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Sulfation of potassium-based lean NO_x trap while cycling between lean and rich conditions

I. Microreactor study

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Abstract

Exposure of $Pt/K/Al_2O_3$ to 15 ppm SO_2 reduces the NO_x activity at 200, 300, and 400 °C at significantly different rates—1.5, 8.5, and 18.0 μmol NO_x/(h g_{cat}), respectively. During the initial sulfation, NO_x conversion is directly linked to lean phase storage capacity, and sulfation does not impact the reduction kinetics since the amount of unconverted NO_x was constant or decreased with increasing sulfation time. A portion of sulfur stored at 200 °C desorbs upon mild heating to 400 °C while cycling between lean and rich conditions. This apparently is a result of sulfur being released from Al_2O_3; however, performance is not significantly recovered as much of the sulfur is re-adsorbed on the K-phase. This is apparent from analysis of the NO_x storage and release profiles. Additional analysis of these profiles suggests that SO_2 initially adsorbs near Pt before interacting with other sites further away from Pt at 300 °C. At 400 °C, it appears that SO_2 either preferentially adsorbs near Pt and then quickly diffuses along the surface to other less proximal sites, or it directly adsorbs on sites further away from Pt.

De-sulfurization up to 800 °C using a temperature programmed reduction (TPR) procedure and rich conditions with both CO_2 and H_2O restored 73–94% of the LNT performance at 300 and 400 °C. However, the recovered performance measured at 200 °C was only 34–49% of the original NO_x reduction activity. H_2S and SO_2 were the primary de-sulfurization products with H_2S having a maximum release between 690 and 755 °C, while SO_2 had a peak release between 770 and 785 °C. The sulfation temperature does not have a significant impact on the recovered performance, the de-sulfurization products or the sulfur release temperature.

Keywords: Lean NO_x traps; NO_x storage reduction; Sulfur; Potassium; NO_x abatement; Platinum; Alumina

1. Introduction

Lean NO_x trap (LNT) catalyst systems, also known as NO_x storage reduction (NSR) or NO_x adsorber catalysts (NAC), are a leading emissions control solution for both future lean-burn gasoline engines and the impending diesel regulations [1]. They are based on the ability of alkali and alkaline earth elements to trap NO_x under lean conditions in the form of nitrates [2–4]. The stored nitrates are then released and reduced in a brief rich interval, ideally producing benign N_2, although N_2O and NH_3 are also possible products [5–11]. These catalysts require an oxidation component, typically a noble metal like Pt or Pd, a storage component, commonly Ba, a high surface area support such as γ-Al_2O_3, and a reduction component, typically Pt or Rh. Potassium is another element that has shown potential as a storage component with a significant benefit at higher temperatures where the K-based nitrate is more stable than the typical Ba nitrate [12–18]. LNTs containing Ba have a typical operating regime of 200–450 °C [14,19], and the addition of an alkali washcoat component has been shown to allow operation up to 575 °C [14–16].

During operation in diesel exhaust LNTs will be exposed to fuel- and lube oil-borne sulfur, typically in the form of SO_2. LNTs are effective at trapping and storing SO_2 much like NO_x, but the required temperature to release the stored sulfur is significantly higher than that required for nitrates and nitrites. The benefit of more stable nitrates in the potassium system becomes unfavorable with sulfur, as a higher temperature

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is required to remove the storage-site blocking sulfur [14,19]. The high temperature operation required for sulfur removal and the resulting aging effects are the most significant impediment to wide-spread commercialization of LNTs in diesel emissions control. Through an understanding of the process of sulfur-poisoning, how sulfur impacts specific storage sites during normal operation, and how catalyst history impacts de-sulfurization, it may be possible to design de-sulfurization strategies that minimize the impact of both sulfur poisoning and thermal aging incurred during high temperature de-sulfurization.

This study aims to analyze the effect of SO_2 exposure on a model K-based LNT at 200, 300, and 400 °C while cycling between lean and rich conditions. The focus on a potassium-based system was motivated by specific interest of a catalyst supplier with whom we have worked closely and because it is a system that has not been studied in great detail even though it is a proposed constituent of some commercial LNTs. SO_2 was chosen as the sulfur species since it is the primary form of sulfur expected in exhaust gas. To accelerate the poisoning process, the catalyst will be exposed to 15 ppm SO_2. While this is higher than the ~1 ppm SO_2 concentrations expected in exhaust streams, a study by Engstrom et al. has suggested that the key variable during sulfur poisoning is the dose amount rather than the concentration [20]. Several studies have shown that sulfur impacts the LNT very differently in lean operation compared to rich operation [21–24], so the catalyst will be exposed to sulfur while cycling between lean and rich conditions. H_2O and CO_2 can also have a dramatic effect [25], especially during de-sulfurization [26–27], so both of these gases will be included in all experiments.

The sulfation will be performed for over 17 h and thus minimal activity will be expected at its conclusion. This allows observation of the various stages of LNT operation as they are effectively "turned off". For each of the sulfation temperature experiments (T_s = 200, 300, or 400 °C), the NO_x reduction activity will be measured at 200, 300, and 400 °C. These measurements will occur for the fresh, sulfated, and de-sulfurized LNT states. This approach will show the effect of sulfation temperature on the rate of deactivation for each temperature. De-sulfurization will be performed using a temperature programmed reduction under rich conditions containing CO_2 and H_2O; several de-sulfurization studies have demonstrated the appropriate temperature to remove sulfur and thus regain activity [28,29]. De-sulfurized LNT performance measurements will indicate if sulfation temperature had a lasting impact after de-sulfurization.

2. Experimental

The model catalyst used in this study was 8.0 wt.% K_2CO_3 on 1 wt.% Pt/Al_2O_3 ($Pt/K/Al_2O_3$)[1]. An 8% loading of K_2CO_3 corresponds to 64% of a theoretical monolayer [30]. The powder catalyst was ground and sieved to obtain particles between 65 and 90 μm. To decrease the pressure drop across the packed bed, the powder was then mixed 1:1 by mass with 250–500 μm ground quartz. The packed bed was loaded between two quartz plugs. A powder-based microreactor, equipped with a quadrupole mass spectrometer to evaluate effluent gas concentrations, was used to measure NO_x conversion[2]. This microreactor has been previously described [31,32]. Essentially, it consists of a 6-mm i.d. quartz reactor with a pneumatically controlled 4-way valve upstream to enable fast switching from lean to rich. The 4-way valve is equipped with a pressure transducer at each of its outlet streams and a back pressure regulator on the exhaust outlet. These features allow the exhausted line to be maintained at the same pressure as the reactor line such that the switch from lean to rich is isobaric. This minimizes the impact of switching on the reactor flow and mass spectrometer response.

Table 1
Evaluation protocol employed to study the effects of sulfation temperature (T_s) on $Pt/K/Al_2O_3$

	T_s (°C)		
	200	300	400
1. Pretreat	450	450	450
2. Initial performance	400	400	400
	300	300	300
	200	200	200
3. Sulfate for T_s > 17 h	200	300	400
4. Sulfated performance	400	400	400
	300	300	300
	200	200	200
5. TPR de-sulfurization	400–800	400–800	400–800
6. De-sulfurized performance	400	400	400
	300	300	300
	200	200	200
7. Remove sample			

Sulfation and NO_x reduction measurements were performed at 200, 300, and 400 °C while operating at a space velocity of 30,000 h^{-1}; space velocity is based on the volumetric gas flow at STP and the volume of the powder/quartz bed. The typical flowrate was 75 cm^3 (STP)/min for all conditions. The evaluation protocol consisted of a six step process as outlined in Table 1 and Fig. 1. The procedure is detailed below:

1. Pre-treat freshly loaded catalyst at 450 °C under rich conditions for 1 h.
2. Evaluate initial catalyst NO_x conversion while cycling between lean and rich conditions; begin at 400 °C, followed by 300 °C, and finally 200 °C.
3. Sulfate catalyst by introducing 15 ppm SO_2 at temperature of interest, T_s = 200, 300, or 400 °C. For this study, sulfation was continued for at least 17 h.

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[1] *EmeraChem*, LLC provided all catalysts for this study.

[2] The mass spectrometer is a quadrupole residual gas analyzer that cannot distinguish between NO and NO_2 with the settings employed in this study; however, the response for NO and NO_2 is the same, and thus, is calibrated for total NO_x.

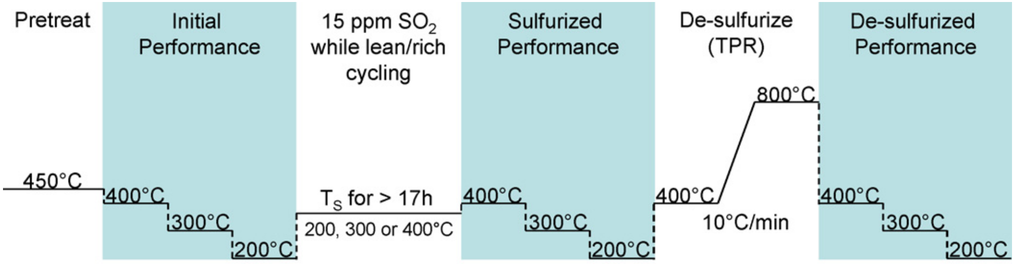

Fig. 1. Schematic of the experimental protocol employed to study the impact of sulfation temperature (T_s) on $Pt/K/Al_2O_3$.

4. Evaluate sulfated catalyst NO_x conversion beginning at 400 °C and decreasing to 200 °C. Switch flow to rich conditions and heat to 400 °C.
5. De-sulfurize the catalyst in rich conditions while ramping from 400 to 800 °C at 10 °C/min. Measure H_2S and SO_2 with mass spectrometer.
6. Evaluate de-sulfurized catalyst NO_x conversion beginning at 400 °C and decreasing to 200 °C.
7. Remove catalyst, and load fresh catalyst for next sulfation temperature.
8. Repeat steps until sulfation and de-sulfurization has been performed at all three sulfation temperatures (T_s).

The cycling conditions are listed in Table 2. For each step, we allow the cycles to continue until the cycle-to-cycle variation is minimal, typically greater than 1 h. This is as close to a ‘‘steady-state’’ as can be achieved for the inherently dynamic LNT process. All gases had purity levels of 99.999% except for NO (99.0%), CO_2 (99.99%) and SO_2 (99.8%).

3. Results

The focus of this paper is the impact of sulfur on NO_x stored during the lean phase, unconverted NO_x released during the rich phase, and overall NO_x conversion. The NO_x stored during the lean phase is the difference between the blank reactor NO_x profile and the experimental NO_x profile during the 6.5 min lean phase; these profiles are shown in Fig. 2 with the lean to rich phase transition marked. The unconverted NO_x released is calculated from the NO_x measured during the 60 s rich phase. The overall NO_x conversion is calculated from the following equation:

$$\text{Overall NO}_x\,\text{conversion} = \left[\frac{\text{NO}_x\,\text{stored} - \text{unconverted NO}_x\,\text{released}}{\text{NO}_x\,\text{fed to reactor}}\right]. \quad (1)$$

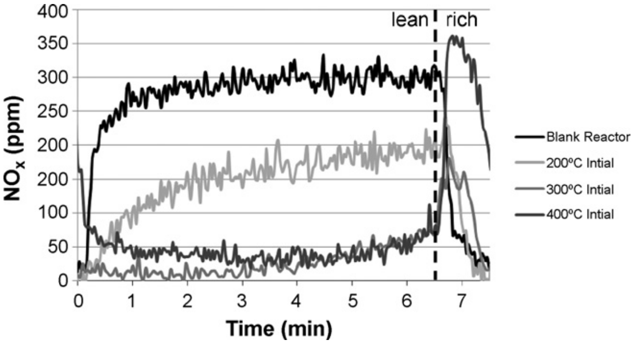

Fig. 2. NO_x concentration profiles at 200, 300, and 400 °C prior to sulfation.

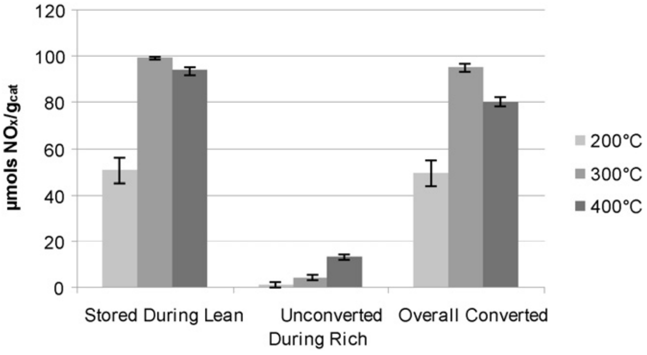

Fig. 3. Quantification of the NO_x species during lean and rich phase operation at 200, 300, and 400 °C prior to sulfation. Error bars represent range of values recorded for the three initial measurements (step 2).

Fig. 2 shows the NO_x concentration profiles at 200, 300, and 400 °C prior to sulfation. From this figure it is clear that there is more NO_x stored at 400 °C compared to 200 °C, but there is also significantly more unconverted NO_x released during the rich phase. The total NO_x stored, unconverted NO_x released and overall NO_x conversion values are shown in Fig. 3 for each evaluation temperature. As shown in Table 1, this initial measurement was performed three times (step 2), once each time a catalyst was loaded for a new sulfation step; therefore, these values represent an average of the three measurements. The reproducibility is given by the error bars in Fig. 3.

Table 2
Reactor conditions used in microreactor while cycling between lean and rich conditions

Condition	Time (s)	NO (ppm)	O_2 (%)	CO (ppm)	H_2 (ppm)	CO_2 (%)	H_2O (%)	Ar
Lean	390	300	10	–	–	5	5	Balance
Rich	60	–	–	5625	3375	5	5	Balance

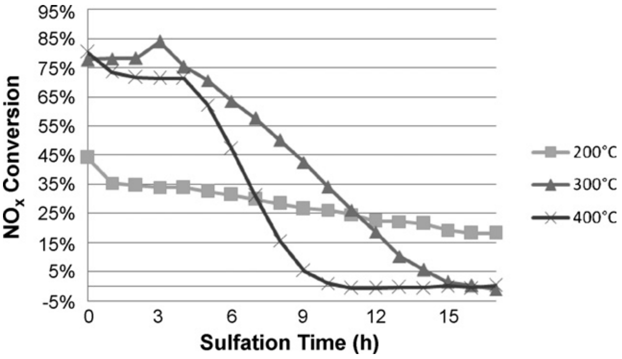

Fig. 4. NO_x conversion for $T_s = 200$, 300 and 400 °C as a function of time.

Throughout the remaining figures an error bar will be included for the initial measurements to reflect this average.

Fig. 4 shows the NO_x conversion during each of the sulfation experiments. After 4 h, conversion decreases steadily, with the rate of deactivation increasing significantly with increasing temperature. There is no activity remaining for $T_s = 300$ and 400 °C after 16 and 10 h, respectively. Although there is a moderate level of activity at 200 °C after 18 h, it is expected that the LNT will also completely deactivate with longer sulfation times. In addition to the differences in rates of deactivation, the NO_x profiles are also affected differently depending on T_s. Fig. 5a shows the NO_x profiles during sulfation at a T_s of 200 °C, Fig. 5b shows the profiles at $T_s = 300$ °C and Fig. 5c shows the profiles for $T_s = 400$ °C. While sulfating at 200 °C, it is evident from these figures that only the NO_x storage is affected. A closer inspection of the profiles for $T_s = 300$ and 400 °C highlights distinct trends with respect to NO_x storage and unconverted NO_x release. Fig. 6 displays the transition from lean to rich for these profiles during the first 3 h of sulfation. For $T_s = 300$ °C, the unconverted NO_x decreases first followed by the storage. For $T_s = 400$ °C, the NO_x storage is affected first, followed by a simultaneous loss in both storage and unconverted release. These qualitative observations are quantified in Fig. 7 for the entire sulfation experiment.

After sulfation, the catalysts were evaluated for NO_x conversion beginning at 400 °C, as outlined in step 4 of the catalyst evaluation protocol given in Section 2. This entailed heating the catalysts sulfated at 200 and 300 to 400 °C for evaluation. For $T_s = 200$ °C, there were distinct differences after exposure to temperatures higher than the sulfation temperature. Fig. 8 shows the NO_x profile changes for the catalyst sulfated at 200 and 300 °C before and after exposure to 400 °C. The change in the amount of NO_x released is remarkable for the 200 °C case, while only small differences are observed in the storage profile. These changes decrease the NO_x conversion from 22% for the freshly sulfated case to 6% after heating to 400 °C. This result is also plotted in Fig. 7b for the unconverted NO_x release, '200 °C (after 400 °C)'. For

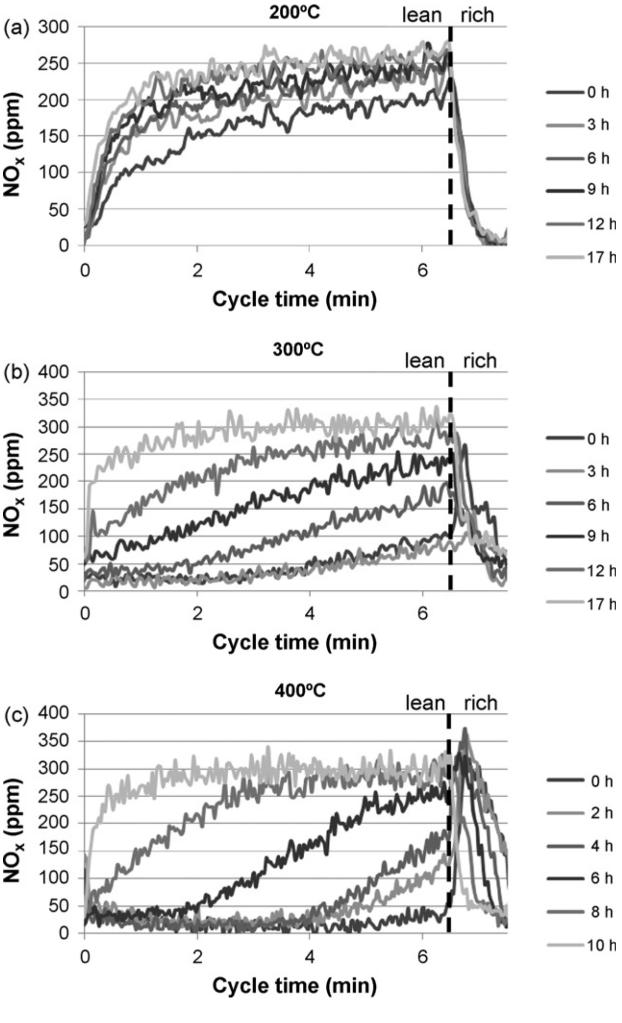

Fig. 5. NO_x profiles as sulfation proceeds for a T_s of (a) 200, (b) 300 and (c) 400 °C.

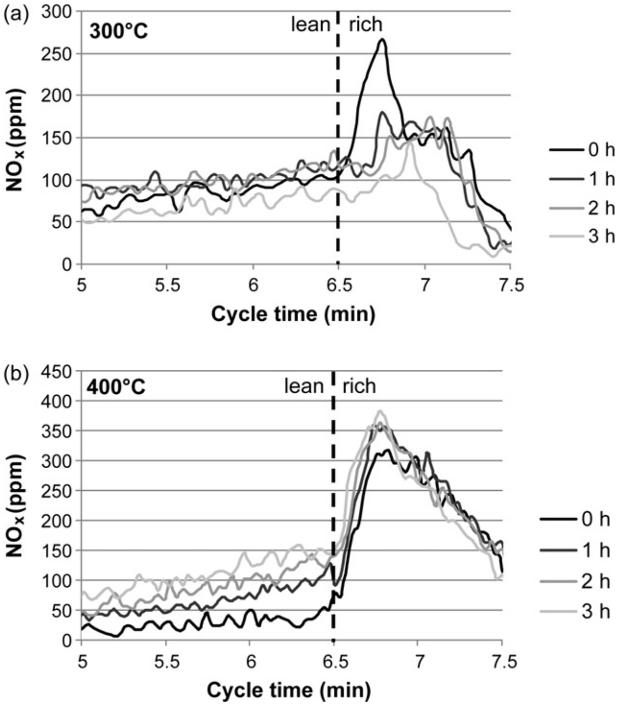

Fig. 6. NO_x profiles during the lean to rich transition at (a) $T_s = 300$ and (b) $T_s = 400$ °C.

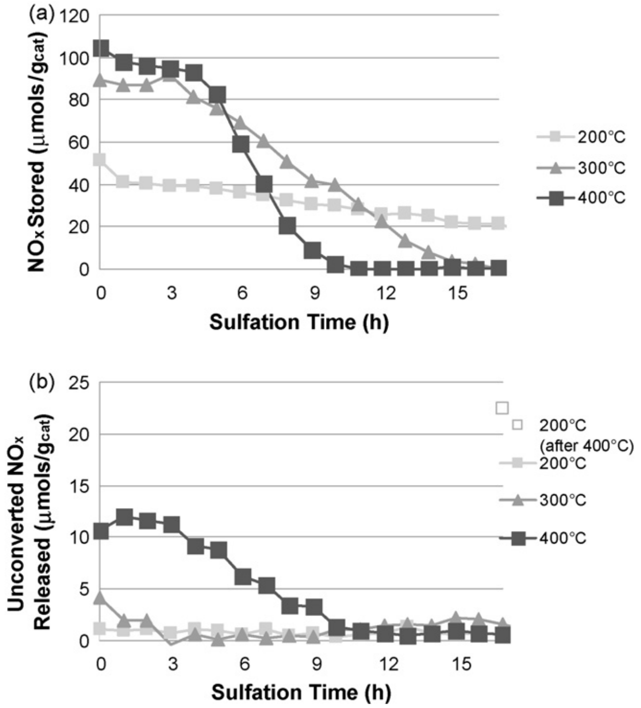

Fig. 7. Calculated (a) lean-phase NO_x storage and (b) rich-phase NO_x release for T_s = 200, 300, and 400 °C.

T_s = 300 °C, heating to 400 °C for the sequential evaluation has very little impact on both the NO_x storage and release profiles. The increased NO_x release when evaluating at 200 °C is not unique to T_s = 200 °C. Fig. 9 summarizes the unconverted NO_x release at each evaluation temperature for each sulfation experiment, T_s = 200 (■), 300 (■) and 400 °C (■); the initial values are shown for reference (□). Evaluations at 200 °C show the unconverted NO_x released increases regardless of T_s. There

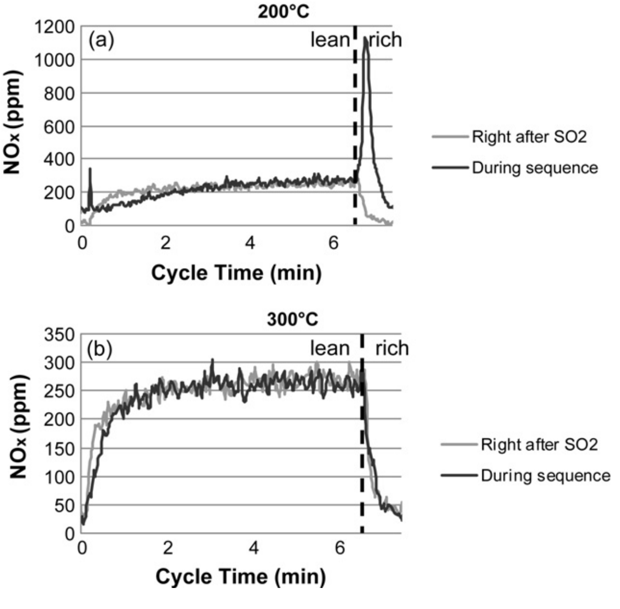

Fig. 8. NO_x profiles for catalysts sulfated at (a) 200 and (b) 300 °C taken directly after sulfation and during the sequential evaluation measurements, i.e. after operating at 400 °C.

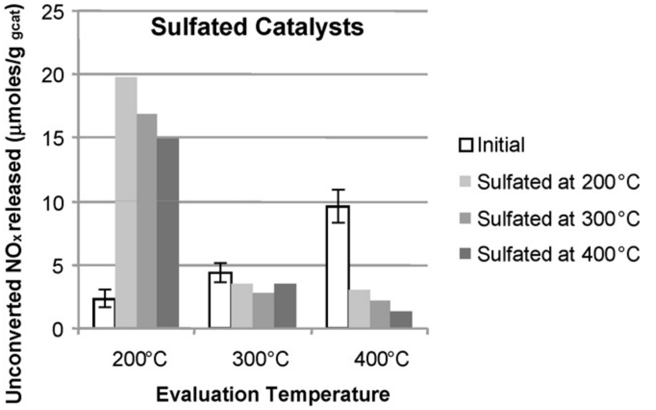

Fig. 9. Initial and sulfated unconverted NO_x released as a function of sulfation and evaluation temperatures.

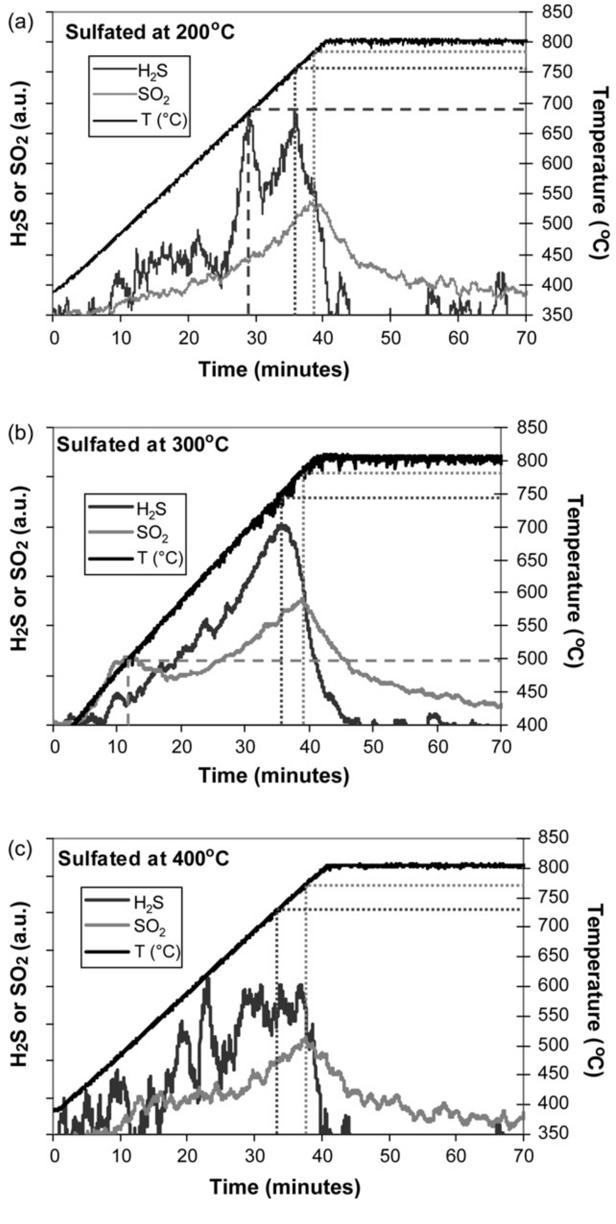

Fig. 10. De-sulfurization using a TPR procedure with rich conditions flowing continuously after sulfating at (a) 200, (b) 300, and (c) 400 °C.

Table 3
Characteristic features associated with $Pt/K/Al_2O_3$ storage, sulfation and de-sulfurization

Evaluation or sulfation temperature	200 °C	300 °C	400 °C
Total storage on K (μmol NO_2/g_{cat})	820	645	270
Rate of deactivation (μmol $NO_2/(h\ g_{cat})$)			
NO_x converted	1.45	8.48	18.0
NO_x stored	1.47	8.45	19.4
Temperature of de-sulfurization maxima (°C)			
H_2S	690 + 755	745	∼735
SO_2	785	780	770

is not a significant trend for the NO_x release at 300 °C, but at 400 °C it is apparent that the unconverted NO_x release is significantly less than the initial value for each T_s.

De-sulfurization was performed using a TPR procedure with the rich conditions described in Table 2 flowing continuously. This resulted in sulfur removal in the form of both SO_2 and H_2S for each T_s, as shown in Fig. 10, with the maximum desorption temperatures highlighted and listed in Table 3. Fig. 11 displays the de-sulfurized NO_x conversion, NO_x storage and unconverted NO_x released at each evaluation temperature; the initial values are shown for reference. The de-sulfurized catalyst performance was recovered to varying degrees: 34–49% of the initial NO_x conversion at 200 °C, 79–81% at 300 °C and 73–96% at 400 °C. These results show very little impact of T_s on both NO_x conversion and NO_x storage. However, there is a noticeable increase in the unconverted NO_x released that coincides with increasing sulfation temperature, T_s. This is apparent at each evaluation temperature.

4. Discussion

Lean NO_x traps have been heavily studied since the approach was first introduced by Miyoshi et al. in 1995 [2,3]. The field has grown to the point where an understanding has been developed for several key steps of the process and what temperature ranges are applicable. The NO_x storage process has been the most heavily studied area to date and a general consensus has been reached that the primary storage pathway involves NO oxidizing to NO_2 before forming nitrites and nitrates on the alkali or alkaline earth metal [19]. A clear picture regarding the location of these storage sites with respect to the precious metals and their relative activity is still the subject of much debate. The loading level of the storage phase is typically sufficient to be greater than a monolayer, or at least high enough that a bulk phase is expected to occur [27,33–36]. The activity of the bulk phase is not well known—it is clear that these sites are able to store nitrates, but it is not certain that they are being released during the brief rich phase and thus active for NO_x abatement [19]. It has also been suggested that the bulk sites account for the ‘‘slow’’ sites [37,38], while others have proposed that the ‘‘slow’’ sites are surface sites that are sufficiently far from the precious metal that the catalytically formed NO_2 must desorb then readsorb on these surface storage sites [19,39]. Either way, there is a general consensus that ‘‘fast’’ sites and ‘‘slow’’ sites exist, and that the fast sites are the most critical for actively storing and regenerating NO_x during cycling. The dependence of the fast sites and slow sites on temperature is also not well understood, but it is clear that the absolute number of sites decreases with increasing temperature [18]. However, LNT performance depends not only on the total number of sites, but also on the ability to efficiently release the nitrates from the storage sites. Thus, the performance window of Ba- and K-based LNTs peaks between 300 and 450 °C where both storage and release are efficient [14].

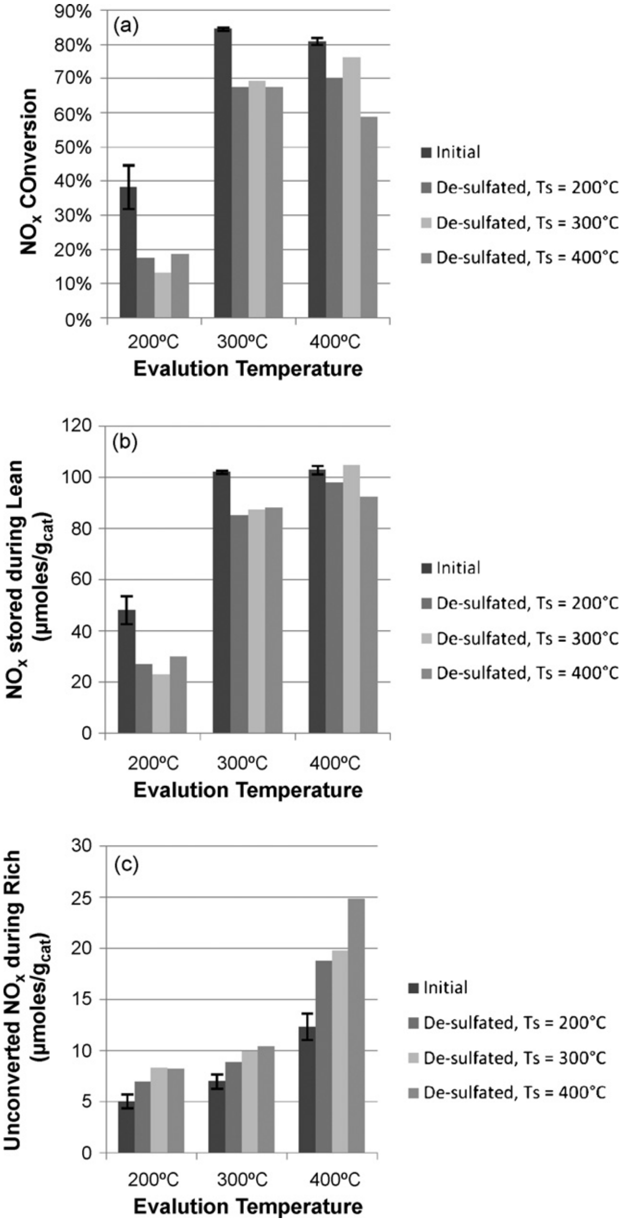

Fig. 11. Initial and de-sulfurized (a) NO_x conversion, (b) NO_x storage and (c) unconverted NO_x released as a function of sulfation and evaluation temperatures.

The importance of understanding these process details and site affiliation is specifically critical to the modeling community. The inherently dynamic LNT process is difficult to simulate with kinetically accurate chemical reactions that capture rates of oxidation, desorption, readsorption, disproportionation, surface diffusion, and bulk phase diffusion. This complex list accounts for only the storage portion of the operation cycle; additionally, the model must accurately describe the release and reduction while also capturing the time- and space-dependent product formation. When sulfur is included, the process becomes even more complex since it is important to understand which sites sulfur is impacting and the nature of that impact, i.e. is it simply a reduction of storage sites or does the presence of sulfates limit surface and bulk diffusion. Sulfur will not be released in significant quantities during the rich phase [22], but it might diffuse from one site to another [40]. If a model includes both slow and fast sites, it is important to determine which sites are impacted by sulfur first. Furthermore, all of these steps will have strong temperature dependence, and it is expected that sulfur will have a degree of mobility within the LNT as suggested by Fig. 8. The results described here help address some of these questions.

4.1. Sulfation

One of the obvious observations from this study is that during sulfation the rate of decrease in NO_x conversion (Fig. 4) is very similar to the rate of decrease in NO_x storage (Fig. 7a). This result indicates that the loss of active storage sites is limiting LNT performance during these long sulfation experiments. If, on the other hand, sulfur was selectively deactivating the reduction of released NO_x, we would expect to see an increase in the amount of unconverted NO_x. As shown in Fig. 7b this is clearly not the case.

Another observation from this study is how the rate of deactivation depends on temperature. Once NO_x conversion begins to decrease, the rate of deactivation is significantly different for each temperature. The slopes of the approximately linear portions of the NO_x storage curves in Fig. 7a were used to quantify this difference, and the results are shown in Table 3. Fitting a line to the linear portion of the deactivation profile in Fig. 4 allows the quantification of the rate of sulfur's impact on NO_x conversion at each sulfation temperature. A linear regression from 5 to 17 h for T_s = 200 °C yielded a deactivation rate of 1.5 μmol NO_x/(h g_{cat}); a rate of 8.5 μmol NO_x/(h g_{cat}) was observed from 5 to 13 h for T_s = 300 °C, and from 5 to 8 h the deactivation rate was 18 μmol NO_x/(h g_{cat}) for T_s = 400 °C.

A reason that the deactivation rate varies is the temperature-dependent nature of the storage sites. A previous study on this catalyst demonstrated the total number of sites available for storage of NO_2 on the potassium phase was 820, 645, and 270 μmol K/g_{cat} at 200, 300, and 400 °C, respectively [18], as shown in Table 3 (the contribution of the alumina phase has been subtracted). This temperature-dependent storage capacity is akin to the temperature dependence of adsorption isotherms, so the increase in capacity at lower temperatures is expected. Since $Pt/K/Al_2O_3$ stores only 40–50 μmol NO_x/(g_{cat} cycle) initially at 200 °C (Fig. 7a at t = 0 h), there is an abundance of unused sites that SO_2 can occupy without necessarily impacting NO_x conversion. For instance, during the initial evaluation at 200 °C there are over 770 μmol K/g_{cat} that are thermodynamically capable of adsorbing NO_x, but do not participate in the storage and release process. Similarly at 300 and 400 °C, where 90–100 μmol K/g_{cat}/cycle are utilized at t = 0 h, there are 545 and 170 μmol K/g_{cat} that do not participate, respectively. Using this analysis, at 200 °C the LNT is utilizing 5.5% of the available K storage sites for NO_x storage and reduction, 14% at 300 °C, and 37% at 400 °C. The lower total number of sites and corresponding higher site utilization at 300 and 400 °C, leads to the faster deactivation.

One goal motivating much of the sulfur-based LNT research is determining which sites adsorb sulfur. Since NO_x is expected to adsorb through either spillover near the Pt or through disproportionation of NO_2 on sites away from Pt [5,18,41–49], it makes sense that both of these routes are also possible with SO_2. A current hypothesis suggests that the NO_x immediately released upon transitioning from lean to rich conditions, i.e. the "puff," has a correlation to the sites adjacent to Pt [19,50–51]. This hypothesis is based on the theory that reductants spillover at the Pt interface, causing a quick release of the stored nitrates. If the reduction kinetics are slower than the release kinetics the exhaust composition will consist of a spike or "puff" of NO_x. If we assume this hypothesis to be true, we are able to use the changing nature of the NO_x puff during our experiments to offer conjectures on the location of the sulfur within the catalyst. At 300 °C, there is evidence that sulfur impacts both the amount of NO_x stored and the amount of unconverted NO_x released. Fig. 2 clearly shows that there is a substantial puff observed at 300 °C under the initial conditions, and investigation of Fig. 6a shows that this initial NO_x release decreases significantly during the first 3 h of sulfation. Fig. 7b shows that the unconverted NO_x released steadily decreases during the first 4 h, while the overall storage is minimally impacted; in fact, the NO_x conversion even moderately increases after 3 h of sulfation. Applying the proposed hypothesis suggests that the sulfur is initially being stored on sites near Pt. As these sites become occupied with sulfur, they are not available for NO_x storage and therefore the sites away from Pt are used for NO_x storage and reduction. At 300 °C, it appears that the disporportionation reaction is able to overcome these losses, or that nitrate diffusion on the surface is sufficiently fast that the sites away from Pt are effectively used and storage is not impacted until a threshold level of sulfur is reached.

As shown in Fig. 2, the initial puff associated with 400 °C is substantial. Interestingly, during the first 3 h of sulfation the puff does not diminish (Fig. 6b), but instead the NO_x storage begins to decrease. Only after 4 h of sulfation does the puff begin to subside. From this point until complete deactivation at 10 h, both storage and unconverted release decrease steadily. One explanation of this observation is that sulfur is adsorbing near Pt and then quickly migrating or diffusing to other sites. This surface diffusion or adsorbate mobility would certainly be expected to increase with temperature, which is in line with the observed differences between 300 and 400 °C. Eventually all sites are susceptible to sulfur and both the sites near Pt and away are sulfated.

Since there was not a significant puff initially at 200 °C or during sulfation (Fig. 5a), it is not possible to directly apply this hypothesis to the observations during sulfation. However, an interesting transformation was observed after the sulfated catalyst (T_s = 200 °C) was heated to 400 °C and then subsequently cooled to 200 °C. The NO_x profile immediately after sulfation, Fig. 8a, shows a very small amount of NO_x stored during the lean phase and virtually no unconverted NO_x released during the rich. Upon heating to 400 °C, there is slightly more NO_x stored (28 μmol NO_x/g_{cat} vs. 20 μmol NO_x/g_{cat}), but almost all of the stored NO_x is released during the rich phase and is unconverted. These contrasting profiles demonstrate that there has been a significant shift in the chemical nature of the catalyst. Additionally, while a controlled TPR was not performed when heating the sulfated catalyst from 200 to 400 °C, lean-rich cycling did continue and SO_2 was observed in the effluent. This release and the profile transformation demonstrate that adsorbed sulfur has a degree of mobility in the typical temperature range of operation, i.e. 200–400 °C. A theory to explain this observation relies on the ability of alumina to store sulfates at 200 °C and release them upon heating to 400 °C. Previous studies have demonstrated the ability of alumina to store and release NO_x similar to Ba and K but at significantly lower temperatures, i.e. 150–300 °C [52], and if Al_2O_3 adsorbs nitrates it will also adsorb sulfates. Furthermore, since its temperature of operation is considerably lower than potassium the relative stability of both nitrates and sulfates would be decreased. Since a significant improvement in the NO_x conversion was not observed after heating to 400 °C, the effluent sulfur observed in the ramp to 400 °C apparently originated from weakly bound sulfur desorbed from Al_2O_3. While some of this desorbed sulfur was emitted in the exhaust, a portion must have been readsorbed on the K-phase. The result of this selective desorption and readsorption is that upon cooling to 200 °C, more potassium and less alumina would be sulfated. Thus, previously sulfated alumina sites would be available for NO_x storage and reduction but less potassium sites would be available. Therefore, the NO_x storage and release profile at 200 °C with the large amount of NO_x released, after heating to 400 °C, is indicative of the chemical behavior of Al_2O_3 at 200 °C. Fig. 9 shows that this large amount of unconverted NO_x released during the sequential NO_x conversion measurements at 200 °C, was also observed at 200 °C after sulfating at 300 and 400 °C.

We now revisit the hypothesis that the NO_x puff is related to storage sites proximal to Pt and apply it to $T_s = 200$ °C. Since it has been proposed that alumina is primarily responsible for the NO_x storage and reduction after the sulfated catalyst has been heated to 400 °C, the hypothesis would simply correspond to alumina sites near Pt. This implies that the large NO_x puff observed in Fig. 8a is a result of nitrates stored on alumina sites near Pt. Specifically, the majority of the weakly bound sulfur removed from the alumina during the ramp to 400 °C and transferred to the K-phase was removed from alumina sites near Pt. This is reasonable since it would be expected that the reductants required to remove the sulfates would spillover from the nearby Pt surface [51].

4.2. De-sulfurization

The de-sulfurization profiles in Fig. 10 show that, regardless of sulfation temperature, the general product formation and sulfur release are similar. The peak SO_2 release occurred at 785, 780, and 770 °C for sulfation at 200, 300, and 400 °C, respectively. SO_2 was generally released at higher temperatures than the formation of H_2S; however, there was a simultaneous release of both H_2S and SO_2 below 500 °C. There is also a small early release of SO_2 when sulfating at 400 °C. Several papers have proposed that this early release of SO_2 is indicative of Al_2O_3-based sulfates [35,52–54]. At 200 and 300 °C the peak formation of H_2S is clearly evident with a dual peak at 690 and 755 °C for the sulfation at 200 °C and a single peak at 745 °C for the sulfation at 300 °C. The H_2S formation is significantly noisier for the sulfation at 400 °C, but the shape is somewhat similar to 300 °C with an approximate "peak" formation at 735 °C. The dual peak observation is unique to the sulfation at 200 °C, but H_2S curves for sulfation at 300 and 400 °C also have a significant component at the lower temperature release point. Ultimately, the differences in the profiles and release temperatures are not significant enough to suggest that sulfation temperature significantly impacts de-sulfurization product distribution or the stability of the sulfur adsorbate using this evaluation protocol.

As shown in Fig. 11a, the catalyst performance was recovered to varying degrees after de-sulfurization. Performance at 200 °C was most significantly impacted during the sulfation and de-sulfurization processes as only 34–49% of the initial performance was recovered. The NO_x storage, release and reduction process is limited by kinetics at 200 °C rather than by storage sites, so this observation is most likely due to Pt sintering during the 800 °C de-sulfurization. Fig. 11c shows that there is a noticeable increase in the unconverted NO_x released following de-sulfurization at each evaluation temperature. This should also relate to Pt sintering, since there would be fewer Pt sites available for the reduction of NO_x.

While there are points that can be made in comparing the de-sulfurized measurements to the initial measurements, there is not a significant trend in the measurements with respect to sulfation temperature. This is clearly the case with respect to both NO_x conversion (Fig. 11a) and NO_x stored (Fig. 11b), but there does appear to be an increasing trend in the unconverted NO_x released that coincides with increasing sulfation temperature, T_s. However, if you compare these differences to the error bars determined from the three initial measurements, this increasing trend does not appear to be statistically significant. Therefore, these results show very little impact of T_s on the recovery of NO_x conversion, NO_x storage and NO_x release.

5. Summary

This study demonstrates that the sulfation of $Pt/K/Al_2O_3$ proceeds at 200, 300, and 400 °C at significantly different rates. During initial sulfation, NO_x conversion is directly linked to lean phase storage capacity, and sulfation does not appear to significantly impact the reduction kinetics since the amount of unconverted NO_x decreased or was constant with sulfation time. Sulfur interactions with the LNT have a distinct temperature dependence. Sulfur stored at 200 °C is either released or diffuses along the surface of the LNT upon mild heating to 400 °C. This apparently is a result of sulfur being released from the Pt-proximal Al_2O_3 sites and readsorbing on the K-phase. Based on the hypothesis that the NO_x puff, observed when transitioning from lean to rich conditions, can be correlated to available storage sites near Pt, these results show that at 300 °C SO_2 adsorbs near Pt initially before interacting with the other sites away from Pt. At 400 °C, it appears that SO_2 either adsorbs near Pt and quickly diffuses to other sites, or it directly adsorbs on sites away from Pt.

De-sulfurization up to 800 °C using a TPR procedure and rich conditions with both CO_2 and H_2O, restored most of the LNT performance at 300 and 400 °C; however, only 34–49% of the NO_x conversion was recovered at 200 °C. Sulfation temperature did not significantly impact the temperature required to remove the sulfur or in the form of the sulfur that was removed. Sulfation temperature also did not have a significant impact on the percentage of performance recovered after de-sulfurization.

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