Catalysis Letters Vol. 111, Nos. 3–4, November 2006 (© 2006)
DOI: 10.1007/s10562-006-0153-4

NO_x uptake mechanism on $Pt/BaO/Al_2O_3$ catalysts

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Received 30 May 2006; accepted 8 August 2006

The NO_x adsorption mechanism on $Pt/BaO/Al_2O_3$ catalysts was investigated by performing NO_x storage/reduction cycles, NO_2 adsorption and NO + O_2 adsorption on $2\%Pt/(x)BaO/Al_2O_3$ (x = 2, 8, and 20 wt%) catalysts. NO_x uptake profiles on $2\%Pt/20\%BaO/Al_2O_3$ at 523 K show complete uptake behavior for almost 5 min, and then the NO_x level starts gradually increasing with time and it reaches 75% of the inlet NO_x concentration after 30 min time-on-stream. Although this catalyst shows fairly high NO_x conversion at 523 K, only ~2.4 wt% out of 20 wt% BaO is converted to$Ba(NO_3)_2$. Adsorption studies by using NO_2 and NO + O_2 suggest two different NO_x adsorption mechanisms. The NO_2 uptake profile on $2\%Pt/20\%BaO/Al_2O_3$ shows the absence of a complete NO_x uptake period at the beginning of adsorption and the overall NO_x uptake is controlled by the gas–solid equilibrium between NO_2 and $BaO/Ba(NO_3)_2$ phase. When we use NO + O_2, complete initial NO_x uptake occurs and the time it takes to convert ~4% of BaO to $Ba(NO_3)_2$ is independent of the NO concentration. These NO_x uptake characteristics suggest that the NO + O_2 reaction on the surface of Pt particles produces NO_2 that is subsequently transferred to the neighboring BaO phase by spill over. At the beginning of the NO_x uptake, this spill-over process is very fast and so it is able to provide complete NO_x storage. However, the NO_x uptake by this mechanism slows down as BaO in the vicinity of Pt particles are converted to $Ba(NO_3)_2$. The formation of $Ba(NO_3)_2$ around the Pt particles results in the development of a diffusion barrier for NO_2, and increases the probability of NO_2 desorption and consequently, the beginning of NO_x slip. As NO_x uptake by NO_2 spill-over mechanism slows down due to the diffusion barrier formation, the rate and extent of NO_2 uptake are determined by the diffusion rate of nitrate ions into the BaO bulk, which, in turn, is determined by the gas phase NO_2 concentration.

KEY WORDS: NO_x storage/reduction; $Pt/BaO/Al_2O_3$; NO_2 adsorption; NO + O_2 adsorption; spill-over; bulk diffusion; kinetic control.

1. Introduction

The control of NO_x, (NO and NO_2) emission from combustion processes, including vehicle engines, remains a challenge particularly for systems operating at high air-to-fuel ratios (so-called 'lean' combustion). The current ''3-way'', precious metal-based catalytic converters are unable to selectively reduce NO_x with reductants (e.g., CO, H_2, and residual unburned hydrocarbon) in the presence of excess O_2. In the last few years, worldwide environmental regulations regarding NO_x emissions from diesel engines (inherently operated 'lean') have become significantly more stringent resulting in considerable research efforts to reduce NO_x under the highly oxidizing engine operation conditions. Urea selective catalytic reduction (SCR) and non-thermal plasma assisted NO_x reduction have been explored as possible technologies to treat the emissions from lean NO_x sources [1,2]. In the mid 1990s, alkaline and alkaline earth oxide-based NO_x storage/reduction catalysts (especially $Pt-Rh/BaO/Al_2O_3$) were developed by Toyota, and have shown promising activities for lean-NO_x reduction [3,4].

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The PM (precious metal, in particular Pt or Rh) components of NO_x storage/reduction catalysts have dual catalytic functions [5]. One is the oxidation of NO to NO_2 which is subsequently taken up as nitrates by the base metal oxide components of the system under lean conditions, and the other is reduction of the released NO_x under rich conditions. The actual NO_x storage material is BaO in most practical applications. Although it is understood that NO_2, formed on Pt, is stored on the BaO phase as $Ba(NO_3)_2$ and that the interaction between Pt and BaO is important, the effect of this interaction on the reactivity is still not clear [6]. Olsson and Fridell report the relationship between platinum dispersion and activity [7], and explain an observed decrease in NO oxidation rates with increasing Pt dispersion on the basis of platinum oxide formation, presumably occurring more readily on smaller Pt particles. The $Pt/BaO/Al_2O_3$ catalyst was shown to be less active than Pt/Al_2O_3, both for the oxidation of NO and for the reduction of NO_2, because PtO formation on BaO/Al_2O_3 is more facile [8]. Contrary to these findings, Fridell and coworkers [9] find the highest catalytic activity at the highest Pt dispersion.

There are several models for the interpretation of NO_x adsorption mechanisms. Generally, a single-site NO_x adsorption mechanism is applied in kinetic models

[10,11]. Furthermore, it is suggested that bulk and surface sorption sites on the BaO phase have different diffusion rates, resulting in different reactivities [8]. Nova and coworkers propose two different mechanisms to form nitrates based on FT-IR and pulse experiments: stepwise oxidation of surface nitrites into nitrates at a Ba site in the proximity of a Pt site, and direct adsorption of NO_2 to form $Ba(NO_3)_2$ according to a disproportionation reaction [12,13]. Similarly, Epling *et al.* [6,14] suggest the presence of two different Ba sites, which differ in 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. Although these interpretations explain many aspects of NO_x uptake properties of $Pt/BaO/Al_2O_3$ systems, still the complete uptake at the early stage of NO_x uptake is not clearly explained.

In this contribution, we will elucidate the role of Pt and BaO components, and show the importance of the interaction between these two constituents in the early stages of the NO_x storage/reduction process by studying $Pt - BaO/Al_2O_3$ catalysts with varying BaO loadings, and the NO_x uptake from gas streams containing different NO_x species (NO_2; NO + O_2).

2. Experimental

A series of catalysts with different barium oxide loadings were prepared by conventional impregnation methods. First,$Ba(NO_3)_2$ was loaded by repeated incipient wetness and drying on a high surface area γ-alumina (Condea, 200 m^2/g), followed by impregnation with an aqueous $Pt(NH_3)_4(NO_3)_2$ solution using the same incipient wetness and drying procedures. The dried samples were then calcined at 773 K for 2 h in flowing air, which resulted in 2 wt% Pt and 2, 8, and 20 wt% BaO supported on Al_2O_3.

The reaction studies were carried out in a fixed bed quartz reactor under continuous lean-rich cycling using 0.117 g of catalyst. Reactants consisted of a continuous flow (300 cm^3/min) of 200 ppm NO, 10% CO_2 and 10% H_2O balanced with He with either rich (1330 ppm C_3H_6, 4% CO and 1.33% H_2) or lean (12% O_2) gas added. All of the gases were controlled by mass flow controllers (Brooks). The NO_x concentration at the inlet (~200 ppm) and outlet of the reactor were measured with a chemiluminescence NO_x analyzer (Thermo Electron, 42C). The NO_x uptake is defined as the ratio of the amount of NO_x stored to the amount of inlet NO_x during the lean cycle for different time intervals (typically 4 and 30 min), prior to a rich cycle of 1 min. NO + O_2 and NO_2 adsorption experiments with different NO_x concentrations were performed at 523 K using the same experimental setup.

3. Results and discussion

Figure 1a shows the NO_x uptake profiles of a $2\%Pt/20\%BaO/Al_2O_3$ catalyst at different temperatures for 30 min lean periods where the inlet NO_x is present as NO (200 ppm). At the maximum NO_x conversion temperature, 523 K, the profile shows the typical NO_x uptake characteristics [4,5]. Just after the change to the lean condition, the NO_x level drops to essentially zero, suggesting the complete uptake of NO_x by the catalyst. This complete uptake behavior sustained for almost 5 min, and then the NO_x level started gradually increasing with time and it reached ~150 ppm after 30 min lean time-on-stream. The profiles are very similar to those reported by

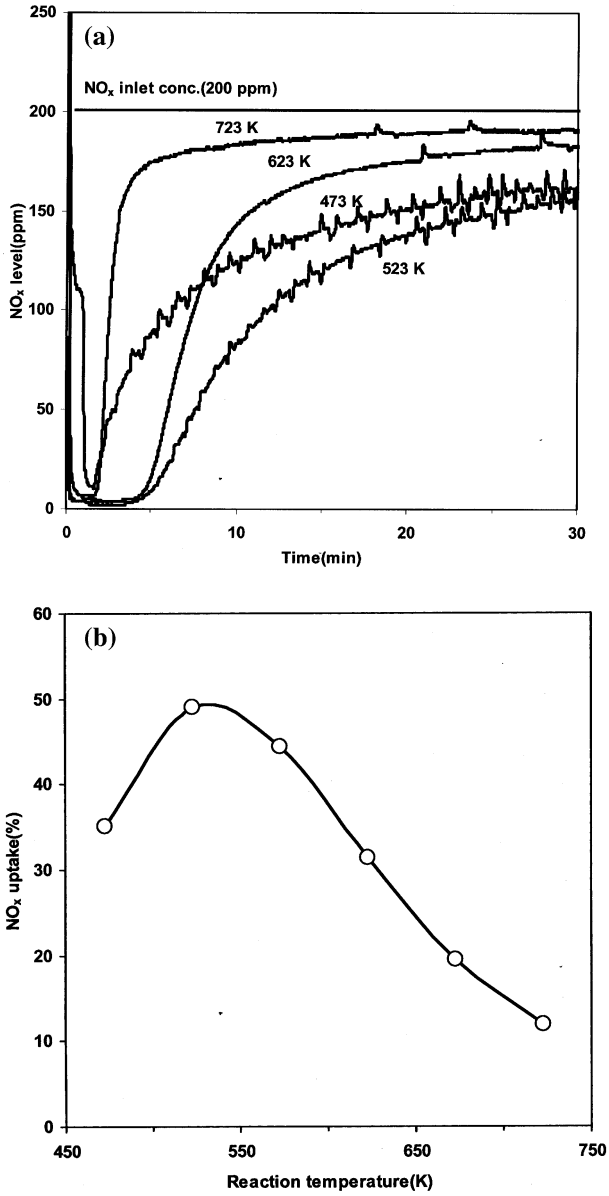

Figure 1. NO_x uptake profiles at different temperatures (a), NO_x uptake for 30 min as a function of temperature (b) ([NO] = 200 ppm).

Epling *et al.* [6], who divided the profiles into three zones. First, for an initial period of time, complete uptake of NO_x was attained. Then, NO_x break-through or slip began, but still rapid uptake of NO_x occurred for some period of time. During this time period, the trapping rate of NO_x decreased continuously. At the last stage of adsorption, a very slow, but measurable uptake of NO_x takes place. These observations are consistent with our results. Epling *et al.* [6] interpreted the NO_x uptake behavior by the presence of two different types of BaO sites, which differ based on their proximity to Pt. They focused on the oxygen source (O_2 or NO_2) for further oxidation of NO_2 to the respective nitrate species. In their model, Ba sites in the proximity of Pt, store NO_2 with the participation of O_2 as an oxidant, while the remote Ba sites rely on the disproportionation mechanism [15]: $3NO_2 + BaO \rightarrow Ba(NO_3)_2 + NO$. They propose that the disproportionation mechanism dominates at the later stages of adsorption. However, the behavior during the initial period of complete NO_x uptake is not as well understood.

At higher temperatures, the NO_x uptake properties are similar to those observed at 523 K. However, after the NO_x breakthrough the NO_x level increased faster than at lower temperature. At 623 K and 30 min time-on-stream, ~180 ppm NO_x level was observed. The complete NO_x uptake time decreased to ~1.5 min as the reaction temperature was further increased to 723 K. At this temperature, after the NO_x breakthrough, the NO_x level increased rapidly to 180 ppm and then, slowly to ~190 ppm at 30 min time-on-stream. The fast NO_x uptake period we have seen at 523 K is very short, as the catalyst temperature increases to 723 K. At lower reaction temperature, such as 473 K, the complete NO_x uptake region is essentially absent. The NO_x concentration stays at a minimum level and then it increases with time at a relatively slow rate. At 473 K, the NO_x level after 30 min is significantly lower than that at 623 K. At the low reaction temperature of 473 K, the NO_x uptake may be limited by the formation rate of NO_2. At this low temperature, not all the NO is oxidized to NO_2 on the Pt particles, therefore, there is no complete NO_x uptake initially. The NO_2 that is formed on the Pt particles are completely retained, but there is still significant amount of unreacted NO present in the gas stream.

The total NO_x uptake after 30 min of lean operation as a function of reactor temperature is shown for a $2\%Pt/20\%BaO/Al_2O_3$ catalyst in figure 1b. The maximum uptake over this catalyst is ~50% and it is measured at a reaction temperature of 523 K. With increasing temperature, the activity of $2\%Pt/20\%BaO/Al_2O_3$ decreases gradually, and drops to below 10% at 723 K. Although this catalyst shows fairly high NO_x conversion at 523 K, only ~2.4 wt% out of 20 wt% BaO is converted to $Ba(NO_3)_2$. The question that these results bring to light is why only such a small fraction of BaO is converted to $Ba(NO_3)_2$. For comparison, we prepared samples with different BaO loadings but the same Pt levels, and conducted NO_x uptake experiments under identical conditions. The 30 min lean NO_x uptake and BaO efficiency results are shown in table 1. It shows that at 523 K, only 1.3 and 2.0 wt% of BaO was participating in the NO_x uptake process for $2\%Pt/2\%BaO/Al_2O_3$ and $2\%Pt/8\%BaO/Al_2O_3$ samples, respectively. One interesting point is that although the BaO loading was increased by 10 times (from 2 to 20%), the wt% of BaO utilized was increased only from 1.3 to 2.4 wt%. These results suggest that the BaO utilization is not linearly proportional to the BaO loading.

It has been known that BaO loading on an NSR catalyst is just one factor that influences the NO_x uptake [12]. The dispersion of the noble metal seems to affect strongly the NO_x uptake as well. As we have mentioned earlier, Olsson and Fridell [7] have reported the relationships between platinum dispersion and catalytic activity, and showed that the activity of platinum decreased with increasing dispersion due to high susceptibility of the small Pt particles toward oxidation. They suggested that the deactivation of Pt by oxide formation is one of the reasons of the observed NO_x uptake behavior. To assess the effect of Pt particle size on the performance of our catalysts with different BaO loadings, we used TEM and hydrogen chemisorption in order to get information about the size of Pt particles on the three catalysts described above. For all three samples, we observed very similar Pt particle sizes of 1–2 nm in the TEM images, and H_2 chemisorption data also suggests that the Pt dispersion is practically identical in all three cases. Therefore, we believe that the oxidation properties of Pt clusters are the same for all three samples studied here.

The results of Olsson and Fridell [7] suggest that $Pt/BaO/Al_2O_3$ samples with lower BaO loadings exhibit higher resistance to the oxidation of Pt particles and it is realized in the NO_x uptake profiles. The NO_x uptake behaviors at 523 K for the three different BaO loaded samples are shown in figure 2. The two most significant effects of BaO loading on NO_x uptake are the change of the initial complete NO_x uptake time, and the increasing slope of the NO_x level increases as a function of time with decreasing BaO loading. The complete NO_x uptake time was ~5 min for 20% BaO sample, ~3 min

Table 1
The effect of BaO loading on the NO_x uptake and BaO conversion to $Ba(NO_3)_2$ at 523 K

Sample	NO_x uptake (%)	BaO converted	
		wt%	Efficiency (%)
$2\%/2\%PtBaO/Al_2O_3$	24.6	1.3	65
$2\%/8\%PtBaO/Al_2O_3$	37.4	2.0	25
$2\%/20\%PtBaO/Al_2O_3$	45.8	2.4	12

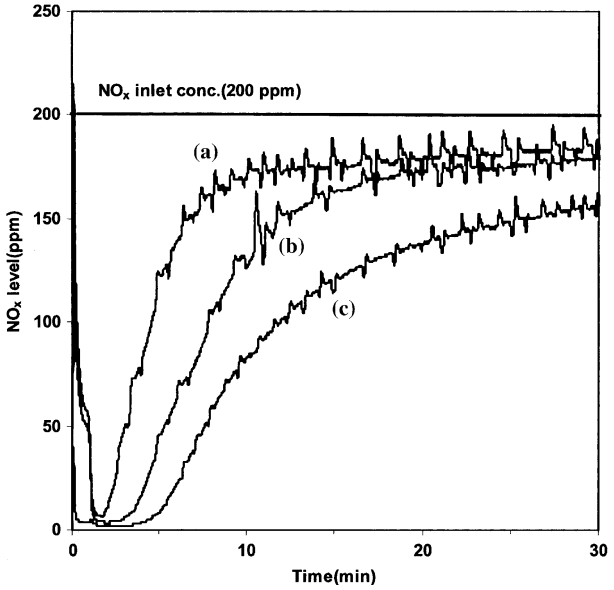

Figure 2. NO_x uptake profile on 2%Pt/xBaO/Al_2O_3 samples for 30 min at 523 K; (a) 2%, (b) 8%, and (c) 20%.

for 8% BaO sample and almost 0 min (no complete uptake) for 2% BaO sample. Even though the time of complete NO_x uptake decreased, there was still a large amount of free BaO remaining in the catalyst (~6 wt% of BaO was free for 2%Pt/8%BaO/Al_2O_3). Recently, we have reported on morphology changes in BaO/Al_2O_3 materials during NO_2 adsorption and release [16]. During thermal decomposition as $Ba(NO_3)_2$ was melting and decomposing, a BaO monolayer was suggested to cover the Al_2O_3 surface. We found that the ~8% BaO loading corresponded to a monolayer coverage on the 200 m^2/g Al_2O_3 surface [17]. However, the amount of barium oxide in the vicinity of the Pt particles may well be higher for the 20% BaO sample. On the other hand, the BaO coverage in the 20%BaO/Al_2O_3 sample was significantly under that of a monolayer, so we can expect relatively poor interaction between BaO and Pt particles. The changes in the complete NO_x uptake time with BaO loading reveals that some specific interaction between Pt cluster (where NO_2 is produced) and BaO (where NO_2 is stored) is important for periods when NO_x is completely taken up by the catalyst, and for the slower uptake periods at longer times. Since the 20%BaO/Al_2O_3 sample has a longer complete NO_x uptake time than the 8% loaded one, the amount of barium species around the Pt particles seems to determine the time period in which complete NO_x uptake occurs. These interpretations are consistent with the recent report about the effect of BaO loading for catalytic activity of Pt/BaO/Al_2O_3 catalysts published by Nova and coworkers [18]. These authors clearly show that the NO_x uptake increased with BaO loading and they point out the importance of the intimate contact between Pt and the Ba-containing phase in the NO_x storage process. These authors suggest the necessity of the intimate interaction between BaO and Pt in order to facilitate the facile transport of activated oxygen (oxygen atoms) to the BaO phase to form BaO_2 that in turn would adsorb NO as nitrite. We argue for direct spillover of the NO_2 molecules formed on the Pt particles onto the BaO phase to form ionic NO_x species.

As we have mentioned above, we also observed the increase of the NO_x slip rate with decreasing BaO coverage (figure 2). If we assume that the NO_2 formation rate over these three catalysts are the same (uptake carried out at the same temperature, same gas flow, and the Pt dispersions are very similar) this observation can be explained by the decreasing amount of BaO that is in close proximity to the Pt particles as the BaO coverage decreases. In the 20 wt% BaO catalyst, there is a large amount of BaO in direct contact or close proximity to the Pt particles, therefore the NO_x uptake by NO_2 spillover is much more facile than in the samples with lower BaO contents. In the 2 wt% o BaO case, the saturation of BaO sites accessible by NO_2 spill-over is very fast (small amount of BaO in close proximity of Pt particles), and most of the NO_2 produced on the Pt particles desorb before they can be taken up by the spill over mechanism.

In order to further understand the NO_x uptake behavior discussed above, we performed NO_x adsorption experiments using 50 and 3700 ppm NO_2/He gas mixtures on 2%Pt/20%BaO/Al_2O_3. Previous reports [6] indicate that the role of Pt under these NO_x uptake conditions will be limited to NO oxidation, therefore, all the available barium sites can be involved in the NO_x storage process. As shown in figure 3, the most significant results of these NO_x uptake experiments with different NO_2 concentrations is the difference of the amount of BaO that is converted to $Ba(NO_3)_2$ (Figure 3c). Around 45% of BaO was converted to $Ba(NO_3)_2$ when the 3700 ppm NO_2 gas was passed through the catalyst for 30 min. However, only 3% of BaO was converted to $Ba(NO_3)_2$ when 50 ppm NO_2 gas was passed through the catalyst bed for 30 min. Even when we continued the adsorption experiment for 10 h with the 50 ppm NO_2 gas, and equilibrium was reached, the amount of BaO converted to $Ba(NO_3)_2$ was only ~10%. The other significant difference we observed in these NO_2 adsorption experiments in comparison with previous NO_x uptake experiments, was the absence of a complete NO_x uptake at the beginning of these experiments. When we introduced 50 ppm NO_2 gas onto the 2%Pt/20%BaO/Al_2O_3 catalyst, we immediately observed NO_x at the exit of the reactor. These NO_2 uptake profiles suggest that the NO_2 uptake in these experiments was completely controlled by the diffusion rate of nitrates from the surface into the bulk. If the NO_x uptake was controlled by multiple NO_x sorption sites, as Epling *et al.* suggested [6], complete NO_x

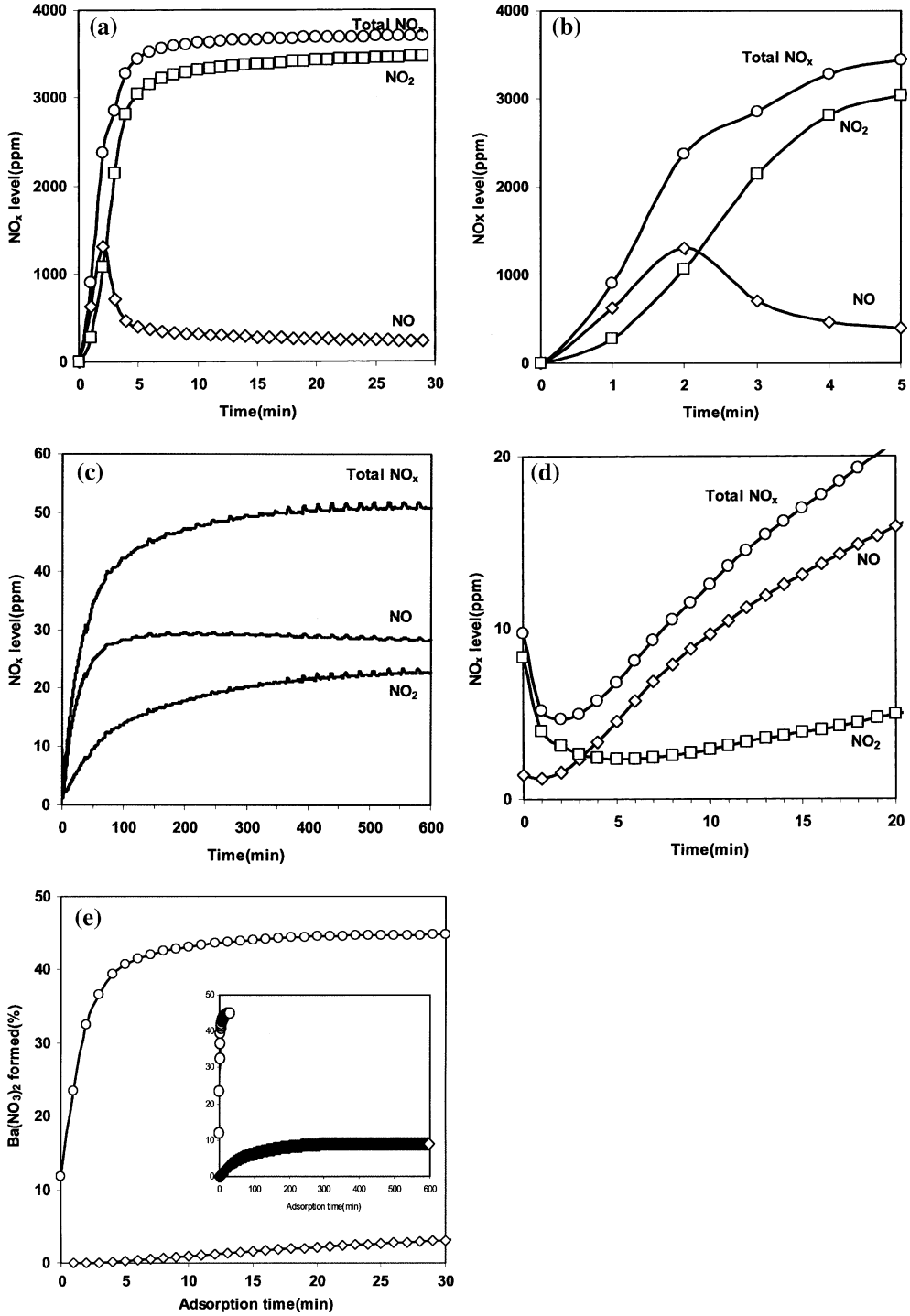

Figure 3. NO_x uptake profiles at different NO_2 concentrations (3700 ppm (a), (b) and 50 ppm (c), (d)) and the extent of BaO conversion to $Ba(NO_3)_2$ at 523 K (e).

uptake should have been observed at low NO_2 concentrations. However, as shown in figure 3b, there is no complete NO_2 uptake at the beginning of the experiment. Immediately, at the point of NO_2 introduction, NO_x was observed to exit from the reactor and even more interestingly, a significant amount of NO_2 was detected. Our results suggest that the NO_2 uptake is kinetically controlled, i.e. it is determined by the diffusion rate of nitrates form the BaO surface into the bulk, therefore, at high NO_2 vapor pressures (e.g. 3700 ppm) much higher fraction of BaO is converted into $Ba(NO_3)_2$ than at low NO_2 pressures (50 ppm). We propose that this kinetic control of the bulk nitrate formation is the primary reason for the low BaO

efficiency observed at low NO_2 levels. However, this interpretation can not explain the initial complete NO_x uptake described earlier.

Next we examined the NO_x uptake on the $2\%Pt/20\%BaO/Al_2O_3$ catalyst using a (NO + O_2/He gas mixture, and evaluated the effect of NO concentration on the NO_x uptake efficiency of BaO. The NO_x uptake profiles obtained at different NO concentrations for 30 min time-on-stream are shown in figure 4. It is evident that complete NO_x uptake occurs even at 50 ppm NO concentration (uptake curve 1). The total NO_x conversion decreased with increasing NO concentration, but the BaO conversion to $Ba(NO_3)_2$ increased. The main difference in the NO_x uptake profiles between NO + O_2 and NO_2, is the presence of complete NO_x uptake at the beginning of the NO_x uptake experiments in the former case. This initial complete NO_x uptake period is absent when NO_2 is used. These results suggest that the Pt particles on which the $NO + O_2 \leftrightarrow NO_2$ reaction takes place also facilitates the uptake of the NO_2 by the active storage phase of BaO, rather than the formation of gaseous NO_2. These results indicate the operation of two different NO_x uptake processes on these $Pt/BaO/Al_2O_3$ based NSR catalyst; i.e. Pt-facilitated NO_2 adsorption leading to complete initial NO_x uptake (NO_2 spill-over from Pt to BaO), and gas-phase NO_2 adsorption, controlled bulk diffusion rate of nitrates.

For comparison, we plot the complete NO_x uptake time and the fraction of BaO converted to $Ba(NO_3)_2$ at that time as a function of input NO concentration in figure 5. We take the time at 10% of NO_x level because of the difficulties of determining the exact NO_x break-through time. Interestingly, the NO_x break-through started after ~4% of BaO was converted to $Ba(NO_3)_2$ independent of the NO_x concentration. On the contrary, the break-through time changed more than 10 times in the NO_x concentration range of this study (50–1200 ppm). This result strongly supports the argument that complete NO_x uptake was not the consequence of gas phase NO_2 adsorption. We propose that this behavior originates from the NO_x adsorption process by spill-over. Initially, the NO + O_2 reaction on the surface of Pt particles produces NO_2 which is

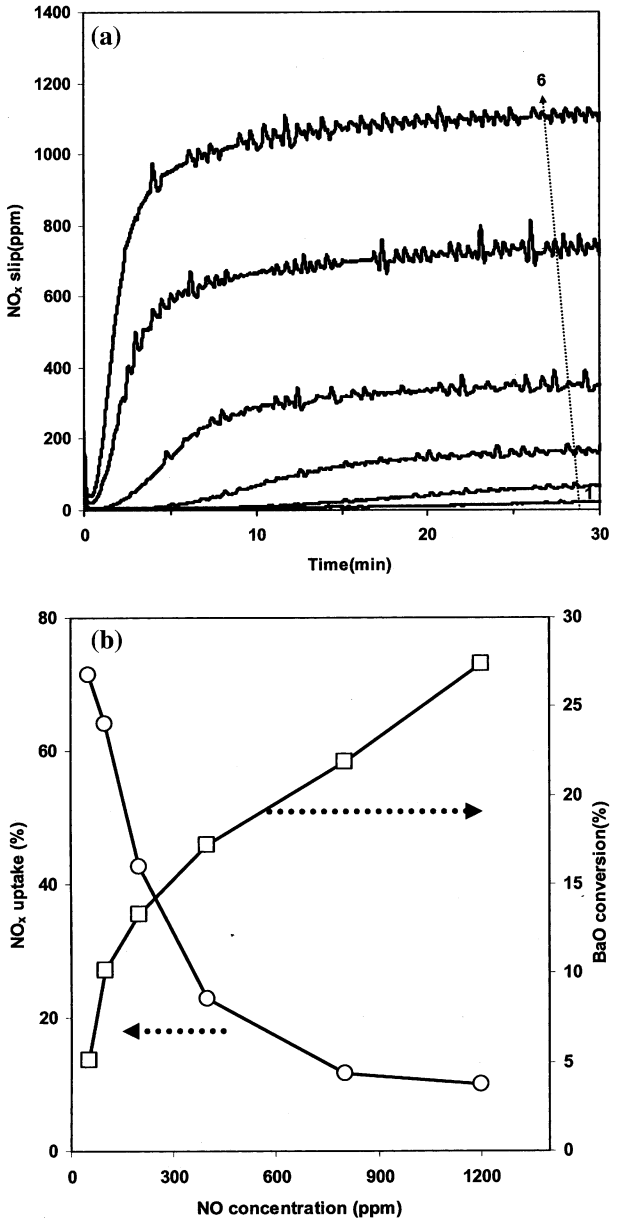

Figure 4. NO_x uptake profiles for NO + O_2 at different NO concentrations (1–6; NO = 50, 100, 200, 400, 800, and 1200 ppm) (a) and comparison of NO_x uptake vs. BaO conversion as a function of NO concentration (b) at 523 K.

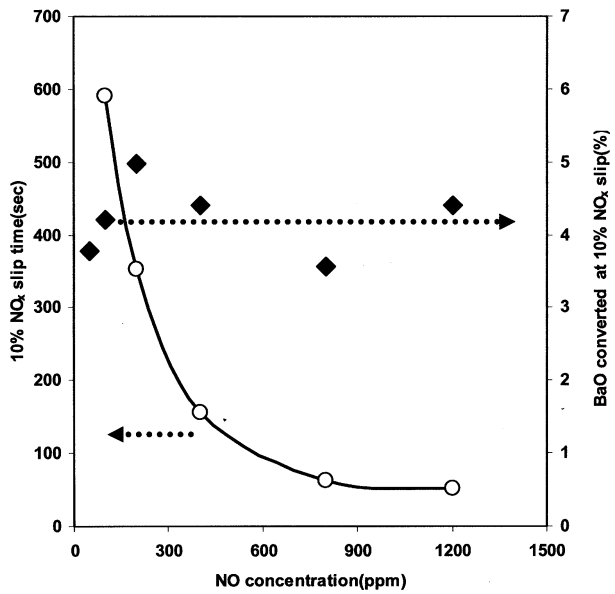

Figure 5. NO_x break-through time and BaO converted at NO_x breakthrough as a function of NO concentration at 523 K.

subsequently transferred to the neighboring BaO phase by spill over. This spill-over process is very fast, and at the beginning of the NO_x uptake, it is able to achieve 100% NO_2 storage. However, as the BaO phase in the immediate vicinity of the Pt particles is converted to $Ba(NO_3)_2$, the NO_2 uptake by this mechanism slows down since the NO_2 molecules formed on the Pt particles need to spill-over to empty BaO sites that are further away. This, however, increases the probability of NO_2 desorption. As more of the BaO sites that are close to Pt particles are filled by the NO_2 spill-over process, the dominant NO_2 uptake mechanism is adsorption from the gas phase. From this point on the rate and extent of NO_2 uptake are determined by the diffusion rate of nitrate ions into the BaO bulk, that is primarily influenced by the NO_2 concentration in the gas phase. A factor that influences the efficiency of NO_2 spill-over from the Pt particles to empty BaO sites is the change in the BaO morphology during NO_2 uptake and release. In our previous report [17], we have clearly shown the formation of $Ba(NO_3)_2$ nano-particles upon NO_2 uptake at room temperature and the growth of these particles into large $Ba(NO_3)_2$ crystals during NO_2 uptake at elevated temperatures. We believe that this kind of morphology change occurring during elevated temperature NO_2 adsorption is one of the reasons for the diffusion barrier formation and the slow down of NO_2 uptake by spill over. Using this interpretation, we can now explain the observed NO_x uptake properties of this catalyst at high temperature. We propose that the short break-through time observed at 723 K originates from the serious segregation of $Ba(NO_3)_2$ phase from the Pt particles while the rapid increase of NO_x concentration after break-through arises from the disproportionation of NO_2 due to the favorable thermodynamic equilibrium toward NO formation (by decomposition of NO_2) at elevated temperatures.

4. Conclusions

The results presented here clearly suggest that there are two different NO_x uptake mechanisms operating during NO_x uptake over $Pt/BaO/Al_2O_3$ catalysts. Initially, the NO + O_2 reaction on the surface of Pt particles produces NO_2 which is subsequently transferred to the neighboring BaO phase by a spill-over mechanism. The absence of complete NO_x uptake in the experiments carried out with NO_2 clearly demonstrates the importance of spill over of NO_2 that is formed on the Pt particles to the BaO phase. This spill-over process is very fast and at the beginning of the NO_x uptake it is able to provide complete NO_x storage. However, the NO_x uptake by this mechanism slows down (NO_x break-through begins) and eventually completely stops after certain amount of $Ba(NO_3)_2$ formed around the Pt particles, and the probability of NO_2 desorption increases. The NO_x uptake further proceeds in this regime (as suggested by theNO_x(inlet)NO_x(outlet)), although, with a significantly reduced rate. In this regime, the rate and extent of NO_2 uptake are kinetically controlled, and determined by the diffusion rate of nitrate ions into the BaO bulk, which, in turn, is primarily influenced by the NO_2 concentration in the gas phase. Our results do not refute the existence of two different types of BaO sites (one in intimate contact with Pt particles and the other not in contact with Pt particles) in these LNT materials. However, rather than explaining the experimental results on the basis on these two obviously different BaO NO_x storage sites, our approach has focused on two different NO_x uptake processes. An NO_x uptake mechanism that involves these two basic processes, as well as the morphology changes occurring during the NO_x uptake process, can now explain unambiguously the three regimes of NO_x uptake discussed in great details in previous studies.

Acknowledgments

Financial support was provided by the US Department of Energy (DOE), Office of Freedom Car and Vehicle Technologies. The work was performed in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL). The EMSL is a national scientific user facility and supported by the US DOE Office of Biological and Environmental Research. PNNL is a multi-program national laboratory operated for the US Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. The authors thank W.S. Epling for helpful discussions.

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