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A study of chemical aging effects on HDD Fe–zeolite SCR catalyst

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Abstract

The effect of phosphorus (P) on iron (Fe)–zeolite based selective catalytic reduction (SCR) monolith catalysts was studied in the absence and the presence of sulfur, and at two different exposure temperatures (220 and 450 °C). It was found that exposure of Fe–zeolite SCR catalyst to P resulted in a loss of NOx conversion and an increase of NH_3 slip relative to a degreened baseline sample. Some of the increased slip was attributed to a loss of NH_3 storage capacity due to P blockage of adsorption sites. Additional increased slip resulted from a rise in the slip to storage ratio, likely due to a shorter effective channel length for NH_3 adsorption since most of the P blocked sites at the sample inlet. DeNOx activity was then reduced due to the decreased amount of adsorbed NH_3. P exposure using zero sulfur fuel resulted in the same amount of deactivation as aging done using low sulfur (350 ppm S) fuel, suggesting that this amount of S did not affect this formulation. An initial loss of activity proved to be due to hydrocarbon exposure, and was reversible simply by ramping the sample up in temperature during the evaluation test. Increasing the exposure temperatures also increased the loss of DeNOx performance. It is proposed that P impacts these catalysts by physically blocking adsorption sites for NH_3, primarily at the monolith channel inlet.

Keywords: DeNOx; SCR durability; Phosphorus; Sulfur; Zeolite; NOx conversion; NH_3 slip; NH_3 storage; Hydrocarbon exposure; NO oxidation; NH_3/NOx ratio; Temperature sweep; XRF analysis

1. Introduction

Increasingly stringent PM and NOx emissions regulations for heavy duty diesel (HDD) engines presents a challenge to the emission control community. Selective catalytic reduction (SCR) catalysts represent one of the most effective strategies for reducing NOx for HDD vehicles. These systems reduce NOx to N_2 via reaction with NH_3, which in turn is generated on board the vehicle via the rapid hydrolysis of urea [1]. To meet the durability requirement of these regulations, an improved understanding of the impact of chemical deactivation on catalyst activity for this application is necessary. A study by Bardasz et al. showed little effect of oil derived contaminants on vanadia based SCR after simulated aging equivalent to 100,000 km and P exposure levels as high as 4.7 g/L of catalyst substrate [2]. On the other hand, a group at Siemens reported a 20–25% decline in NOx conversion due to P exposure, after road testing a similar catalyst for 531,000 km [3]. Work by Bunting et al. on diesel oxidation catalysts (DOCs) has shown the impact of phosphorus (P) on catalyst activity varies with introduction method, and intake manifold injection of P results in deactivation similar to a field aged catalyst [4]. Earlier work by the same research group, using electrospray mass spectrometry, determined that when lube oil was combusted the P in the exhaust gas was in the form of phosphoric acid and the catalyst was poisoned by the diffusion of P into the bulk washcoat [5]. A study of the axial P profile on catalyst indicated that most of the P wound up on the front face of the catalyst, with decreasing concentration throughout the length of the substrate [2].

Recently there has been an interest in using zeolite based catalysts for urea SCR, especially for on-road applications [6–9]. Zeolite offers an advantage of improved NOx conversion efficiency at higher temperatures that might be expected with a vehicle application [10]. For these catalysts, it is proposed that NH_3 adsorption occurs on the acid sites of the zeolite [11,12]. An important step in the zeolite SCR mechanism is NO oxidation, which Devedas et al. indicate occurs over Fe^{3+} ions

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in the zeolite cage. The DeNOx reaction then occurs when NO or NO_2 reacts with the adsorbed NH_3 [12]. Aging studies over zeolite SCR have been primarily concerned with hydrothermal aging, which can result in the dealumination of the zeolite [13–16]. Researchers at Delft University also looked at exposing Ce-ZSM-5 to exhaust contaminants including P, calcium (Ca), zinc (Zn), sulfur (S) and hydrocarbon (HC) [16]. They found little effect of the P on the catalyst activity, but it was at low levels.

In this work, a set of Fe–zeolite based SCR catalysts were exposed to P in the presence and absence of S, and at 220 and 450 °C in the laboratory, and the impact on NOx reduction was evaluated. Comparisons were made to SCR samples previously tested in our laboratory [17], to see the extent of interactions between P and S.

2. Experimental

A Fe–zeolite based SCR formulation provided by Umicore was prepared using methods described elsewhere [18]. The catalyst was supported on 25.4 mm diameter × 76.2 mm long cordierite monolith cores with a cell density of 62 cells/cm^2.

Four different catalyst cores were exposed to 10 g P/L using three different procedures as indicated in Table 1, using a diesel fuel burner. One sample (A) was exposed using low sulfur fuel (350 ppm) at 220 °C, a second sample (B) was exposed to P using zero sulfur fuel at 220 °C, and the third sample (C) was exposed using low sulfur fuel at 450 °C. The fourth sample (D) was a duplicate core to Sample A, aged in the same manner. Diesel fuel (0 or 350 ppm S content) was doped with 10.7 g (~9 cm^3) of tricresyl phosphate per 900 cm^3 of fuel. The fuel flowing at 1.5 cm^3/min was mixed with air flowing at 20.0 L/min and introduced into a combustion furnace at a temperature of 900 °C. The resulting exhaust gas was sent over the catalyst that was held in a downstream tube furnace so that the catalyst exposure temperature could be controlled. The samples were exposed to the equivalent of either 5 or 10 g P/L of substrate. This procedure simulates the intake manifold injection of P mentioned earlier and results in the introduction of combusted P and S over the sample, which is common in HD diesel engines. Furthermore this combusted P was expected to be entirely in the form of phosphoric acid [5].

Each catalyst core was degreened for 24 h at 550 °C in 10% water in air. Testing was done before and after aging. DeNOx activity was measured in a quartz bench reactor at 60,000 h^{-1} space velocity using simulated diesel exhaust composed of 240 ppm NO, 60 ppm NO_2, 300 ppm NH_3, 8.0% CO_2, 9.5% O_2, 5% H_2O, and balance N_2. A steady state temperature sweep test was run from 200 to 550 °C with data taken every 50 °C at constant NH_3/NOx and NO_2/NOx ratios by ramping the temperature between set points at 10 °C/min and holding at each set point temperature for 15 min to allow the reaction to stabilize. An NH_3/NOx ratio sweep from 0.7 to 1.2 was run at a NO_2/NOx ratio of 0.2 and a temperature of 390 °C. The NO oxidation activity of the catalysts was evaluated with a steady-state temperature sweep test from 200 to 550 °C under similar conditions but with 240 ppm NO and 9.5% O_2 as the only reactive gases. NH_3 storage was measured by exposing the samples to 200 ppm NH_3, 5% CO_2, 5% H_2O and balance N_2 at 400 °C for 80 min while monitoring inlet and outlet NH_3, followed by a down ramp to 200 °C at 10 °C/min. The storage capacity tended to increase as the temperature went down. The reactor exhaust gases in each case were analyzed with a Mexa Horiba analyzer and a Thermoelectron FTIR.

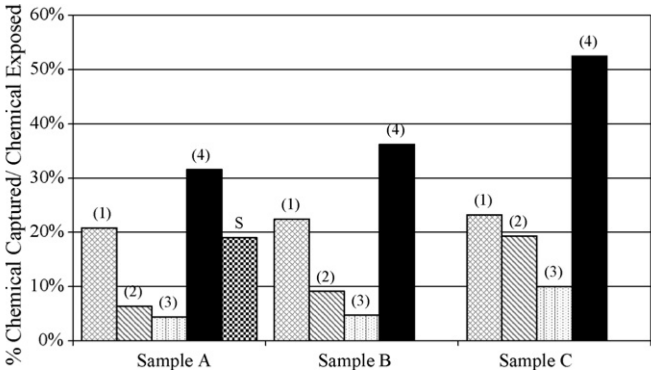

Fig. 1. Axial chemical profiles of P within the monolith channels of each sample, analyzed via XRF: (1) front third; (2) middle third; (3) rear third; (4) total for each monolith core. (S) is total sulfur captured by Sample A, determined via LECO sulfur analyzer. No sulfur analysis was performed for Sample C.

3. Results and discussion

3.1. Characterization of aged samples

The chemical profiles of P and S within the monolith channels of Samples A, B and C were analyzed via XRF. After aging and subsequent activity testing, the samples were sliced into thirds and the resulting concentration profiles are shown in Fig. 1. In each case, the highest P load was found on the front third of the catalyst where more than 20 wt% of the total exposed P was captured. For the middle third of Samples A and B, the total amount of P captured was less than 10 wt%. However the middle third of Sample C captured 19 wt% of the total P, which was nearly as much as its front third. This may

Table 1
Aging conditions for Fe–zeolite SCR catalyst Samples A, B, C and D

Sample designation	Diesel fuel sulfur content (ppm)	Exposure temperature (°C)	Exposure time (h)	P exposure level (g/L)
A	350	220	14	10
B	0	220	7, 14	5, 10
C	350	450	14	10
D	350	220	14	10

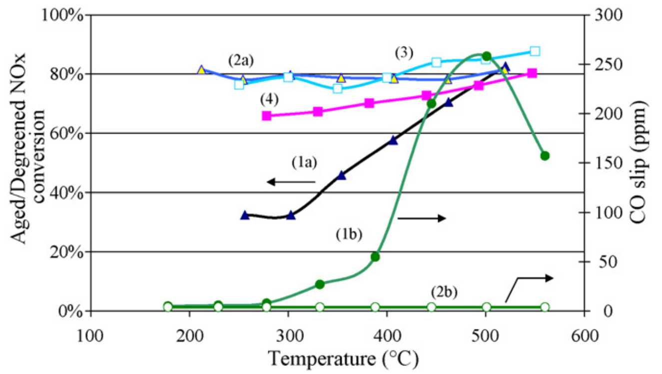

Fig. 2. The ratio of aged to degreened NOx activity over three aged samples as a function of temperature. (1a) Sample A exposed to 10 g P/L with S, run 1; (1b) Sample A, run 1 CO slip; (2a) Sample A, run 2; (2b) Sample A, run 2 CO slip; (3) Sample B exposed to 10 g P/L without S, run 2; (4) Sample C exposed to 10 g P/L with sulfur, run 2.

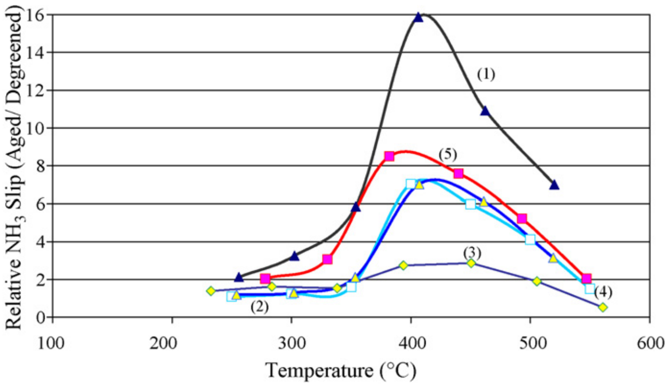

Fig. 3. The ratio of aged to degreened NH_3 slip over three aged samples as a function of temperature. (1) Sample A exposed to 10 g P/L with S, run 1; (2) Sample A, run 2; (3) Sample B exposed to 5 g P/L without S, run 2; (4) Sample B exposed to 10 g P/L without S, run 2; (5) Sample C exposed to 10 g P/L with S, run 2.

indicate higher temperature exposure will increase the penetration of P, most likely due to improved mass transfer as the hotter gas expands further into the channels. The rear third of the samples captured the least amount of P in every case, ranging from 4 wt% of total P for the low temperature exposed samples to 10 wt% of total P for the high temperature exposure. The total amount of P removed from the exhaust over the entire channel length was just 32 wt% for Samples A and B, but as high as 52 wt% in the case of Sample C. A portion of Sample A, which was aged with low sulfur fuel, was separately analyzed for S content using a LECO CS200 sulfur analyzer using ASTM Method E1019. The sample captured 19 wt% of the total amount of sulfur that it was exposed to. The presence or absence of S did not seem to change the P profile significantly.

Based on the assumption that the incoming P was in the form of phosphoric acid, it was proposed that the surface species that resulted on contact with the catalyst was primarily phosphates. Spectroscopic studies will need to be done to confirm this.

3.2. *Effect of aging on DeNOx activity with temperature*

The first run of Sample A started with a 70% loss of activity after aging compared to the baseline (Fig. 2). As the temperature rose, the relative performance increased along with it until there appeared to be only a 20% loss of activity relative to the baseline at 500 °C. A simultaneous plot of CO slip with increasing temperature revealed a significant release at the same time the NOx conversion was improving. Since there was no CO in the inlet feed, the release was attributed to oxidation of HCs, which were most likely adsorbed during the aging procedure. An FTIR analysis of the diesel burner exhaust (not shown) indicated up to 25 ppm of unconverted diesel HC (e.g. C_2H_4, C_3H_6, CH_2O and $>C_5$ alkanes) was present in the gas going over the cores. It is speculated that the poor initial DeNOx activity of this sample was due to hydrocarbon poisoning which was removed during the temperature ramp.

A repeat temperature sweep over Sample A began at a 20% activity loss relative to the baseline, and remained there over the course of the sweep. The relative loss in this case was attributed to the presence of the P. A plot of CO slip for the repeated run suggested no HC oxidation took place. Comparing the repeated runs of Samples A (aged with low sulfur fuel) and B (aged without S), the relative activity loss appeared to be very similar. It appeared that S had little or no impact on the DeNOx activity of this formulation, especially for a total S exposure of 4 g S/L.

The relative activity of Sample C is also shown in this figure. The higher temperature exposure increased the relative activity loss by an additional 7–10%. The amount of P adsorbed during the higher temperature exposure increased by about 50%, and the loss of activity also increased by a similar amount.

During the same test that NOx conversion activity was being evaluated, NH_3 slip was also measured. The relative NH_3 slip as a function of aging condition is shown in Fig. 3 plotted versus temperature. Just as with the NOx conversion, the first run on Sample A shows an NH_3 slip over the aged sample up to 16 times greater than seen with the degreened version. After removing the HC, the slip level over the aged sample dropped to just seven times the baseline, showing the presence of HC likely reduced the NH_3 storage capacity of the sample.

Sample B was tested at the mid point of the aging process, after being exposed to 5 g P/L, and again after 10 g P/L exposure. At the lower level of P exposure, the second run peak NH_3 slip seen in Fig. 3 is only about 3.5 times greater than the baseline. After doubling the P exposure level, the maximum slip doubled as well to seven times more than the degreened sample. The peak slip temperature shifted slightly lower as well with the increased P exposure. When the P exposure temperature was increased, as with Sample C, the relative NH_3 slip increased and the peak temperature decreased. These results can be explained if P was blocking NH_3 adsorption sites, with the effect decreasing going down the monolith channel. As P built up on the front of the catalyst, the effective channel length for NH_3 adsorption would be shorter, allowing slip to occur sooner with the higher P exposure. At higher exposure temperatures, more of the exposed P would become adsorbed P. Interestingly, the slip curve for Sample B after 10 g P/L

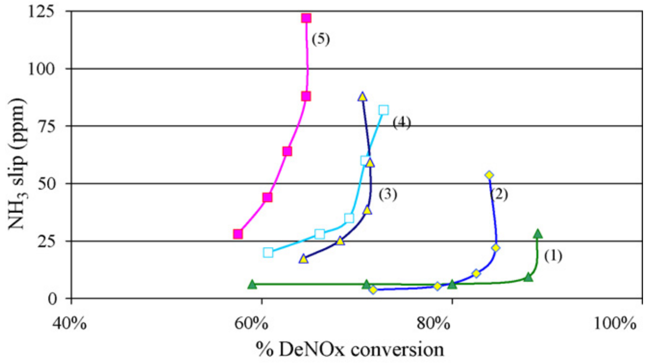

Fig. 4. NH_3 slip vs. NOx conversion as a function of inlet NH_3/NOx ratio and aging conditions at 390 °C. (1) Sample B degreened, peak NH_3/NOx = 1.1; (2) Sample B exposed to 5 g P/L without S, peak NH_3/NOx = 1.03; (3) Sample B exposed to 10 g P/L without S, peak NH_3/NOx = 0.90; (4) Sample A exposed to 10 g P/L with S; (5) Sample C exposed to 10 g P/L with S.

exposure was very similar to the same curve for Sample A, indicating the presence of S did not affect the NH_3 slip.

3.3. Aged DeNOx activity with varying NH_3/NOx ratio

The effect of NH_3/NOx ratio on DeNOx activity as a function of aging condition was studied at a constant temperature of 390 °C. The results in Fig. 4 were plotted as NH_3 slip as a function of NOx conversion. It is clear that peak NOx conversion dropped as the aging severity (P exposure level) increased. Degreened Sample B achieved 90% NOx conversion before the NH_3 slip exceeded 10 ppm, but after exposure to 5 g P/L the maximum NOx conversion dropped to 85%. After 10 g P/L, the maximum NOx conversion was down to 71%. Results for Sample A in the presence of sulfur look remarkably similar to Sample B, again indicating little effect of S on the aging process. If the sample was exposed to P at higher temperature, the NOx conversion dropped to 65% conversion.

Along with the decrease in NOx activity with increased severity of P exposure, Fig. 4 also indicates that peak NOx conversion occurred at higher NH_3 slip as the severity of the P aging increased. This increase in slip was observed over Sample B despite a reduction in the inlet NH_3/NOx ratio for each condition when the severity of aging increased. Degreened sample B had peak NOx conversions with an NH_3/NOx inlet ratio of 1.10. After exposure to 5 g P/L this inlet ratio dropped to 1.03, and then to 0.90 after 10 g P/L. Increasing the inlet NH_3/NOx ratio beyond the peak NOx activity resulted in lower NOx conversion and a further increase in NH_3 slip. This increased slip at peak conversion in spite of decreased inlet NH_3/NOx likely indicates the loss of NH_3 adsorption sites.

3.4. Effect of aging on NO oxidation

After testing the DeNOx activity, a test was done using NO and O_2 as the only reactive gases over Sample A, in order to determine the effect of the P on NO oxidation. NO conversions and NO_2 selectivity over the degreened and aged catalysts are shown in Fig. 5. In this case, NO_2 selectivity was defined as NO_2 produced/NO consumed. The figure shows little difference in the relatively modest NO oxidation conversion between the degreened and the aged sample, suggesting the reaction rate was not affected by P + S exposure. On the other hand, the low degreened activity makes it difficult to see small changes in performance, if they occurred. A comparison of NO_2 selectivity over the degreened and aged samples indicated that the aged catalyst was slightly less selective to NO_2 than the degreened sample. Statistical analysis indicated the observed loss in selectivity is real. However, since the NO oxidation rate is less than 10% over this sample, a small change in NO_2 selectivity would probably not affect the overall SCR reaction rate.

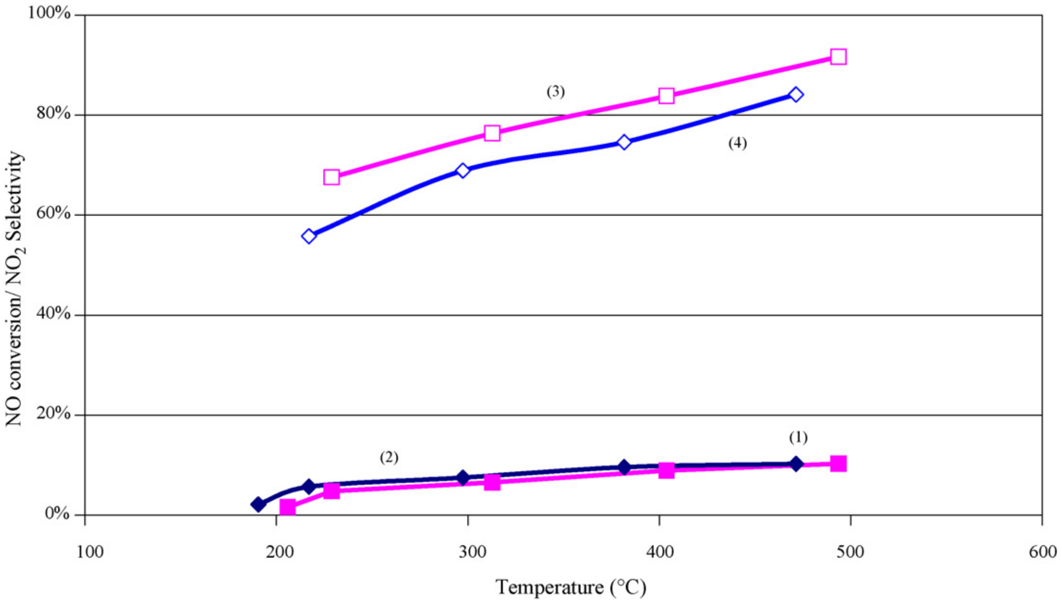

Fig. 5. NO oxidation as a function of temperature over degreened and aged Sample A, exposed to 10 g P/L with S: (1) degreened NO conversion; (2) aged NO conversion; (3) degreened NO2 selectivity; (4) aged NO2 selectivity.

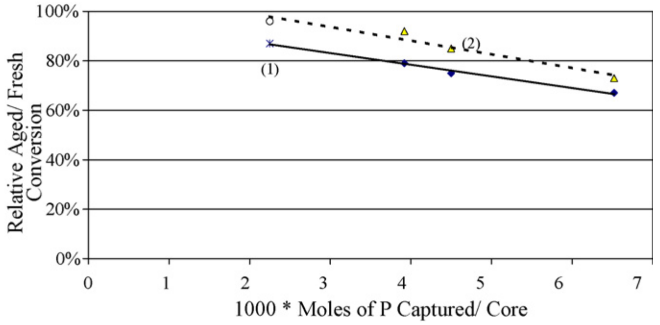

Fig. 6. Relationship between the amount of P captured on a sample core, and its relative aged/fresh NOx or NH_3 conversion: (1) NOx activity; (2) NH_3 activity.

3.5. *Correlation of P load with activity loss*

The results from the catalyst characterization using XRF were compared to the relative aged activity of Samples A, B and C. Fig. 6 reveals the relationship between the amount of P captured on a sample core, and its relative aged/fresh NOx or NH_3 conversion. Since the P content of Sample B after exposure to 5 g P/L was not measured, the amount was estimated based on the assumption that the ratio of P captured/P exposed would be constant, and knowing this ratio from the same sample exposed to 10 g P/L. The P content of all other samples was directly measured. The results indicate a linear relationship between captured P and the relative activities for NOx and NH_3 in the range of exposure levels and conditions studied. This in turn suggests the P is physically blocking sites, with a decrease in activity which is proportional to the P load.

3.6. *Ammonia storage capacity measurements*

In order to confirm the hypothesis that P blocks NH_3 adsorption sites, Sample D was tested for ammonia storage after degreening and again after exposure to 10 g P/L using low sulfur fuel. Fig. 7 shows the relative NH_3 storage capacity for the catalyst. The figure indicates that about 10% of the total NH_3 storage capacity of the catalyst is lost after P exposure compared to the degreened condition, across the entire temperature range. This finding supports the idea that P blocks some of these sites which in turn results in a loss of NOx conversion activity. A comparison of the NH_3 slip to storage ratio over the degreened catalyst compared to the P aged sample shows a significant increase in the slip to storage ratio after aging, especially at higher temperatures. If P is predominantly depositing in the front of the brick, then the increased slip may be a result of a decrease in the effective NH_3 adsorption length. This shorter length would then result in a disproportionate increase in slip relative to the amount of NH_3 storage loss, especially if the adsorption profile is sharp.

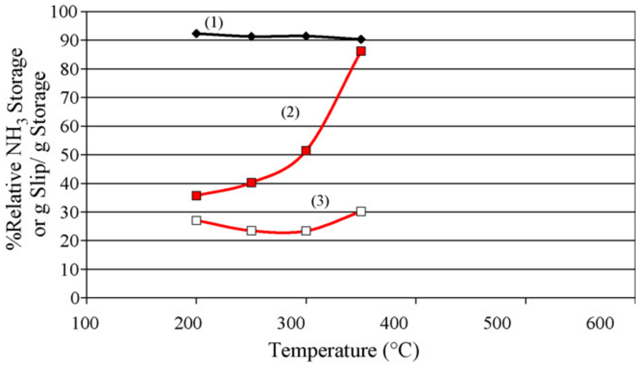

Fig. 7. Sample D relative NH_3 storage and slip/storage ratios for degreened and 10 g P/L aged samples: (1) aged NH_3 storage capacity/degreened NH_3 storage capacity; (2) NH_3 slip/NH_3 storage over aged catalyst; (3) NH_3 slip/NH_3 storage over degreened catalyst.

4. Conclusions

It was found that exposure of Fe–zeolite SCR catalyst to P resulted in a loss of NOx conversion and an increase in NH_3 slip relative to a degreened baseline sample. This increased slip was partly attributed to a loss of NH_3 storage capacity due to P physical blockage of adsorption sites. An additional loss of stored NH_3 resulted from an increase in the slip to storage ratio, likely due to a shorter effective channel length for NH_3 adsorption after most of the P blocked sites at the sample inlet. Lower levels of adsorbed NH_3, in turn, led to decreased DeNOx activity. Exposure to 10 g P/L at 220 °C led to a 20% loss of NOx conversion relative to the degreened sample, similar to the literature reported road test results after 531 K km [3]. Increasing the temperature of P exposure led to an increase in NH_3 slip at lower temperature as P migrated deeper into the bed.

HC introduced during the aging procedure greatly increased NH_3 slip and reduced NOx conversion during the first temperature sweep test immediately following aging. The effect of the HC was transient and could be easily removed via a high temperature excursion. A repeated temperature sweep showed no effect of HC exposure on performance.

A comparison of the relative aged activity of catalysts aged in the presence and absence of S indicated little difference in DeNOx or NH_3 conversion. The assumption is that moderate amounts of S did not significantly deactivate this formulation.

A correlation between the P content of the tested monolith cores and their relative activity for NOx and NH_3 revealed a linear relationship. This can be explained if P is physically blocking sites, so that the activity loss is proportional to the P captured.

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