture, NO_x begins to slip through the catalyst. This indicates that the catalyst-trapping ability is decreasing, which is expected as the sorbate sites fill. However, for NSR catalysts, this does not represent long-term deactivation. For NSR catalysts, steady state conversion is a function of cycles. Over a brief period of time (minutes), the trapping efficiency decreases as the sorbate sites fill and NO_x slip increases. However, the catalyst operates in a cyclic pattern and after the end of each cycle returns to its original state. Over a long time period, hours or days etc., a very high conversion can be maintained.

Increasing the operating temperature of the catalyst from 175 to 278 °C lengthens the time in which complete capture occurs from 0.5 to 1.4 min. Furthermore, once NO_x does begin to slip, the rate of escape, signified by the slope of the breakthrough curve, is smaller at 278 °C than at any of the other temperatures examined. The increased trapping performance, with respect to the temperature increase from 175 to 278 °C can originate from several possible mechanisms or rate changes. It is understood that the kinetics of reaction change with temperature, but a consensus on the key parameter(s) that influences this catalyst has not been reached. Possible mechanisms, kinetic or rate changes are as follows:

- Catalytic NO oxidation to NO_2 (needed for nitrate formation) increases with temperature and is not significantly regulated by equilibrium until < 300 °C [12].
- If the mechanism includes the nitrate precursor diffusing along a surface path from Pt to a Ba site, an increase in temperature will increase diffusion and the nitrate precursor can diffuse to sites further from the Pt [7].
- At lower temperatures, the nitrate species may only form on the surface of the sorbate crystals and not diffuse into the bulk. As the temperature increases, diffusion into the bulk of the sorbate crystal increases, freeing more sites for nitrate formation [6].
- An activation barrier may exist for decomposition of the sorbate precursor species (e.g. BaO). Once some stability threshold is exceeded, an accessible nitration site becomes available [2,5]. This can be extended to include the equilibrium ratio of Ba oxide/hydroxide/carbonate/nitrate species.
- O_2 dissociation to atomic oxygen for nitrate formation or some other source of an oxygen atom (e.g. from NO_2 via dissociation) is necessary for the final product to be formed [1,3]. Temperature may increase the access to the reactant oxygen via increased Pt dissociation of O_2, migration or separation of oxygen from another oxide source or from NO_2.
- Although the nitrate forms, the decomposition of the nitrate during regeneration may be limited, leaving less sites available for the next sorption. Incomplete

regeneration would decrease as the temperature is increased since the nitrate species become less stable.

One of the listed mechanisms may be dominant or all could be significant and occurring coincidentally or further complicating matters, and the importance of each mechanism may change as a function of temperature. For example, at low temperatures (<200 °C) the NO oxidation reaction is kinetically limited but at slightly higher temperatures (200–300 °C), the O_2 dissociation reaction may kinetically limit the process. Although some of the possibilities have been discussed in previous studies, which of these is the primary driver, which of these has no affect on performance or which of these simply does not exist has yet to be confirmed.

Incomplete regeneration is listed above and occurs when some of the nitrate species formed during sorption cannot be removed during regeneration. In this study, an excess amount of H_2 was used to accelerate regeneration of the catalyst. No differences were observed in performance between the second and third cycles of the experiments, which indicates that if incomplete regeneration was occurring, it must occur during the first cycle. When the three cycles at one test temperature were complete, the sample was ramped to the next temperature setpoint during the sorption phase. Therefore, if changes in regeneration efficiency were the sole cause of the observed NO_x uptake changes, then the first breakthrough curve at a new temperature would mimic the last observed at the lower temperature. This did not occur; the NO_x uptake increased during this first sorption. Therefore, regeneration efficiency may be a factor, but at least one of the other mechanisms on the list was simultaneously influencing the performance of the catalyst.

As the data in figure 1 and in table 2 show, after the reactor temperature exceeds 278 °C the catalyst trapping performance decreases. This is most likely due to a decrease in nitrate stability, but can be influenced by NO/NO_2 equilibrium changes. First, as the temperature passes 250 °C, NO oxidation can decrease because of these NO/NO_2 equilibrium limitations. However, since NO_2 is being sorbed, the equilibrium barrier is shifted toward oxidation. As the temperature is further increased, the equilibrium limitations become stricter and may affect performance. At higher temperatures the nitrate stability decreases. The nitrate formation reaction is a reversible process, and as the temperature is increased, the rate of the reverse reaction increases faster than that of the forward reaction [3]. These factors lead to a change in the stable equilibrium or ratio between the $OH/CO_3/O/NO_3$ sorbate species. It is the stability of the nitrate in relation to the other species that causes the observed decrease in trapping performance as the temperature increases beyond 278 °C.

The NO_x releases during the regeneration phase at 175, 278 and 420 °C are shown in figure 2. This NO_x was trapped during the lean phase and released from the surface when the reductant was added, but *not* reduced to N_2. The reduction efficiency listed in table 2 is the percentage of NO_x trapped during the sorption phase that is converted to N_2. This inherently assumes that no N species accumulate on the catalyst so the mass balance is comprised only of the known quantities of NO_x entering and released and the sorbed NO_x that is reduced to N_2 (the reduction efficiency). Since no changes in performance are noted between cycles 2 and 3, the absence of accumulation between these cycles is a reasonable assumption. As shown in table 2, most of the trapped NO_x is reduced to N_2. For the 20-min cycle time, the highest conversion of trapped NO_x is 93.1% at 250 °C but surprisingly drops as the operating temperature is increased beyond 250 °C. This may be due to the

- larger amount of NO_x trapped on the surface that is released with reductant introduction (however, at temperatures >303 °C the amount trapped decreased),
- decreased stability of the nitrate species (as discussed above),
- decreased efficiency of the Pt species or in forming the Pt species responsible for reduction.

As shown in figure 2, the NO_x is released during the first 2.5 min of regeneration, but changes in NO_x release rates during this 2.5 min suggest that release occurs through more than one mechanism or from more than one site. The first release of NO_x occurs almost immediately with the start of the regeneration phase. A second release becomes apparent between 1 and 2 min later when the catalyst is tested at temperatures higher than 200 °C. This release occurs at a slower rate and may represent a compilation of varying reaction energies or release along the catalyst length. Overall, between 200 and 303 °C, the reduction efficiency remains rather

Table 2
Catalyst performance in the presence of both CO_2 and H_2O

Temperature (°C)	Overall NO_x conversion (%)	Trapping efficiency (%)	Reduction efficiency (%)
175[a]	46.5	54.5	85.3
200[a]	62.9	69.6	90.4
225[a]	72.9	77.9	93.6
250	58.6	63.0	93.1
278	61.2	66.3	92.4
303	59.9	66.2	90.4
330	57.0	65.3	87.3
360	50.8	61.9	82.1
390	40.9	55.5	73.8
420	30.2	47.2	64.0

[a] These data points were obtained from shortened sorption/regeneration cycles (10-min total cycle versus 20-min total cycles for the others) since the NO_x breakthrough pattern had already evolved.

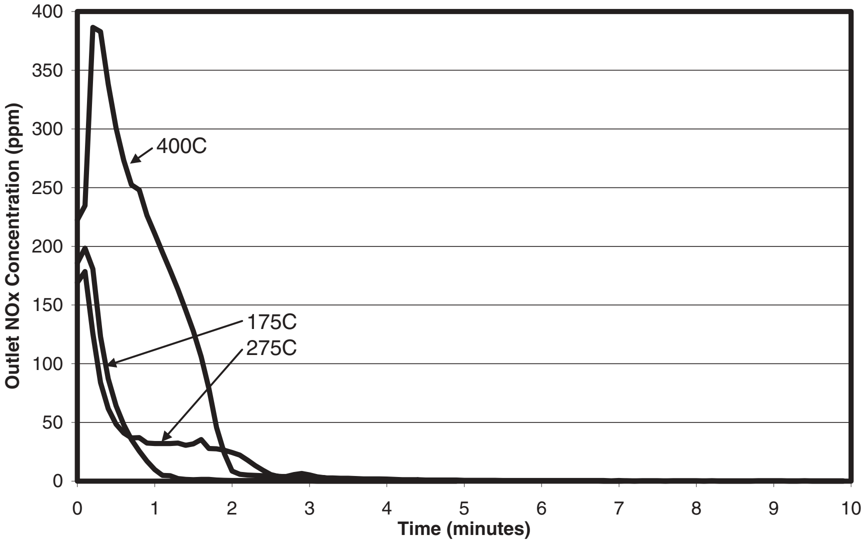

Figure 2. NO_x release profiles during regeneration at 175, 275 and 400 °C with both H_2O and CO_2 present. Regeneration gas consists of H_2O, CO_2, 150 ppm CO and 1500 ppm H_2 in a balance of N_2.

stable. Although more NO_x is released with each increase in temperature, the catalyst trapped more NO_x during the associated sorption before regeneration, resulting in a stable reduction efficiency coincident with an increasing NO_x release. The first release accounts for ~4% of the reduction inefficiency if the temperature is between 200–360 °C and remains at the same relative intensity until 360 °C is exceeded. At temperatures exceeding 303 °C, there is an increase in the NO_x released from the later mechanism, which accounts for loss in reduction efficiencies listed in table 2. At 390 and 420 °C, the intensity of the first release also grows, which results in accelerating the loss.

The presence of multiple NO_x releases complicates the understanding of the surface reactions, however, a few ideas have been introduced. The noble metal site becomes reduced during the rich phase of the cycle. It has been suggested that these reduced sites are responsible for the reduction of NO_x to N_2 [1,13]. Unlike the conditions used in this study, in both of these previous studies [1,13] NO_x was also introduced to the reactor during the rich phase. The two authors, however, suggest different mechanisms for the increase in NO_x concentration (NO_x release) at the beginning of the rich phase. One study attributed the NO_x release observed during the rich phase to the nitrate decomposition being more rapid than Pt oxide reduction when the rich phase began [13]. With sudden nitrate decomposition to NO_x and no reduced Pt sites available to carry out reduction, a large amount of NO_x exited the reactor. The opposing argument is that noble metal sites are rapidly reduced, decreasing their ability to sorb NO_x, and the rate-limiting step for reduction is the nitrate decomposition step [1]. The observed sharp increase in NO_x concentration when the rich phase began was attributed to the decreased ability of reduced Pt to sorb incoming NO_x along with the coincident nitrate decomposition. In the present study, NO_x was not introduced during the regeneration phase and the data shown in figure 2 indicate that significant NO_x release still occurs. This eliminates the need for Pt to sorb the extra incoming NO_x. These data therefore support the mechanism where the rate of Pt reduction is slower than nitrate decomposition [13]. Some of the NO_x that is released escapes at the beginning of the regeneration without being reduced because there are not enough efficient Pt sites initially available. It is also apparent that the introduction of the reductant (and in this study the removal of NO_x) drives nitrate decomposition. Lietti *et al.* [2] argue that the release of NO_x from $Ba(NO_3)_2$ should not be attributed to the small temperature rise that occurs during regeneration. In that study, a 3–5 °C gas temperature rise was observed [2]. An identical temperature rise was observed in this study near the beginning of the regeneration phase. It can be argued that a small rise in the gas temperature can still be attributed to a large rise in catalyst surface temperature. Heat is absorbed into the catalyst media as well as by the rapidly flowing gas, thereby suppressing the observed increase in temperature when an exothermic reaction occurs at the surface. This heat generated at the surface would accelerate nitrate decomposition and therefore NO_x release. The beginning of the temperature rise at the catalyst outlet was detected at 0.9 min when operating at 175 °C and at 1.4 min when operating at 420 °C. Although observed after the first NO_x release was complete, the heat release or temperature rise closer to the front of the catalyst occurs earlier. Therefore, a temperature profile with time evolves along the catalyst at the beginning of regeneration. This heat may be responsible for the development of the second NO_x release observed between 1 and 2 min. Overall, however, these data do suggest that the temperature rise does not result in the first NO_x release, since the temperature rise through the whole of the catalyst is observed after the first NO_x release has occurred. With these data, however, the evolution of the second peak cannot be decoupled from the heat release.

3.2. *Elimination of* H_2O *and* CO_2

The overall conversions, trapping and reduction efficiencies as a function of reaction temperature, with neither H_2O nor CO_2 in the sorption and regeneration phases of the reaction cycle, are listed in table 3. It is apparent when comparing tables 2 and 3 that the catalyst performs better in the absence of H_2O and CO_2. The peak overall conversion for 20-min cycles is 87.2% and occurs at an operating temperature of 303 °C, whereas in the presence of both H_2O and CO_2 the peak conversion occurs at 278 °C and is 61.2%. Overall, the changes in reduction efficiency with temperature are similar for both sets of experiments. The reduction efficiencies at temperatures lower than 390 °C are consistently lower by about 3–5% when CO_2 and H_2O are introduced. At 390 and 420 °C, the reduction efficiency difference is greater. It is the trapping efficiency, however, that dictates the change in temperature where the peak conversion occurs, and, furthermore, the trapping efficiency is more significantly affected by the presence of the two components. The maximum trapping efficiency for the entire 10-min trapping interval is 66.3% when H_2O and CO_2 are present and 92.9% when absent.

Two sets of NO_x breakthrough and release profiles, obtained while operating the reactor at 175 and 420 °C, are shown in figure 3. These plots include a full cycle of data, i.e. both sorption and regeneration phases are shown. As stated above, it is primarily the trapping efficiency that is affected (increased) with the removal of CO_2 and H_2O. Furthermore, the introduction of CO_2 and H_2O changes the rate of NO_x breakthrough after slip begins and NO_x release during regeneration, indicating changes in surface reaction pathways, mechanisms or rates. An obvious explanation for the decreased capacity and coincident conversion is the introduction of competitive species. Without H_2O and CO_2, barium hydroxide and carbonate species will not exist (unless hydroxyl species form from the H_2 reductant source and carbonates form from the CO introduced during both phases). Therefore, BaO could be the dominant species of the sorber after a regeneration phase. Previous research has shown that BaO is the first of the sorbate species on a $Pt/Ba/Al_2O_3$ catalyst to convert to nitrate in the presence of NO_x [2]. Hydroxides were converted next and the carbonates last. As the hydroxides and carbonates are more stable, the presence of CO_2 and/or H_2O during sorption could suppress or change the rate of nitrate formation via competitive adsorption or equilibrium considerations. The data shown in figure 2 and listed in table 3 along with the previous research discussed above, support this argument.

Table 3
Catalyst performance without CO_2 and H_2O present

Temperature (°C)	Overall NO_x conversion (%)	Trapping efficiency (%)	Reduction efficiency (%)
175[a]	72.6	80.2	90.4
200[a]	85.7	91.0	94.2
225[a]	91.9	95.6	96.1
250	81.7	85.1	96.0
278	85.4	88.9	96.1
303	87.2	91.6	95.3
330	86.1	92.9	92.7
360	81.2	92.3	88.0
390	73.3	89.5	81.9
420	62.5	83.9	74.6

[a] These data points were obtained from shortened sorption/regeneration cycles (10-min total cycle versus 20-min total cycles for the others).

Removing CO_2 and H_2O also results in a shift in the temperature where the maximum conversion is attained due to a shift in the temperature where the maximum trapping efficiency occurs. This result indicates the significance of the influence of CO_2 and/or H_2O as a function of temperature. Since the maximum conversion temperature is shifted downwards with the presence of these two gases, the effect of the two components on the chemistry must be more prominent at higher temperatures. As discussed previously, the stability of the $O/OH/CO_3/NO_3$ species and, more importantly, their relative stability will change with temperature. It is apparent that the stability of the hydroxide or carbonate species increases in comparison to the nitrate at the higher temperatures. Not only does the presence of these two components influence the capacity and temperature where the peak capacity is attained, they change the shape of the breakthrough profile of NO_x. NO_x slip occurs earlier when CO_2 and H_2O are present and, once slip begins, the rate of NO_x escape changes. Again, this could be related directly to competition of the species with $Ba(NO_3)_2$ formation. This will be more extensively discussed below in the sections addressing the individual effects of the two components.

The presence of CO_2 and H_2O also influences the regeneration phase. With CO_2 and H_2O present, more NO_x could be driven off owing to surface species equilibrium considerations. Indeed, previous studies show that NO_x release is enhanced by the presence of CO_2 in the rich or NO_x-free phase of a cycle [8,9]. However, no conclusive demonstration of the effect of CO_2 on the conversion of NO_x to N_2 was discussed. In other words, although more NO_x was released, was more converted to N_2 if more sorbed in the previous cycle? Did more or less of the sorbed NO_x remain on the surface with the addition of CO_2? The first NO_x release

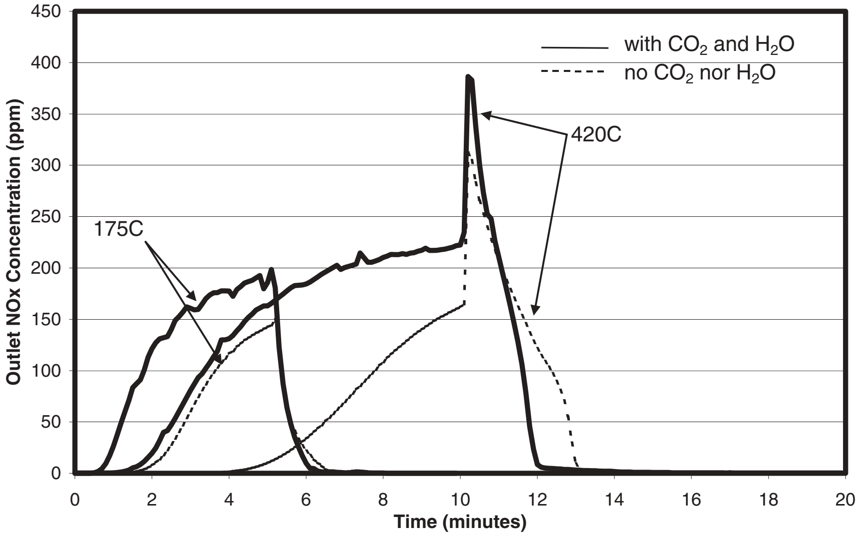

Figure 3. NO_x breakthrough and release profiles at 175 and 400 °C with (1) both H_2O and CO_2 present and (2) neither H_2O nor CO_2 present. Sorption gas also contains O_2, 150 ppm CO and 250 ppm NO in a balance of N_2. Regeneration gas also contains 150 ppm CO and 1500 ppm H_2 in a balance of N_2.

is more intense with CO_2 and H_2O present at 390 and 420 °C, but at lower temperatures no significant differences are noticeable. This finding indicates that the first NO_x release is only affected by the presence of CO_2 and H_2O at the elevated temperatures even though more NO_x is trapped on the catalyst in their absence and the same amount of reductant was used in each experiment. It is apparent from the data shown in figure 3 that the second NO_x release is actually increased in the absence of CO_2 and H_2O and this was true at all the temperatures tested. The data in table 3, however, show that the reduction efficiency is enhanced by the removal of H_2O and CO_2. The apparent discrepancy is due to the larger amount of NO_x trapped on the catalyst during sorption when CO_2 and H_2O are absent from the simulated exhaust gas. When H_2O and CO_2 are present and when operating at 420 °C, 13.8 cc of NO_x sorbed during the 10-min NO_x exposure and with neither component present, 24.1 cc NO_x sorbed. The ratio of trapped NO_x to reductant therefore increases 75%. Since the same amount of reductant is used in both experiments, only a certain amount of this increased amount of NO_x stored can be reduced. Since the total amounts of NO_x released during the regeneration phases are similar, the catalyst that trapped more NO_x reduced more NO_x, accounting for the increased reduction efficiency listed in table 3. Under the conditions of this test, the reaction is not reductant limited. Therefore, CO_2 and/or H_2O influence the reduction or release rates of the sample.

Overall, it is apparent that the absence of CO_2 and H_2O results in improved catalyst performance. Their presence reduces the trapping capacity and changes the regeneration chemistry and reduction efficiency of the sample. This work was carried further to investigate the influence of the two components individually; i.e., does H_2O or CO_2 individually cause all the differences noted in the preceding section?

3.3. *Absence of H_2O (influence of CO_2)*

The overall conversions, trapping and reduction efficiencies as a function of reaction temperature, with no H_2O in either the sorption or regeneration phases of the reaction cycle, are listed in table 4. CO_2 was present throughout.

Reintroducing CO_2 into the reactant stream significantly suppresses the catalyst's activity toward NO_x conversion to N_2. The presence of CO_2 results in decreased trapping capacity, especially at the higher temperatures. Slightly higher reduction efficiencies are attained at the lower temperatures, while at the higher temperatures the reduction efficiency is lower.

Table 4
Catalyst performance without H_2O present

Temperature (°C)	Overall NO_x conversion (%)	Trapping efficiency (%)	Reduction efficiency (%)
175[a]	62.2	68.5	90.9
200[a]	79.0	83.7	94.4
225[a]	88.3	92.2	95.8
250	77.2	81.8	94.4
278	77.4	83.1	93.1
303	74.2	82.2	90.3
330	67.2	78.4	85.7
360	56.4	71.4	79.0
390	43.0	61.3	70.2
420	29.4	49.7	59.2

[a] These data points were obtained from shortened sorption/regeneration cycles (10-min total cycle versus 20-min total cycles for the others).

NO_x breakthrough and release profiles obtained at 175 °C are shown in figure 4. Complete NO_x capture occurs for the same amount of time whenever CO_2 is present. Although CO_2 significantly influences the initial interval of NO_x trapping, the data indicate that CO_2 has a smaller influence on the capture efficiency after breakthrough begins to occur. These results, compared with those in figures 1 and 3, demonstrate that multiple trapping mechanisms or sites exist at the catalyst surface. The first mechanism occurs and dominates at the initial stage of capture and is characterized by a rapid rate of NO_x uptake and results in complete NO_x capture at the beginning of a sorption phase. Once these highly active sites fill and breakthrough begins, a second mechanism or site becomes evident. This mechanism is characterized by a slower rate of NO_x removal but continues for a long period of time. The result of the slower mechanism is that the rate of NO_x slip decreases with sorption time; therefore, the outlet NO_x level asymptotically approaches the inlet concentration value. At 175 °C, CO_2 suppresses the first mechanism and has less influence on the second. On the basis of these data, this coincidentally suggests that when CO_2 is present, H_2O plays a role in affecting the second mechanism but has little or no influence on the first. This will be verified below. The data shown in figure 5 were obtained at a reactor temperature of 420 °C. The breakthrough profile of the sample tested with both CO_2 and H_2O is almost identical to that tested with CO_2 present but with H_2O absent. This indicates that CO_2 significantly influences the reaction chemistry of the catalyst at the higher temperature, while H_2O has little or no influence on trapping at the higher temperature when CO_2 is present. It may be that at the elevated temperatures, most or all of the relevant hydroxyl groups are displaced by carbonates from the sites participating in the reaction sequence.

The regeneration phase is also affected by CO_2, but only at the higher temperatures. At 175 °C, no significant differences in the NO_x release profiles are evident. At 420 °C, the first release of NO_x is larger when just CO_2 is added. The CO_2 causes a larger initial NO_x release, but, apparently, the addition of H_2O suppresses this effect since, when both components are present, the release is smaller although the amount trapped appears similar. Again, the data show that the second release becomes more prominent with increasing temperature. However, the second release of NO_x is less significant whenever CO_2 is present. The time duration that NO_x is released also becomes shorter with CO_2 addition, for example, when operating at 420 °C the NO_x release decreases from 3.2 min with neither component present to 2.0 min with CO_2. Unfortunately, it is not possible to decouple the lowered trapping capacity from the smaller second release. The extra NO_x that is trapped in the absence of CO_2 may be the NO_x that results in a larger second release. The first release is increased either by the direct involvement of CO_2 in the release or reduction reaction or the indirect involvement that results in a decrease in appropriate trapping sites.

3.4. *Elimination of CO_2 (influence of H_2O)*

The overall conversions, trapping and reduction efficiencies as a function of reaction temperature, with no CO_2 in either the sorption or regeneration phases of the reaction cycle, are listed in table 5. H_2O was present in both.

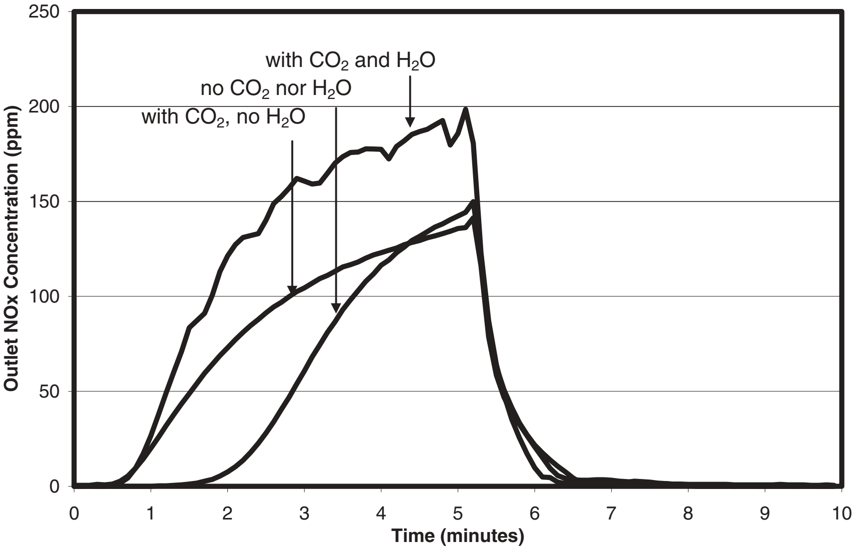

Figure 4. NO_x breakthrough and release profiles at 175 °C with (1) both H_2O and CO_2 present, (2) neither H_2O nor CO_2 present and (3) H_2O absent and CO_2 present. Sorption gas also contains O_2, 150 ppm CO and 250 ppm NO in a balance of N_2. Regeneration gas also contains 150 ppm CO and 1500 ppm H_2 in a balance of N_2.

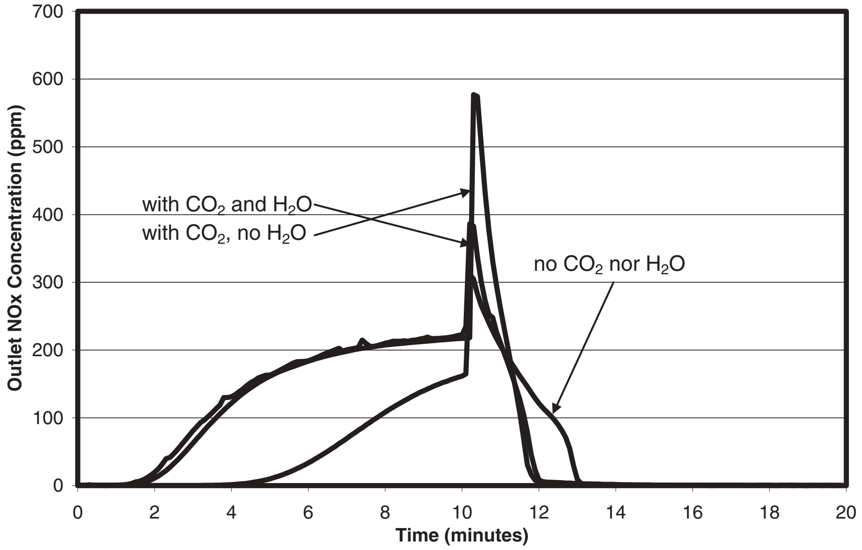

Figure 5. NO_x breakthrough and release profiles at 400 °C (1) both H_2O and CO_2 present, (2) neither H_2O nor CO_2 present and (3) H_2O absent and CO_2 present. Sorption gas also contains O_2, 150 ppm CO and 250 ppm NO in a balance of N_2. Regeneration gas also contains 150 ppm CO and 1500 ppm H_2 in a balance of N_2.

It is apparent in comparing the data in tables 3 and 5 that the presence of H_2O has little or no effect on the reduction efficiency, but the overall conversion and trapping efficiencies are decreased. On the basis of the data shown in tables 4 and 5, CO_2 suppresses the trapping capacity more than H_2O does. In order to gain a better picture of these results, the trapping efficiency and reduction efficiency at each temperature are plotted in figures 6(a) and (b) respectively. These plots clearly show that the effect of H_2O on trapping is consistent through most of the temperature range examined. The effect of CO_2, however, is more evident at the higher temperatures. A similar pattern is evident when analyzing the reduction efficiencies. The effect of water is consistent through the entire range (little or no effect), while that of CO_2 is observed at the higher temperatures. This loss in reduction efficiency cannot solely be attributed to a greater NO_x uptake since the maxima in reduction efficiency and NO_x uptake as a function of temperature do not coincide.

Table 5
Catalyst performance without CO_2 present

Temperature (°C)	Overall NO_x conversion (%)	Trapping efficiency (%)	Reduction efficiency (%)
175[a]	61.3	67.5	91.4
200[a]	76.6	80.9	95.0
225[a]	84.5	87.9	96.3
250	72.1	75.0	96.4
278	75.6	78.6	96.4
303	78.9	82.3	95.9
330	79.9	84.5	94.6
360	77.7	84.9	91.6
390	70.4	81.9	86.1
420	56.7	73.2	77.7

[a] These data points were obtained from shortened sorption/regeneration cycles (10-min total cycle versus 20-min total cycles for the others).

The temperature at which the maximum trapping efficiency occurs is

- 278–303 °C with CO_2 and H_2O present,
- 330–360 °C with neither present,
- 278 °C with just CO_2 present (no H_2O) and
- 360 °C with just H_2O present (no CO_2), the highest temperature.

This is yet further evidence that the effect of CO_2 on trapping performance becomes stronger as the temperature is raised. It also supports the argument that the effect of H_2O on trapping efficiency is consistent throughout the temperature range examined. The incontinuity between 225 and 250 °C in figure 6(a) is due to the change in cycle time from 10–20 min. The overall trapping efficiency is offset to a higher value since a shorter trapping time is used prior to 250 °C. Interestingly, however, a much smaller incontinuity is observed in the reduction efficiency profile, figure 6(b). This reflects the catalyst's strong ability to reduce the NO_x that is released when regeneration occurs under the conditions examined.

The NO_x breakthrough data obtained during each of the four experiments at 175 °C are shown in figure 7. The time that complete NO_x capture occurs lengthens in the order, neither CO_2 nor H_2O > just H_2O > just CO_2 = both CO_2 and H_2O. This shows that H_2O influences the reaction chemistry involved with the initial rapid uptake of NO_x only when CO_2 is absent. With the addition of H_2O, the shape of the NO_x breakthrough profile after slip begins resembles that when both components are introduced, which indicates that the mechanisms are potentially the same once slip

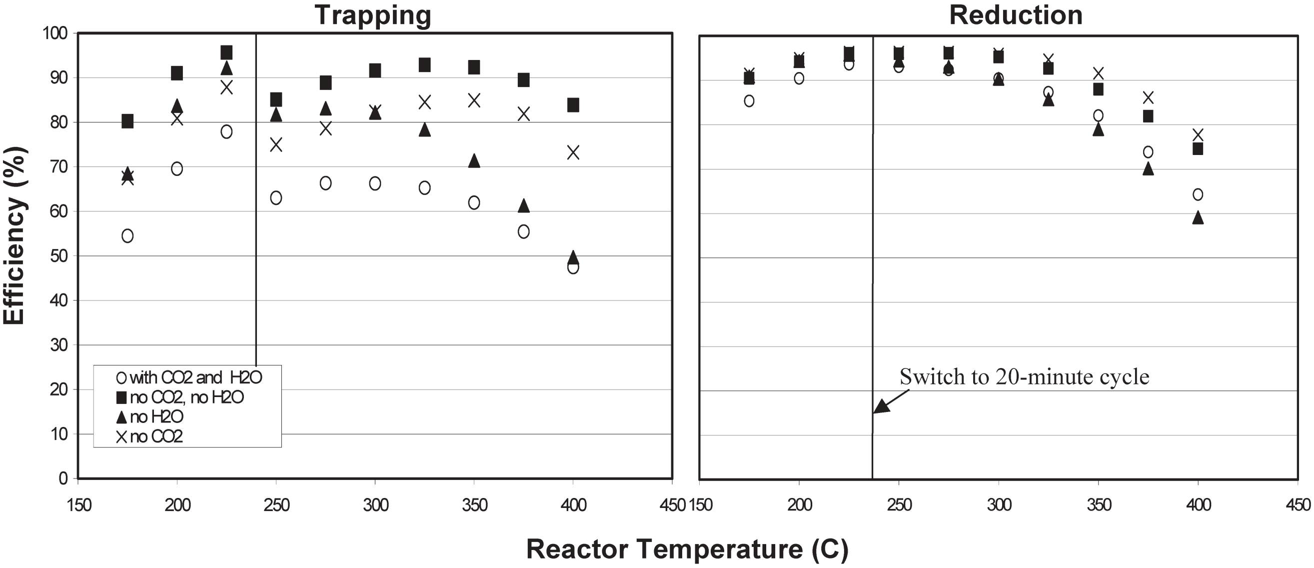

Figure 6. Individual and collaborative effects of H_2O and CO_2 on trapping and reduction efficiencies.

begins. As discussed in the previous section when just CO_2 is present, the profile after slip begins is significantly different from that obtained when both components are present. This further indicates that the effect of H_2O is more significant than CO_2 after slip begins. Unlike the initial phase of NO_x uptake, at low temperatures this effect is not influenced by the presence of CO_2. Overall, these data demonstrate that H_2O influences the reaction chemistry at low temperatures, but the influence is observed at different times depending on the presence of CO_2. The breakthrough profiles obtained at 420 °C during each of the four experiments are shown in figure 8. When H_2O is removed, but CO_2 remains, the profile is identical to that obtained when both components are present. When H_2O is added but not CO_2, complete capture ends earlier and towards the end of the sorption phase, the concentrations actually converge. The convergence of the two profiles is due to the slower elimination of available sorption sites as they are all being consumed in nitrate formation. Therefore, the influence of H_2O on NO_x capture is less significant at higher temperatures, but is only observed in the absence of CO_2.

At 175 °C, all of the NO_x release profiles are identical once the regeneration phase begins. The small differences in the profiles at around 6 min (1 min into the rich phase) may be the evolution of a NO_x release. However, this is difficult to resolve owing to the sharp decline in NO_x concentration during that short time interval. The NO_x concentration profiles obtained at 420 °C during regeneration whenever CO_2 is absent are similar although when H_2O is present, the NO_x release is

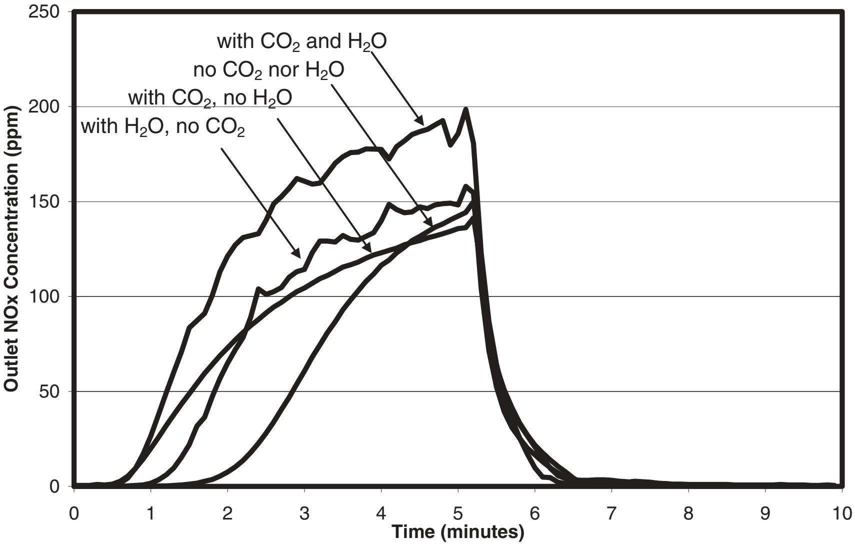

Figure 7. NO_x breakthrough and release profiles at 175 °C with (1) both H_2O and CO_2 present, (2) neither H_2O nor CO_2 present, (3) H_2O absent and CO_2 present and (4) H_2O present and CO_2 absent. Sorption gas also contains O_2, 150 ppm CO and 250 ppm NO in a balance of N_2. Regeneration gas also contains 150 ppm CO and 1500 ppm H_2 in a balance of N_2.

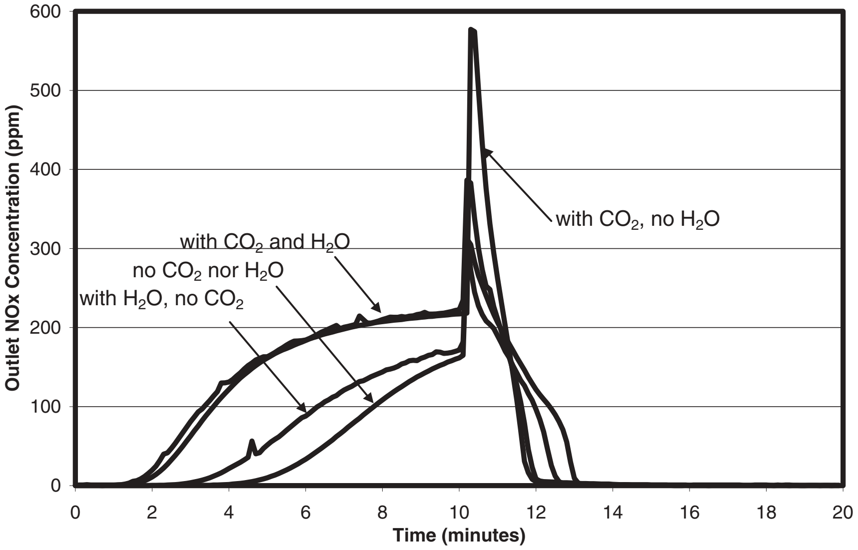

Figure 8. NO_x breakthrough and release profiles at 400 °C with (1) both H_2O and CO_2 present, (2) neither H_2O nor CO_2 present, (3) H_2O absent and CO_2 present and (4) H_2O present and CO_2 absent. Sorption gas also contains O_2, 150 ppm CO and 250 ppm NO in a balance of N_2. Regeneration gas also contains 150 ppm CO and 1500 ppm H_2 in a balance of N_2.

somewhat suppressed. However, the amount trapped is also smaller when H_2O is present. Furthermore, when CO_2 is absent and more NO_x is trapped, NO_x is released about 2 min into the regeneration phase. This again suggests that at higher temperatures the increased NO_x release that occurs at about 1 to 2 min into the regeneration is related to the NO_x that is trapped in the absence of CO_2. The first, earlier, release of NO_x is not associated with any extra uptake of NO_x, since it actually decreases when CO_2 is absent and is suppressed with the addition of H_2O.

The data presented in this study indicate that multiple NO_x sorption and release mechanisms or sites exist on the catalyst surface. These sites, mechanisms or pathways become significant or change significance with temperature. Under the conditions of these experiments, two apparent sorption pathways exist, one that is rapid and evident at the beginning of sorption and the other that is slower and becomes evident after NO_x slip begins. This latter mechanism accounts for the slow approach of the NO_x slip concentration toward the inlet NO_x value. The outlet NO_x levels never achieve the inlet values under the conditions examined in this study. Results using IR spectroscopy [14] indicate that on another model sorber catalyst the alumina washcoat will sorb NO_x if H_2O is absent while in the presence of H_2O no NO_x sorption on the alumina occurs. Therefore, H_2O completely suppresses the alumina involvement. The data presented in this study show an effect of H_2O, but not to the extent that the IR data suggest. Therefore, H_2O may play yet another role in the sorption mechanism beyond suppressing the alumina involvement. Further research being conducted at Oak Ridge National Laboratory, using modeling techniques, also suggest multiple site sorption pathways [15]. The results of the modeling effort indicate that at least two, if not more energetically different, reactive sites exist at the surface. The data presented above show that CO_2 causes the duration of complete capture to shorten, which demonstrates the initial, rapid NO_x uptake mechanism is influenced by CO_2. H_2O, when CO_2 is absent, has a similar effect but it is much smaller. H_2O plays a larger role in influencing the second uptake mechanism. The influence of H_2O on NO_x uptake diminishes with increasing temperature and at the highest temperature examined, 420 °C, the influence of CO_2 is dominant. Together, these data also indicate that multiple NO_x release mechanisms exist. Furthermore, all of the data support the claim that CO_2 changes the chemistry of the regeneration mechanism (in relation to the absence of H_2O and CO_2), although some of the changes in trapping and regeneration may be related to each other. The data taken at intermediate temperatures display a blend of these findings.

4. Conclusions

In conclusion, these data show that multiple sorption and NO_x release mechanisms or sites exist on a NO_x storage/reduction catalyst during standard bench-top reactor tests. At the beginning of sorption, there is a rapid uptake of NO_x. A second pathway or site for sorption also exists and is observed once NO_x slip begins. This mechanism is characterized by a slower NO_x uptake rate, but is observed over a longer period of time. H_2O and CO_2 significantly alter the chemistry of the catalyst and have different effects on the two sorption pathways observed. At lower temperatures, CO_2 shortens the time that complete NO_x trapping occurs but does not significantly suppress the trapping ability of the catalyst once NO_x slip begins. H_2O also shortens the time of complete trapping but when both components are present, it is not an additive effect. H_2O suppresses the second mechanism that is observed once NO_x slip begins. Thus, it is apparent that CO_2 has a larger influence on one pathway (a rapid rate of NO_x uptake characterized by complete NO_x capture), while H_2O has a larger influence on the other (a slower rate of NO_x uptake that is observed once slip begins). The effect of CO_2 becomes more dominant as the operating temperature is increased. Actually, the effect of H_2O is only apparent at the lower operating temperatures since the CO_2 effect dominates at higher temperatures. These results demonstrate the need of including CO_2 and H_2O in standard tests and model development to capture the chemistry that occurs during NO_x storage and reduction.

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