NO_x Reduction on Fully Formulated Lean NO_x Trap Catalysts Subjected to Simulated Road Aging: Insights from Steady-State Experiments

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Abstract: Fully formulated lean NO_x trap (LNT) catalysts of the type Pt/Rh/BaO/Al₂O₃ were prepared with and without incorporation of CeO₂-ZrO₂ in the washcoat, and their NO_x reduction behavior was evaluated in steady-state, continuous flow experiments. In the fresh state, the CeO₂-ZrO₂ addition was found to exert little effect on NO_x reduction activity using H₂, CO, and NH₃ as the reductants. However, after simulated road aging, NO_x reduction activity was significantly impaired for the CeO₂-ZrO₂-free catalyst, whereas the performance of the CeO₂-ZrO₂-containing analog was affected to only a minor degree. These differences are explained on the basis of high-resolution transmission electron microscopy measurements showing that Pt supported on CeO₂-ZrO₂ remained highly dispersed after aging, whereas Pt supported on BaO/Al₂O₃ underwent significant sintering. In addition, the Pt/CeO₂-ZrO₂ component did not accumulate sulfur during aging, unlike Pt/BaO/Al₂O₃ for which significant sulfation of the Ba phase occurred. For both catalysts, selectivity to NH₃ in NO and NO₂ reduction by H₂ increased after the catalyst aging, indicative of a change in the relative surface coverages of N and H ad-atoms on the precious metal sites.

Key words: lean NO_x trap; NO_x storage-reduction catalyst; steady state; NO_x reduction; ceria-zirconia; catalyst aging

CLC number: O643

Document code: A

Received 28 February 2011. Accepted 8 April 2011.

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This work was supported by the U.S. Department of Energy (DOE) under award No. DE-EE0000205.

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

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Lean-burn engines provide more efficient fuel combustion and lower CO₂ emissions compared with traditional stoichiometric engines [1]. However, the effective removal of NO_x from lean exhaust represents a challenge to the automotive industry. Conventional three-way catalysts are highly effective for control of nitrogen oxides, CO, and hydrocarbons from stoichiometric engine exhaust but are not effective for NO_x mitigation under lean conditions. Of the various approaches proposed for lean NO_x removal, lean NO_x trap (LNT) catalysts represent a promising technology, particularly for lean-burn gasoline and light-duty diesel applications [1,2]. LNT catalysts are typically composed of at least one precious-metal component and one alkali or alkaline-earth component which are supported on a high surface area refractory oxide. These catalysts operate in a cyclic manner, whereby the catalyst stores or "traps" NO_x as

nitrate species during lean period of operation. Periodically a short rich pulse is introduced so that the trapped NO_x is released and reduced to N₂, thereby regenerating the trapping capacity of the catalyst [3].

In previous work [4,5] we observed that the addition of a Ce-Zr mixed oxide to a fully formulated Pt/Rh/BaO/Al₂O₃ LNT catalyst significantly improved NO_x storage-reduction performance under lean-rich cycling conditions. This was particularly evident after catalyst aging under simulated road conditions [5]. Several other recent studies have likewise shown that the addition of ceria-containing mixed oxides can impart beneficial properties to model LNT catalysts. For example, ceria possesses significant NO_x storage capacity [6–10], particularly at low to moderate temperatures (< 400 °C), which may help to supplement the NO_x storage capacity of the main alkaline earth or alkali metal

storage component. Ceria also promotes H₂ formation under rich conditions via the water-gas shift (WGS) reaction [11], which can be expected to facilitate catalyst regeneration and desulfation. Furthermore, LNTs incorporating ceria show improved resistance to deactivation during sulfation (as reflected by the NO_x storage efficiency), and require lower temperatures to restore the NO_x storage efficiency to its pre-sulfation value [12–16]. Ceria and ceria-zirconia can also be beneficially employed as a support for the Ba phase in Ba-based LNTs [17–20].

Another effect associated with the presence of ceria in LNTs is increased selectivity for N₂ during NO_x reduction (at the expense of NH₃), which can be attributed in part to the oxygen storage capacity (OSC) of ceria. Specifically, NH₃ formed in the front of the LNT can subsequently undergo reaction with stored oxygen in the rear of the catalyst to afford N₂ (and possibly NO and N₂O) [21–23], in addition to reacting with stored NO_x [24]. Furthermore, oxygen stored in the front of the catalyst can be expected to consume a portion of the reductant as the reaction front moves through the catalyst, thereby decreasing the effective reductant/NO_x ratio and favoring the formation of N₂ over NH₃. Finally, it should be appreciated that differences may also arise on the basis that Pt supported on BaO/Al₂O₃ and CeO₂ (or its mixed oxides) may possess intrinsic differences with respect to their activity and selectivity in NO_x reduction with reductants such as H₂, CO, and NH₃.

In this work, we sought to study the effect of adding CeO₂-ZrO₂ to a Pt/Rh/BaO/Al₂O₃ catalyst on its NO_x reduction properties before and after aging. The transient nature of lean-rich cycling experiments, coupled with the integral nature of monolithic catalysts, results in complex spatial and temporal phenomena within the catalyst sample with respect to reactant and product concentrations [21,22]. These phenomena make it difficult to directly relate the outlet gas composition to the chemistry taking place inside the catalyst. Therefore, in this study steady-state, continuous flow experiments were performed in an attempt to avoid these difficulties in data interpretation. The key step in eliminating the transient behavior of the LNT is to decouple the NO_x storage/release process from the reduction reactions [23]. This was accomplished by flowing NO_x and reductant species simultaneously over the catalyst. In this paper we report our findings.

1 Experimental

1.1 Catalyst preparation

Two fully formulated Ba-based LNT catalysts were used in this study, the compositions of which are shown in Table 1. The catalysts are denoted as 30-0 and 30-100Z, where

“30” refers to the loading of BaO in the catalyst (in g/L) and “0” or “100Z” refers to the loading of CeO₂-ZrO₂ (i.e., 0 or 100 g/L). As shown in the table, the catalysts have the same nominal loadings of Pt and Rh. The BaO component (21.5 wt%) was supported on alumina, while bare alumina was also used as a balance to bring the total washcoat loading up to 260 g/L. A detailed breakdown of the Pt loadings on the three different types of powder in the catalyst washcoats is given in Table 2. Details of the catalyst preparation have been described elsewhere [4,5]. In both cases, the washcoat was applied to 4" × 6" cordierite monolith substrates, possessing a cell density of 400 cpsi and a wall thickness of 6.5 mil.

Table 1 Composition of catalysts used in this work

Sample	Catalyst loading ^a (g/L)				
	Pt	Rh	BaO	CeO ₂ -ZrO ₂ ^b	Al ₂ O ₃ ^c
30-0	3.53 (100)	0.71 (20)	30	0	balance
30-100Z	3.53 (100)	0.71 (20)	30	100	balance

The numbers in brackets are in g/cuft.

^aNominal loadings. Total washcoat loading = 260 g/L.

^bCe/Zr = 70/30.

^cStabilized with 3 wt% La₂O₃

Table 2 Pt loading in the three component powders used for catalyst washcoat preparation

Sample	Pt loading (g/L)			
	Total	Pt-Rh/Al ₂ O ₃ ^a	Pt/BaO/Al ₂ O ₃	Pt/CeO ₂ -ZrO ₂
30-0	3.53	0.71	2.83	—
30-100Z	3.53	0.71	1.65	1.18

^aRh loading same as for Pt loading.

1.2 Catalyst characterization

Surface area and pore volume measurements on the fresh and aged catalysts were performed according to the BET method by nitrogen adsorption at −196 °C using a Micromeritics Tri-Star system. Prior to the measurements catalyst samples (washcoat and monolith) were ground to a fine powder and outgassed overnight at 160 °C under vacuum. The dispersion of precious metal (Pt+Rh) was determined with a Micromeritics AutoChem II Analyzer by means of pulsed H₂ chemisorption at dry ice temperature (−78 °C). OSC values of the catalysts were determined under lean-rich cycling conditions as described previously [4]. High-resolution transmission electron microscopy (HRTEM) investigations were performed using a 200-keV field emission analytical transmission electron microscope (JEOL 2010F) equipped with an Oxford energy dispersive X-ray spectrometer and Gatan 794 CCD (charge coupled) camera. Materials for TEM analysis were powdered samples and minute amounts were supported on copper grids.

1.3 Catalyst aging procedure

Catalyst aging was performed on a synthetic gas bench using cores (2.1 cm diameter $\times$ 7.4 cm long) drilled out from the LNT monoliths. The protocol used for the rapid aging has been detailed in earlier publications [5]. This method is designed to simulate the road aging of a LNT catalyst used in conjunction with a diesel particulate filter (DPF). Each aging cycle is composed of three modes: sulfation, desulfation, and simulated DPF regeneration. A maximum mid-bed catalyst temperature of (770 ± 10) °C was observed during desulfation due to the exotherm resulting from the fast lean-rich cycling. Depending on actual fuel sulfur levels, one aging cycle is estimated to be equivalent to 1000–1500 miles of road aging. 50 cycles were used for the aging runs, requiring a total aging time of ca. 100 h per sample. At the end of each aging run, a final desulfation was performed under constant rich conditions, corresponding to 2% H₂ in the presence of 5% H₂O and 5% CO₂ at 750 °C for 10 min, in order to remove as much as the residual sulfur as possible. This was done to ensure that the aged catalysts were not subject to desulfation phenomena during subsequent steady-state NO_x reduction tests.

1.4 Temperature ramp experiments

Temperature ramp experiments were performed using 2.1 cm diameter $\times$ 2.54 cm long catalyst cores operating at a high gas hourly space velocity (GHSV, 120000 h⁻¹) in order to ensure a fast approach to steady-state. The catalyst was allowed to equilibrate under the gas flow at 125 °C, after which the temperature was ramped to 500 °C at a rate of 5 °C/min. The feed NO or NO₂ concentration in the experiments was fixed at 300 ppm, while the reductant concentration was varied as indicated in the text. CO₂ (5%), H₂O (5%), and N₂ (as a balance) were also included in the feed.

2 Results and discussion

2.1 Catalyst characterization

N₂ physisorption data for both fresh and aged catalysts are compared in Table 3. Aging resulted in a decrease in washcoat BET surface area (A_{BET}) and pore volume, associated with the collapse of some of the smaller pores (reflected in an increase in average pore radius after aging). Relative to the ceria-free catalyst 30-0, 30-100Z displayed a more pronounced decrease in BET surface area, which can be correlated to the more severe sintering of the CeO₂-ZrO₂ phase in 30-100Z relative to the La-stabilized γ -Al₂O₃ support [5]. H₂ pulsed chemisorption results show that aging induced severe sintering of the precious metals (PMs), as

Table 3 Physical properties of fresh and aged catalysts

Catalyst	Washcoat BET SA (m ² /g)	Pore volume (cm ³ /g)	Average pore ra- dius (nm)	PM dispersion (%)	OSC (mmol/L)
30-0 (fresh)	121	0.148	6.82	34.0	21.5
30-0 (aged)	107	0.137	7.23	8.5	19.4
30-100Z (fresh)	140	0.176	6.44	45.5	73.2
30-100Z (aged)	74	0.119	8.42	9.2	69.5

evidenced by a significant drop (75%–80%) in the overall PM dispersion for both catalysts. As discussed in our previous paper [5], PM sintering is likely to occur both during desulfation (corresponding to a catalyst inlet temperature of 700 °C and mid-bed temperature of 770 °C) and subsequent DPF regeneration at 650 °C under continuous lean conditions. In addition to precious metal sintering, the loss of PM surface area for 30-100Z after aging may be due in part to sintering of the CeO₂-ZrO₂ support, which can result in encapsulation of the PM [25]. Also of note is the comparison of the OSC measured at 350 °C under cycling conditions (Table 3), which revealed that the addition of CeO₂-ZrO₂ significantly increased OSC, and that only a slight decrease in OSC occurred as a result of aging.

HRTEM studies were also performed on the catalysts. Characterization of 30-0 has been reported in a previous paper [5]. To summarize the findings, in the fresh catalyst Pt particles supported on Al₂O₃ display a narrow size range, with the majority of particles being ~2 nm in size. Pt on Ba-rich surfaces shows a broader size range from 1 to 4 nm. After aging, the catalyst has a markedly denser surface appearance compared with the fresh material and rather large Pt crystals are observed, some as large as 25 nm. The Al₂O₃ support hosts only minor amounts of Pt particles that are still in the original 2 nm size range. The majority of Pt occurs within regions that are coated by a BaSO₄ phase, this being the result of sulfur accumulation on the catalyst during aging.

Shown in Fig. 1 are TEM images of the fresh and aged 30-100Z catalyst samples. Given that the Pt/BaO/Al₂O₃ component in 30-100Z is the same as that in the previously characterized 30-0, in the following discussion we focus on the Pt/CeO₂-ZrO₂ component. As shown in Fig. 1(a), in the fresh catalyst the CeO₂-ZrO₂ crystals are polyhedral with sharp crystal edges and a size range of typically 10–15 nm in diameter. The supported Pt is highly dispersed, typical particle sizes ranging from 1.5 to 3 nm. After aging, the CeO₂-ZrO₂ particles show more rounded edges relative to the fresh state, with the size range shifted to larger grains. This suggests that the CeO₂-ZrO₂ has undergone some degree of recrystallization. At the same time, the Pt particles range in size from 2 to 7.5 nm, indicative of a decrease in the Pt dispersion, although relatively few Pt particles are

observed in the upper end of the size range. The Pt nanoparticles tend to exhibit a hexagonal morphology, especially in the larger sized particles. Compared to Pt located on the Ba/Al₂O₃ phase in aged 30-0, Pt supported on the CeO₂-ZrO₂ host in 30-100Z is more highly dispersed after aging, which can be attributed to the ability of ceria-containing supports to stabilize small Pt particles via strong Pt-O-Ce interactions [5,18].

Of particular note is the fact that no sulfur was detected by EDS when areas of the Pt/CeO₂-ZrO₂ phase in the aged 30-100Z catalyst were analyzed. A series of EDS analyses was performed on 20 different CeO₂-ZrO₂ particles, in which a beam window was selected so as to include the entire grain surface. In no cases was sulfur detected, an example being shown in Fig. 2(a), with a close-up in Fig. 2(b). Figure 2(c) shows a high resolution STEM image of a CeO₂-ZrO₂ particle that supports a Pt particle on its surface. Sulfur analysis was performed along a trace-line (the red

line in Fig. 2(c)) that stretched across the CeO₂-ZrO₂ particle (avoiding the Pt particle). As shown in Fig. 2(d), no sulfur was detected along the line. These results contrast with results obtained for the Pt/BaO/Al₂O₃ component in samples 30-0 and 30-100Z. Specifically, as detailed previously for 30-0 [5], STEM/EDS analyses reveal the presence of S associated with the Ba phase, while XPS data confirmed that the sulfur was present as sulfate. Indeed, for 30-0, the S/Ba atomic ratio measured by XPS was 0.452, the bulk ratio according to elemental analysis being 0.342.

2.2 NO_x reduction with H₂

Figure 3 shows the results of steady-state NO reduction by H₂ over the four catalysts at NO:H₂ ratios of 1:1 and 1:2.5. From the data it is apparent that NO reduction lights off at very low temperatures (< 100 °C) over the catalysts and that the NO conversion at low temperatures is improved

Fig. 1. HRTEM analysis of fresh (a) and aged (b) 30-100Z catalyst. Arrows indicate the positions of Pt particles.

Fig. 2. (a) EDS spectrum obtained for CeO₂-ZrO₂ particle in aged 30-100Z. (b) Close-up of sulfur region of EDS spectrum shown in (a). (c) STEM image showing position of EELS trace-line. (d) Result of sulfur analysis along trace-line shown in (c).

Fig. 3. Results of NO reduction with H_2 . Feed: (a) 300 ppm NO + 300 ppm H_2 ; (b) 300 ppm NO + 750 ppm H_2 ; both feeds also contained 5% CO_2 , 5% H_2O , balance N_2 ; GHSV = 120000 h^{-1} .

by increasing the H_2 concentration in the feed. Comparing the catalysts, 30-0 is found to be slightly less active than 30-100Z at the 1:1 $\text{NO}:\text{H}_2$ ratio, while both catalysts show slightly lower activity after aging. At this $\text{NO}:\text{H}_2$ ratio the two catalysts show similar behavior with respect to the selectivity of NO_x reduction, significant NH_3 formation occurring at low temperatures ($< 250^\circ\text{C}$). In agreement with the literature [23,27–29], selectivity for NH_3 is highly dependent on the $\text{NO}:\text{H}_2$ ratio, NH_3 being the main product across a wide temperature range when a $\text{NO}:\text{H}_2$ ratio of 1:2.5 is used. Particularly noteworthy is the finding that the selectivity for NH_3 is increased after catalyst aging; as reported in our previous study [5], this is also the case when NO_x reduction is performed under lean-rich cycling conditions. Furthermore, it is evident that at the $\text{NO}:\text{H}_2$ ratio of 1:2.5, catalyst 30-0 shows higher selectivity for NH_3 than 30-100Z at most temperatures, both in the fresh state and after aging. It is worth noting that N_2O formation was also observed over the catalysts at low temperatures (data not shown). At 100°C the selectivity for N_2O approached 60% for both fresh and aged 30-0 and 30-100Z at the 1:1 $\text{NO}:\text{H}_2$ ratio, although the N_2O selectivity rapidly decreased with increasing temperature, such that N_2O formation was insignificant above 175°C . Changing the $\text{NO}:\text{H}_2$ ratio to 1:2.5 resulted in decreased N_2O formation, N_2O being a minor product even at 100°C ($\sim 35\%$ selectivity); again, negligible N_2O formation was observed above 175°C . At both ratios, selectivity for N_2O was not significantly affected by catalyst aging.

Turning to the $\text{NO}_2 + \text{H}_2$ reaction, Fig. 4 shows steady-state results at $\text{NO}_2:\text{H}_2$ ratios of 1:2 and 1:3.5. In general, the trends are similar to those observed for the $\text{NO} + \text{H}_2$ reaction, although the light-off temperature is sig-

nificantly higher than for the $\text{NO} + \text{H}_2$ reaction. As suggested in the literature [23], this may be due to the presence of strongly adsorbed NO_2 on the precious metal surface sites at low temperatures, thereby preventing the dissociative adsorption of H_2 . Similar to the $\text{NO} + \text{H}_2$ reaction, NH_3 formation is observed only at low temperatures when a stoichiometric amount of H_2 is used for NO_2 reduction, whereas at the higher $\text{NO}_2:\text{H}_2$ ratio of 1:3.5 NH_3 is formed with high selectivity across a wide temperature range. Comparing 30-0 and 30-100Z, it is evident that the activity of 30-0 decreases significantly after aging, whereas 30-100Z is hardly affected. For both catalysts, selectivity for NH_3 is significantly increased after aging, 30-0 showing slightly higher selectivity for NH_3 than 30-100Z.

2.3 NO_x reduction with CO

Given that CO is generally the most abundant reductant present in diesel and gasoline exhaust gas, steady-state NO_x reduction experiments were conducted with CO. Figure 5 summarizes the results of experiments using $\text{NO}:\text{CO}$ ratios of 1:1 and 1:2.5. Comparison of these results with those obtained using H_2 (Figs. 3 and 4) reveals that the light-off temperatures for NO conversion are significantly higher for the CO experiments, the lowest T_{50} value (i.e., the temperature corresponding to 50% NO conversion) being around 175°C for the latter. Furthermore, with the exception of aged 30-0, the light-off temperature increases slightly as the CO concentration in the feed is increased. These observations are indicative of CO poisoning at low temperature. Previously we have reported the results of a DRIFTS study on powder catalysts of the type $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$, with and without Pt/CeO_2 added as a physical mixture [30]. For

Fig. 4. Results of NO₂ reduction with H₂. Feed: (a) 300 ppm NO₂ + 600 ppm H₂; (b) 300 ppm NO₂ + 1050 ppm H₂; both feeds also contained 5% CO₂, 5% H₂O, balance N₂; GHSV = 120000 h⁻¹.

Fig. 5. Results of NO reduction with CO. Feed: (a) 300 ppm NO + 300 ppm CO; (b) 300 ppm NO + 750 ppm CO; both feeds also contained 5% CO₂, 5% H₂O, balance N₂; GHSV = 120000 h⁻¹.

Pt/BaO/Al₂O₃ alone, DRIFTS spectra contained a strong Pt-CO band at temperatures below ca. 250 °C, suggesting that there is indeed a high surface coverage of CO on Pt at these temperatures. However, the band disappeared at a lower temperature (between 200 and 250 °C) when Pt/CeO₂ was present, due to the high WGS activity of the Pt/CeO₂ component. Similarly, the high WGS activity of the Pt/CeO₂-ZrO₂ component of catalyst 30-100Z explains its lower light-off temperature compared to 30-0. It is also noteworthy that after aging the T_{50} value of 30-100Z is virtually unchanged, whereas the T_{50} for 30-0 increases significantly.

Turning to the selectivity of NO reduction, at the NO:CO ratio of 1:1, N₂ is formed as the main reduction product, although some NH₃ formation occurs at low temperatures (<

250 °C). N₂O formation (data not shown) is negligible. Increasing the NO:CO ratio to 1:2.5 results in the formation of NH₃ as the main product at temperatures below 400 °C (with the exception of aged 30-0), which is to be expected if NO reduction proceeds mainly via H₂ generated from the WGS reaction. Comparing the fresh and aged catalysts, it is apparent that 30-0 becomes more selective for N₂ formation (less selective for NH₃) after aging, whereas 30-100Z becomes less selective for N₂ (more selective for NH₃). The latter is expected since it follows the trend for the NO + H₂ reaction, while the increase in selectivity for N₂ observed for 30-0 is presumably the result of a decrease in WGS activity after aging, thereby decreasing the effective concentration of H₂ available for NO reduction.

Shown in Fig. 6 are the results of NO₂ reduction with CO.

The trends are very similar to the NO + CO reaction, although one difference is the shift of the light-off temperature to lower values when the CO concentration in the feed is increased. This reflects the strong adsorption of NO₂ on the precious metal sites (in contrast to NO); evidently, significant NO₂ adsorption occurs at low temperatures (< 150 °C), even in the presence of excess CO.

2.4 NO_x reduction with NH₃

NO_x reduction by NH₃ is an important reaction during LNT regeneration. Figure 7 shows steady-state data for the NO + NH₃ reaction (in the absence of O₂) over the four catalysts. The light-off temperatures for the fresh catalysts are very similar, T_{50} being ~170 °C. However, after aging T_{50} increases to 250 °C for 30-0, while the activity of aged 30-100Z shows almost no change from the fresh state. Comparison of the NO and NH₃ conversion curves shows

that for each catalyst a substantial fraction of NH₃ remained unconverted at the temperature corresponding to complete NO conversion. This observation is consistent with a stoichiometry in which NO reduction requires less than 1 equivalent of NH₃, i.e.:

In the absence of O₂, consumption of the excess NH₃ at high temperatures must be associated with NH₃ decomposition to N₂ and H₂. Indeed, in separate experiments (data not shown), the four catalysts were found to show similar activity for catalyzing NH₃ decomposition (in the absence of NO and O₂) with a T_{50} value of ~375 °C. We note that similar findings have been reported by Pihl et al. [23] for a commercial LNT catalyst. It is also worth noting that the selectivity of NO_x reduction to N₂ was typically very high (> 95%, data not shown), the exception being at temperatures below 200 °C when the selectivity for N₂O approached 35%.

Fig. 6. Results of NO₂ reduction with CO. Feed: (a) 300 ppm NO₂ + 600 ppm CO; (b) 300 ppm NO₂ + 1050 ppm CO; both feeds also contained 5% CO₂, 5% H₂O, balance N₂; GHSV = 120000 h⁻¹.

Fig. 7. Results of NO reduction with NH₃. (a) NO conversion; (b) NH₃ conversion. Feed: 300 ppm NO + 300 ppm NH₃, 5% CO₂, 5% H₂O, balance N₂; GHSV = 120000 h⁻¹.

2.5 Discussion

The steady-state reaction of NO with H₂ over precious metals has been extensively reported in the literature [28]. For a given metal, it is apparent that the activity and selectivity of a given metal is determined by the relative concentrations of N, H, and O on the surface [29,31]. In this study, the strong dependence of the selectivity of NO_x reduction on the NO_x:H₂ ratio was confirmed. It was also found that the light-off temperature for the NO₂ + H₂ reaction decreased with increase of the H₂ concentration. Xu et al. [27] reported a similar finding for NO reduction by H₂ over Pt/Al₂O₃ and Pt-BaO/Al₂O₃ catalysts, and took this as an indication that the reaction order is positive in H₂. In the case of the NO + H₂ reaction, comparison of catalyst activity in the low temperature region at the two NO:H₂ ratios is not possible due to the fact that at the 1:1 NO:H₂ ratio the NO conversion is H₂-limited at low temperatures; this is a direct consequence of NH₃ formation, which requires a 1:1.5 NO:H₂ stoichiometry. At these low temperatures (< 175 °C) NO conversion via the NO + NH₃ reaction is insignificant (as shown in Fig. 7), hence a certain fraction of the NO remains unconverted.

In contrast to NO_x reduction by H₂, an inhibition effect is observed for NO reduction by CO at low temperatures, indicative of a negative reaction order in CO. As for NO_x reduction by H₂, the selectivity of both NO and NO₂ reduction by CO was found to be highly dependent on the concentration of CO in the feed. If NO_x reduction proceeds to a large degree via H₂ generated in the WGS reaction, then this observation is readily explained since the concentration of H₂ generated in situ is a function of the CO concentration. However, it is also possible that NH₃ is generated via hydrolysis of intermediate isocyanate (–NCO) species, as has been proposed by several research groups [32–34]. Increasing the ratio of adsorbed CO:N on the precious metal sites should result in more effective trapping of the N ad-atoms by CO and hence increased isocyanate formation. At present, the relative importance of these two pathways for NH₃ formation from CO remains unclear [34].

NH₃ also functions as an efficient reductant for NO under anaerobic conditions. However, comparison of the conversion curves for NO reduction with H₂ and NH₃ reveals that the NO + H₂ reaction lights-off earlier than the NO + NH₃ reaction, H₂ clearly being a more active reductant than NH₃ at temperatures of 200 °C and below. Again, this is consistent with results reported for Pt/BaO/Al₂O₃ model catalysts [28].

Turning to the effect of catalyst composition, relatively little difference is observed in the activity for NO_x reduction exhibited by catalysts 30-0 and 30-100Z in the fresh state. As reported in our previous study [5], the fresh catalysts

also show similar behavior under lean-rich cycling conditions with respect to NO_x storage efficiency, LNT regeneration (that is, decomposition of nitrates) and reduction of the NO_x liberated from nitrate decomposition. However, it was observed that after aging the cycle-averaged NO_x conversion efficiency of 30-0 was significantly impaired, whereas the performance of 30-100Z was affected to only a minor degree. The deteriorated performance of 30-0 was found to result from decreased NO_x storage efficiency, as well as decreased regeneration efficiency and decreased NO_x reduction activity (resulting in increased NO_x slip during rich phase regeneration). As shown above, the steady-state data confirm that catalyst aging results in significant deterioration of the activity of 30-0 for NO_x reduction with H₂, CO, and NH₃. This decrease in activity can be attributed to the significant PM sintering that resulted from the catalyst aging procedure applied (Table 3). Indeed, as reported in the literature for three-way catalysts [35], decreased NO_x reduction activity is typically associated with PM sintering. It is generally accepted that the reductant needs to be first adsorbed on the PM before NO_x reduction can occur. Given that sintering results in decreased PM surface area and hence a decrease in available sites for NO_x dissociation and reductant adsorption, the rate of NO_x reduction is expected to decrease.

In contrast to 30-0, the NO_x reduction activity of catalyst 30-100Z is not significantly deteriorated after aging. As indicated above, this agrees with the results of lean-rich cycling experiments performed with 30-100Z [5]. The superior activity of the aged 30-100Z can be attributed to the presence of the Pt/CeO₂-ZrO₂ phase in the catalyst. As shown by HRTEM observations, Pt supported on CeO₂-ZrO₂ remains highly dispersed after aging, in contrast to Pt supported on the BaO/Al₂O₃ component. In addition, the facile desulfation of the Pt/CeO₂-ZrO₂ component means that it does not accumulate sulfur during aging (as indicated by TEM-EDS analysis), unlike Pt/BaO/Al₂O₃ [5]. Consequently, the Pt/CeO₂-ZrO₂ component in 30-100Z should not be blocked by accumulated sulfate with respect to NO_x adsorption on the Pt or CeO₂-ZrO₂ surface. In this context, it is also worth noting that CeO₂-ZrO₂ is an active catalyst in its own right for the selective catalytic reaction of NO with NH₃ [36,37].

The most unexpected finding from the steady-state experiments is that selectivity for NH₃ in the NO/NO₂+H₂ reactions increases after catalyst aging. In principle, this could be due to the fact that once NH₃ is formed, it can undergo subsequent reactions with unreacted NO_x in the feed or can undergo decomposition to N₂ and H₂. Hence, a relative decrease in the rates of the NO/NO₂+NH₃ or NH₃ decomposition reactions relative to the NO/NO₂+H₂ reaction might explain the increased selectivity for NH₃. However,

comparison of the data in Figs. 3 and 7 reveals a significant increase in NH_3 selectivity at 150 °C after aging, which is below the light-off temperature for the $\text{NO} + \text{NH}_3$ reaction over both the fresh and aged catalysts. In other words, the $\text{NO} + \text{NH}_3$ reaction does not affect the overall selectivity of NO_x reduction to NH_3 at these low temperatures. Furthermore, data for fresh and aged 30-0 and 30-100Z show that NH_3 decomposition is negligible below 250 °C and that catalyst activity for the decomposition reaction does not change appreciably after aging (data not shown). Hence, this potential explanation can also be excluded.

Based on the foregoing we conclude that the increased selectivity for NH_3 after catalyst aging must be due to an increase in the intrinsic selectivity of the catalyst for NH_3 production. This in turn implies a change in the relative surface coverages of N and H ad-atoms on the PM sites, i.e., increased coverage by H at the expense of N. The reasons for this are unclear, although logically it must be related to the PM dispersion. One possible implication is that as the PM particles become larger, and hence more metallic in character, dissociative adsorption of NO_x decreases, while H_2 dissociation is affected to a lesser degree. While there have been many studies of NO reduction by H_2 and CO on metal surfaces, the effect of metal dispersion on product selectivity does not appear to have been addressed. However, Pirug and Bonzel [38] have reported that product distribution as a function of temperature in the $\text{NO} + \text{H}_2$ reaction shows a striking similarity over polycrystalline Pt foil in vacuo and Pt dispersed on Al_2O_3 at 1 atm total pressure. This tends to rule against the above explanation.

Another possible explanation involves the transport of NO_x to the PM sites. It is pertinent to mention here that under cycling conditions selectivity for NH_3 is generally increased after catalyst aging. As noted previously [5,22], there are a number of possible factors which can account for this increase. One of the principal reasons is believed to be Pt sintering, which results in a decrease in the Pt-Ba interfacial perimeter and hence a decrease in the rate of transport of stored NO_x to Pt sites during regeneration. As noted by Clayton et al. [39], if this rate is slower than the H_2 feed rate, then H_2 will break through the catalyst with a substantial amount of NO_x remaining on it. Consequently, the Pt surface will be predominantly covered by hydrogen, and as the stored NO_x migrates to the Pt particles, NH_3 will be preferentially formed. Recent modeling studies by Bhatia et al. [40] confirm this idea: NH_3 formation is favored when solid-phase diffusion of NO_x to the Pt/Ba interface is the rate determining process, which becomes increasingly likely as the Pt dispersion decreases. Somewhat similarly, it can be postulated that if — under steady-state conditions — NO_x reduction on Pt proceeds to a significant degree via initial adsorption on the BaO/ Al_2O_3 or CeO_2 - ZrO_2 phases, fol-

lowed by migration to the PM sites, then sulfation of the Pt/BaO/ Al_2O_3 phase, together with the decreased PM-support interfacial perimeter, will result in decreased NO_x adsorption on Ba and a decreased rate of NO_x transport from Ba to Pt. This in turn would lead to a higher H: NO_x ratio at the PM sites.

LNT selectivity for NH_3 is an important issue given the toxic nature of NH_3 . However, it is also possible to take advantage of NH_3 formation by means of so-called “hybrid” LNT-SCR systems. In this concept, an SCR catalyst is placed downstream of the LNT and is used to trap NH_3 and catalyze its reaction with NO_x that slips through the LNT, thereby achieving higher overall NO_x conversion levels than is possible with the LNT alone [41]. Understanding the chemistry of NH_3 formation over LNT catalysts is therefore essential to the optimal design and operation of LNT-SCR systems. Steady-state experiments in this study clearly show that in NO_x reduction by H_2 and CO, the intrinsic selectivity for NH_3 increases after catalyst aging. This provides an additional explanation for the increased emissions of NH_3 observed for aged LNT catalysts during cyclic LNT operation [5], and holds implications for the operation of LNT-SCR systems. The fact that an unambiguous explanation for this phenomenon is currently lacking indicates a need for further study.

3 Conclusions

The addition of CeO_2 - ZrO_2 to a fully formulated Ba-based LNT catalyst was found to exert little effect on steady-state NO_x reduction activity in the fresh state. However, after aging, NO_x reduction activity with H_2 , CO, and NH_3 was significantly impaired for the CeO_2 - ZrO_2 -free catalyst, whereas the performance of its CeO_2 - ZrO_2 -containing analog was affected to only a minor degree. These differences are explained on the basis of HRTEM measurements which show that Pt supported on CeO_2 - ZrO_2 remained highly dispersed after aging, in contrast to Pt supported on the BaO/ Al_2O_3 component. In addition, it was found that Pt/ CeO_2 - ZrO_2 did not accumulate sulfur during aging, unlike the Pt/BaO/ Al_2O_3 component for which significant sulfation of the Ba phase was observed. For both catalysts, selectivity for NH_3 in NO and NO_2 reduction by H_2 increased after catalyst aging. This is suggestive of a change in the relative surface coverages of N and H ad-atoms on the precious metal sites, i.e., increased coverage by H at the expense of N.

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