Sulfur Management of NOx Adsorber Technology for Diesel Light-duty Vehicle and Truck Applications

Howard L. Fang, Jerry C. Wang and Robert C. Yu
Cummins Inc.

C. Z. Wan
Engelhard Corporation

Ken Howden
Department of Energy, Office of Advance Automotive Technologies

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ABSTRACT

Sulfur poisoning from engine fuel and lube is one of the most recognizable degradation mechanisms of a NO_x adsorber catalyst system for diesel emission reduction. Even with the availability of 15 ppm sulfur diesel fuel, NO_x adsorber will be deactivated without an effective sulfur management. Two general pathways are currently being explored for sulfur management: (1) the use of a disposable SO_x trap that can be replaced or rejuvenated offline periodically, and (2) the use of diesel fuel injection in the exhaust and high temperature de-sulfation approach to remove the sulfur poisons to recover the NO_x trapping efficiency. The major concern of the de-sulfation process is the many prolonged high temperature rich cycles that catalyst will encounter during its useful life. It is shown that NO_x adsorber catalyst suffers some loss of its trapping capacity upon high temperature lean-rich exposure. With the use of a disposable SO_x trap to remove large portion of the sulfur poisons from the exhaust, the NO_x adsorber catalyst can be protected and the numbers of de-sulfation events can be greatly reduced.

Spectroscopic techniques, such as DRIFTS and Raman, have been used to monitor the underlying chemical reactions during NO_x trapping/regeneration and de-sulfation periods, and provide a fundamental understanding of NO_x storage

capacity and catalyst degradation mechanism using model catalysts. This paper examines the sulfur effect on two model NO_x adsorber catalysts. The chemistry of SO_x/base metal oxides and the sulfation product pathways and their corresponding spectroscopic data are discussed.

INTRODUCTION

NO_x adsorber technology relies on a storage-reduction approach that involves removal of NO_x from the exhaust under lean conditions by adsorption, followed by periodic regeneration of the adsorbent along with reduction of the released NO_x under rich conditions (1-9). The operational temperature range of the NO_x adsorber catalyst is governed by the low and high limits. The low limit is controlled by the light-off temperature required for the catalysts to oxidize NO into NO₂ and the upper limit is determined by the temperature of thermodynamic stability of the trapped NO_x species (e.g. nitrates of barium or alkali metals). The adsorbent function is extremely susceptible to deactivation from sulfur oxides in the exhaust by the formation of sulfated species that hinder adsorption sites available for NO_x storage. SO_x competes for the same active sites for NO_x adsorption to form thermodynamically more stable sulfate species. The sites covered by these sulfated species are difficult to regenerate at normal operation temperatures (e.g. < 500°C). Even with the availability of 15 ppm sulfur diesel

fuel, NO_x adsorber will be totally deactivated within a fraction of the useful life if there is no effective sulfur management in place.

There are two general approaches to sulfur management. The first is to use a disposable SO_x trap that can be replaced or rejuvenated offline periodically. The trapping capacity and the thermal stability of the trapped sulfur are the two critical issues for SO_x trap development. The second is the use of diesel fuel injection in the exhaust and high temperature de-sulfation strategy to remove the sulfates in an attempt to recover the NO_x trapping efficiency. The combination of the two approaches provides a robust strategy in tackling sulfur poisoning and system durability. A SO_x trap with high capacity can reduce the number of de-sulfation events, thus, the fuel penalty and prolong the useful life of the NO_x adsorber.

In addition to fuel sulfur, lube sulfur also plays a role in sulfur loading and performance degradation in NO_x adsorber. These include sulfurs derived from ZDDP's, the sulfurized detergents and S-containing antioxidants. It is also expected that phosphorus and ash contents from oil additives may induce certain masking and alloying effects to the catalysts. Although a development of the future emission friendly oil compatible with aftertreatment systems (such as the category of PC-10) is underway, contribution from the oil sulfur needs to be considered to the exhaust system.

To estimate the total sulfur flux and phosphorus flux the catalyst system will encounter in useful life of 150,000 miles, an average fuel economy of 20 mpg (for a vehicle of GVWR between 5000 and 8500 lbs) and a NO_x adsorber catalyst volume of 11.6 liter are used in the calculation. Fuel sulfur will contribute about 235 grams of sulfur based on 10 ppm (average) sulfur fuel and oil sulfur (average 0.2 % [S] and 0.12 % [P]) will add about 45 grams of sulfur and 28 grams of phosphorus to the engine exhaust. It is determined that the NO_x adsorber will be totally deactivated in less than 25,000 miles of operation if there is no sulfur management strategy in place. Without a SO_x trap, the NO_x adsorber needs about 25 events of high temperature desulfation strategy on every 1 g S/L accumulated sulfur flux. With a SO_x trap, the NO_x adsorber will significantly reduce the numbers of de-sulfation events depending upon the size of the SO_x trap and a reasonable SO_x trap replacement schedule.

SULFUR TRAP DEVELOPMENT

A SO_x trap is designed to protect a NO_x adsorber from sulfur poisoning. An ideal SO_x trap shall capture all engine-out SO_x under engine operation conditions for the entire life of the exhaust aftertreatment system. The NO_x adsorber catalyst will then prolong its function without going into difficult deSO_x process to recover from deactivation due to the sulfur poisoning. However, such a system needs a SO_x trap very large in volume that would make the system impractical. A realistic SO_x trap will have a limited volume with a limited total capacity, thus, a limited useful life that is far less than the required life of the exhaust aftertreatment system. If the capacity of a SO_x trap is sufficiently high and only a couple of replacements of the SO_x trap in the useful life of an aftertreatment device is needed, the use of a SO_x trap may become a competitive option in a NO_x adsorber technology system. In addition, a sulfur trap can also act as a scavenger for oil derived poisons such as phosphorus and zinc compounds although the long-term impact of those poisons on NO_x adsorber catalyst performance is not well understood.

To demonstrate the feasibility of the SO_x trap concept for light-duty truck (LDT) application, catalyst samples of a SO_x trap material with various loadings of the trapping component were obtained from Engelhard Corporation. In a laboratory reactor, the SO_x trap samples were exposed to various sulfur flux at 300°C in a simulated diesel exhaust. The aged SO_x trap samples were then analyzed for the sulfur content. The SO_x trapping efficiency defined as the total sulfur collected on the SO_x trap for a given accumulated sulfur flux to which the catalyst sample exposed is presented in Figure 1. The relative sulfur flux at unit one in the Figure is equivalent to a flux quantity of 15 g [S]/L for a SO_x trap with optimal loading. It can be seen that minimum amount of SO_x will breakthrough if SO_x trap is replaced frequently whenever sulfur flux reaches 0.5 relative quantity. Preferably, SO_x trap may be replaced after it is exposed to a total flux of 1.5 times of the relative quantity to allow some sulfur breakthrough. In such case, the use of a SO_x trap can remove 70% of the sulfur from the exhaust for a reasonable useful life. Thus, it reduces the number of de-sulfation events necessary to rejuvenate the downstream NO_x adsorber when compared to a system without the presence of a SO_x trap and that will prolong the life of the NO_x adsorber.

In an engine aging experiment, a SO_x trap of 2.5 liters in volume was aged on a Cummins 5.9L B-engine for 240 hours to simulate 20,000 miles operation. The use of an undersize SO_x trap with reduced component loading was to accelerate the SO_x deposition and to investigate the trapping efficiency under high space velocity conditions. The aging cycle consisted of a combination of three steady state modes (i.e. A18, C25 and C75 defined in EPA supplemental test cycles) each for 20 minutes in the cycle and the aging cycle repeated every hour. The temperatures of the aging ranged from 215°C to 380°C and the space velocities varied from 65K to 120K. Fuel sulfur and total fuel consumption were monitored during the entire aging. The total sulfur flux to the SO_x trap was estimated to be equivalent to 1.25 times the relative flux defined in Figure 1. After the aging, the SO_x trap was analyzed for its sulfur content. It was determined that 80% of the sulfur from engine-out was collected by the SO_x trap. As shown in the Figure 1, the result of the engine-aged SO_x trap follows closely with the laboratory data and that validates the SO_x trap concept.

Figure 1: SO_x trapping efficiency as a function of accumulated sulfur flux.

SPECTROSCOPIC ANALYSES OF SULFATION AND DESULFATION OF MODEL NO_x ADSORBER CATALYSTS

EXPERIMENTAL

DRIFTS (diffused reflectance FTIR) and micro Raman techniques were used to characterize surface adsorbed species. The experimental setups for both units have been described before (1). All DRIFTS spectra were taken with 2 cm⁻¹ resolution and a MCT detector. The IR data were normalized against a KBr background. For surface IR measurement, a caution needs to be paid to the saturation of IR detector due to high diffuse signal. The common practice to minimize such saturation is to dilute the sample with KBr powder in a 1:1 weight ratio. All Raman spectra were collected using a Renishaw microRaman system equipped with holographic Notch filters, an Ar⁺ laser, and a liquid-N₂ cooled CCD detector (10-12). All data analysis was done using standard curve deconvolution algorithm within GRAMS32.

Two model catalysts, alumina-based BaO/Pt/Al₂O₃ and titania-based alkali metal carbonate/Pt/TiO₂, were compared. Both samples were firstly treated by exposing to H₂ gas (4 % in N₂) at 250°C for 1hr in an attempt to remove some unwanted surface adsorbing species. On sulfation, the catalyst powder was loaded in a packed-bed reactor and exposed to 992 ppm SO₂ in air with a flow rate of 30 ml/min at the desired temperatures. To simulate the de-sulfation event, the sulfated samples were exposed to H₂ (4 % in N₂) at the desired temperatures for various length of time duration. It is known that H₂ and CO are more effective reductants than hydrocarbons. After each reaction, sample was rapidly cooled down to room temperature for spectroscopic analysis.

RESULTS AND DISCUSSIONS

Most commercial NO_x adsorbers contain alkali or alkali earth metal oxides (under atmospheric condition surface species are most in carbonates or hydroxides) on Pt/Al₂O₃ or Pt/TiO₂ and subsequently supported onto monolithic structure. We have been applying spectroscopic techniques to identify and quantify surface adsorbing/desorbing species responsible for sulfation and de-sulfation processes. The surface characterization provides insights about the underlying chemistry of the adsorption/desorption processes and the

degradation mechanism (13-26). The temperature and temporal probes of surface adsorbing species permit us to derive thermodynamic and kinetic parameters required for model development (13-18).

Spectroscopy study on sulfation

Disposable SO_x adsorber is developed under a sacrificial strategy in an attempt to avoid or reduce the de-sulfation events. When base metal oxides are exposed to SO_2 , two types of products are generally generated, the bulk sulfate and various surface oxy-sulfur species. The trapping capacity depends on the product distribution between surface and bulk, which in turn is a strong function of surface basicity and temperature. Bulk sulfates are more likely formed on samples with low surface area while more surface oxy-sulfur species are expected for samples with high surface area (16-18). High temperature will favor the formation of sulfates and pyro-sulfates. The bulk sulfate is desirable because of its thermal stability.

The major trapping mechanisms of NO_x and SO_x are displacement reactions involving sorbate materials of base metal oxides or alkali metal carbonates. Both surface and bulk oxy-sulfur species are generated when catalysts are exposed to SO_2 under appropriate conditions. The surface oxy-sulfur species are precursors for bulk sulfate formation. Based on structural rearrangement among M-O bonds, particularly in the vicinity of Pt, the adsorbed SO_2 can couple with substrate oxygen or surface superoxides to form more stable surface sulfates. Surface OH groups may also play important roles in the formation of oxy-sulfur species through displacement or insertion reactions of $\text{>OH} + \text{SO}_x \rightarrow \text{>SO}_x\text{OH}$. The surface bi-sulfites can undergo further oxidation to form bi-sulfates and sulfates. Owing to its higher thermal stability, the formation of bi-sulfate is more favored than bi-sulfite. High temperature and low surface area will favor the formation of bulk sulfates and bi-sulfates. Upon long operation, bi-sulfates may combine to form pyro- or poly-sulfates with the reaction of 2HSO_3^- or $2\text{HSO}_4^- \rightarrow \text{S}_2\text{O}_5^{2-}$ or $\text{S}_2\text{O}_7^{2-} + \text{H}_2\text{O}$. Pyrosulfates are physically bulky and are believed to be the precursors for S-poisoning.

Under higher reaction temperatures ($>500^\circ\text{C}$), pyro-sulfates may decompose to form free sulfates. The bulk sulfate formation is controlled by an overall oxidation mechanism involving reactions of

$\text{SO}_2 + [\text{O}] + \text{MO} \rightarrow \text{MSO}_4$ where $\text{M} = \text{Ba}^{++}, \text{Ca}^{++}$, etc. The reaction rates depend on the ease of generating SO_3 and the basicity of the metal center in controlling the reaction of $\text{MO} + \text{SO}_3 \rightarrow \text{MSO}_4$. Oxidizing reagents such as ceria and catalyzing components such as Pt are commonly used to speed up the reaction. Typical reactions are $\text{SO}_2 + 2\text{CeO}_2 \rightarrow \text{SO}_3 + \text{Ce}_2\text{O}_3$ and $\text{SO}_2 + [\text{O}](\text{Pt-site}) \rightarrow \text{SO}_3$. It is expected that bulk species are more difficult to reduce than the surface species, possibly due to the more ionic nature of the bulk sulfated species.

For more neutral metal oxides such as Al_2O_3 and TiO_2 , surface adsorbed SO_2 , or in general the SO_x ($x=2-4$), are the main species. This is in contrast to the base metal oxides where the formation of metal sulfates is the main pathway. The surface adsorbed SO_2 can be identified through its rotational contour. The transition frequency of Q-branch of vapor-like SO_2 , normally located at 1358 cm^{-1} , is so distinct that it can be unequivocally identified on various substrates. We have established a database regarding the sulfation on various metal oxides, such as BaO, CaO, NiO, Al_2O_3 and TiO_2 , etc. The IR spectra of Al_2O_3 and TiO_2 after exposing to SO_2 in air (at 250°C for 1/2hr) are compared. The major buildups are located at $1358/1180\text{ cm}^{-1}$ for Al_2O_3 and $1369/1180\text{ cm}^{-1}$ for TiO_2 . The 1358 or 1369 cm^{-1} band carrying certain rotation contour with the Q-branch characteristic suggests the surface adsorbed SO_2 . The sulfate formation can be quantified through the buildup of the 1180 cm^{-1} band. The intensity of the sulfate band at 1180 cm^{-1} is stronger in Al_2O_3 than that in TiO_2 . This is expected because TiO_2 is less basic in nature than Al_2O_3 . The trapping capacities of neutral metal oxides are much less than the base metal oxides such as BaO or CaO.

Figure 2 shows the IR spectra of the BaO/Pt/ Al_2O_3 powder sulfated at various temperatures for 1/4 hr. Major spectral changes consist of (1) buildups of the sulfated species on Ba-sites (including 1186 cm^{-1} for bi-sulfates, 1085 cm^{-1} for sulfates and 980 cm^{-1} for sulfites); (2) buildups of the sulfated species on Al-sites (1360 cm^{-1} for sulfates); and (3) the features of the OH loss including OH-stretchings ($3000-3600\text{ cm}^{-1}$) and OH-bendings (1630 cm^{-1}). The 1186 cm^{-1} band can also be assigned as the tri-dentate sulfate where the three S-O bonds are attached to surface (vs. the 1085

cm^{-1} band of bi-dentate sulfate with two S-O bonds attached to the surface). The sulfite band at 980 cm^{-1} diminishes at higher temperature, ($T > 400^\circ\text{C}$). Sulfites can be easily oxidized to more stable sulfates.

The quantification of sulfated species can be normalized against the internal bands of Al_2O_3 . Typical spectral features of Al_2O_3 are 2060 and 2340 cm^{-1} . For $T < 350^\circ\text{C}$, sharp bands at 1620 and 1760 cm^{-1} can also be used. The linear dependence of $\ln(\text{sulfate buildup})$ vs. $1/T(^{\circ}\text{K})$ is also shown in Figure 2 where the slope, equivalent to $-\Delta E_a/R$, should reflect the activation energy through the Arrhenius equation. The ΔE_a for bi-sulfate formation is found to be lower than the value observed for sulfate, 4.3 vs. 6 kcal/mole . Both are kinetically favored reactions.

Figure 2: Sulfation of model $\text{BaO}/1\%\text{Pt}/\text{Al}_2\text{O}_3$ at various temperatures measured by DRIFTS.

Buildups of surface sulfated species must be proportional to the remaining active sites on the surface. Following the Elovich adsorption

mechanism (19), the surface buildup of certain species q at a time t would follow an equation of $dq/dt = k \exp(-\beta q)$ where k is the reaction rate and β is a constant which is independent of pressure and temperature. With an integration of $\bullet \exp(\beta q) dq = \bullet k dt$, we can easily derive a relationship of $q \sim \ln(t)$. If q is plotted as a function of $\ln(t)$, a linear curve should be obtained. Figure 3 shows the Elovich plot for sulfate and bi-sulfate formation on Ba-sites.

Figure 3: Sulfation kinetics and the corresponding Elovich plot measured by DRIFTS

Figure 4 shows the differential IR spectra of the sample of alkali metal carbonate/ Pt/TiO_2 during sulfation at various temperatures for $1/4\text{hr}$. Major spectral changes consist of: (1) the depletion of metal carbonate around 1500 cm^{-1} ; (2) buildups of the sulfated species including sulfite at 980 cm^{-1} , sulfate at $1080/1190 \text{ cm}^{-1}$ and bi-sulfate at 1260 cm^{-1} ; and (3) a slight OH growth in the OH-stretchings around 3500 cm^{-1} . The linear dependence of the plot of $\ln(\text{sulfate loss})$ vs. $1/T(\text{K})$ with the slope of $-\Delta E_a/R$ is also shown in Figure 4. The ΔE_a is found $\sim 7.6 \text{ kcal/mole}$ which is essentially similar to the value observed for

Barium-based catalyst. The spectral change in the OH-stretching region for the titania-system is substantially lower than the one observed for the Barium-system.

Figure 4: Differential IR of sulfation, the fresh sample spectrum is subtracted from the spectrum of the sulfated sample, on model titania-system.

Figure 5 shows the Raman spectra of the sulfation of BaO/Pt/Al₂O₃ system at various temperatures. In the spectral range of 500-1200 cm⁻¹, three features can be seen. They are carbonate at 1053 cm⁻¹, sulfate stretching at 980 cm⁻¹ and sulfate bending at 610 cm⁻¹. Since the decomposition of carbonate is not significant during the temperature window, the sulfate bands can be normalized against the strength of the carbonate. The Arrhenius plot is also shown in Figure 5. The ΔE_a is found ~5 kcal/mole, which is in good agreement with the DRIFTS data.

The Raman data for the sulfation on the model titania-system is shown in Figure 6. The intensity of the sulfate band at 990 cm⁻¹ increases with temperature and its strength can be normalized against the 1635 cm⁻¹ TiO₂ band. The ΔE_a derived

from the slope of the Arrhenius plot is found 7.5 kcal/mole which is also in excellent agreement with the DRIFTS data. Kinetically, sulfation for the titania-system seems to be identical to the Barium-system.

Spectroscopic study on de-sulfation

As described in the previous section, sulfation is a kinetically favored reaction, with fairly low activation energy. Under the reduction condition, the sulfated species need to be reduced to sulfur species with lower oxidation states, where SO₂ and H₂S are expected to be the major products. During desulfation, it is desirable to have the less strongly bound surface SO₂ species since they are much easier to remove than the sulfate. However, sulfate species populate in a sulfated NO_x adsorber sample. Applying spectroscopic techniques, attempt was made to quantify the surface change during the de-sulfation process for model catalysts using H₂ (4% in N₂) as the reductant. For sulfated model samples of Pt/Al₂O₃ and Pt/TiO₂, the most possible chemistry relies on the reactions of $2\text{HSO}_4^- + 5\text{H}_2 \rightarrow \text{S}^= + \text{SO}_2 + 6\text{H}_2\text{O}$, and $2\text{SO}_4^= + 4\text{H}_2 \rightarrow \text{S}^= + 4\text{H}_2\text{O}$ and $\text{SO}_4^= + \text{H}_2 \rightarrow \text{SO}_2 + 2\text{OH}^-$.

Figure 5: Sulfation on BaO/Pt/Al₂O₃ at various temperatures measured by microRaman.

The IR spectra of the BaO/Pt/Al₂O₃ system during de-sulfation at various temperatures are shown in Figure 7. Sample was firstly sulfated at 400°C by exposing to SO₂ (992 ppm in air) for 1 hr. The sulfated sample was then put in a reactor and exposed to H₂ (4 % in N₂) at the desired temperatures for ¼ hr. As shown in Figure 7, major changes consist of: (1) the depletion of the sulfated species on Ba-sites at 1100 and 1186 cm⁻¹; (2) the depletion of the sulfated species on Al-sites at 1350 cm⁻¹; and (3) the features of the OH loss including OH-stretchings around 3000-3600 cm⁻¹ and OH-bendings at 1630 cm⁻¹. The band intensity change of sulfates on Ba-sites is more significant than the one on Al-sites.

Since the integrated strength of the carbonate around 1350 and 1600 cm⁻¹ does not change with the temperature, all absorbance changes of the sulfated species can be quantified by normalizing their absorption strength against the carbonate band. The significant loss of OH suggests a rearrangement of surface hydroxyl groups when adsorbed sulfate is under reduction. Figure 7 also shows the plot of sulfate buildup vs. 1/T(°K) and the ΔE_a for sulfate reduction is determined 17 kcal/mole. Similar procedure was applied to the 1186 cm⁻¹ band of bi-sulfate (or tri-dentate sulfate) and the ΔE_a for such reduction is determined 23 kcal/mole. If the 1186 cm⁻¹ band is assigned to sulfate, it is more difficult to reduce tri-dentate sulfates than normal sulfates.

The Raman spectra of the de-sulfation of BaO/Pt/Al₂O₃ system at various temperatures is shown in Figure 8. In the spectral region of 400~1200 cm⁻¹, four features can be seen and three of them (455, 610 and 980 cm⁻¹) can be attributed to sulfate formation. The 1053 cm⁻¹ band can be assigned to carbonate of BaCO₃ resulting as a reaction product of BaO with CO₂ and moisture. The Raman band ratio between the sulfate and the carbonate can be used to quantify the de-sulfation process. Since the thermal decomposition of carbonate normally requires high temperatures and the carbonate loss during the current temperature window is insignificant, the sulfate loss can be normalized against the strength of the carbonate band. A typical Arrhenius plot is also shown in Figure 8. The ΔE_a is found 17 kcal/mole, which is in excellent agreement with the DRIFTS data.

Figure 6: Sulfation on the model titania-system at various temperatures measured by microRaman

Figure 7: De-sulfation of model BaO/Pt/Al₂O₃ using H₂ measured by DRIFTS.

For the titania-system, the IR spectra during the de-sulfation at various temperatures are shown in Figure 9. Major spectral changes consist of: (1) the depletion of sulfites at 990 cm^{-1} ; (2) the depletion of sulfates at 1180 cm^{-1} ; and (3) the features of the OH loss including OH-stretchings around $3000\text{--}3600\text{ cm}^{-1}$ and OH-bendings at 1630 cm^{-1} . The integrated strength of the carbonate bands around 1350 and 1600 cm^{-1} does not change with the temperature which can be used as reference to quantify the sulfated species. After normalization, a plot of $\ln(\text{sulfate loss})$ vs. $1/T(\text{K})$ gives a straight line with a slope of $-\Delta E_a/R$. This Arrhenius dependence is also shown in Figure 9 where the ΔE_a is found $\sim 11\text{ kcal/mole}$. The difference of $\sim 6\text{ kcal/mole}$ in ΔE_a can account for the slightly lower temperature, 575°C vs. 650°C , for de-sulfation between the two adsorber systems.

Figure 8: De-sulfation on model $\text{BaO/Pt/Al}_2\text{O}_3$ at various temperatures measured by microRaman

The Raman spectra of de-sulfation for Pt/TiO_2 system at various temperatures is shown in Figure 10. With a continuous purge of H_2 , the intensity of

the sulfate band at 990 cm^{-1} decreases with temperature indicating the reduction of sulfates. At 575°C , most of the sulfates have reduced, but the buildups around $800\text{--}900\text{ cm}^{-1}$ still remain in the spectrum.

Figure 9: Temperature dependence of de-sulfation on the model titania-system.

Figure 10: De-sulfation of the model titania-system (using H_2) measured by microRaman.

IR was also used to characterize one commercial SO_x trap material. A fixed amount of the SO_x absorber material was packed within a flow reactor and exposed to SO₂ under the air at various temperatures. The flow rate of SO₂/air is 1000 sccm and the corresponding space velocity is about 5000 (min⁻¹). The temperature range is from room temperature to 340°C. The SO₂ slip was evaluated with a SO_x analyzer placed downstream from the flow reactor. After the sulfation for 2 hrs, the sample was cooled down to room temperature for spectroscopic measurement. Spectral buildup and depletion were analyzed to give clues to reaction rate as well as mass transfer mechanism.

The absorption spectra of the sulfated samples at different reaction temperatures are shown in Figure 11. Both buildup and depletion are seen in the spectra. As shown in Figure 11, a pair of depletion bands is observed at 1530/1410 cm⁻¹ which can be attributed to the loss of certain metal-oxide bonds. The broad buildup observed around 1200 cm⁻¹ can be assigned to the formation of various sulfates and bi-sulfates, including both surface and bulk species. The temperature response of the sulfate buildup shows a V-shape dependence. For T<140°C, the sulfate buildup decreases with the temperature (with negative slope), but increases with the temperature in the range of T>140°C (with positive slope). The slope difference can be attributed to two different mechanisms of sulfation. In T>140°C, the sulfation simply follows a kinetics governed by MO + SO₂ + [O] → MSO₄ which will be accelerated with temperature. At T<140°C, surface adsorbed SO₂ may be the dominant sulfated species where the surface accumulation is inversely proportional to the temperature increase. This is consistent with the results on model metal oxides where surface adsorbed SO₂ can be observed around 1358 cm⁻¹ for BaO, CaO and Al₂O₃, particularly for T<200°C.

CONCLUSION

- (1) Both DRIFTS and Raman techniques are sensitive probes for elucidating underlying chemistry on model catalysts for NO_x adsorbers.
- (2) Disposable SO_x trap with high capacity has been developed which can last for 50,000 miles and substantially reduce the numbers of desulfation events.

- (3) SO_x release due to desorption of the trapped sulfur species under rich condition is evaluated to be very small (in ppb level).
- (4) Both surface adsorbed SO₂ (prefer to form in low temperature) and metal sulfates (prefer to form in high temperature) are observed in SO_x absorber.
- (5) Surface basicity and thermal stability determine the binding strength and trapping capacity of SO_x absorber.
- (6) Surface sulfation is a kinetically favored reaction with fairly low activation energy (ΔE_a) for both titania and Barium systems.
- (7) The ΔE_a of de-sulfation for the titania-system is lower than the one for the Barium-system. It implies that the de-sulfation temperature in the titania-system is lower than the one in Barium-system (12 vs. 17~23 kcal/mole for ΔE_a).

Figure 11: IR spectra and the V-shape response of commercial SO_x trap material sulfated at various temperatures

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