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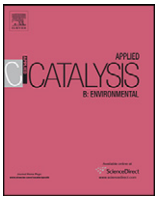

Application of spaciMS to the study of ammonia formation in lean NO_x trap catalysts

Vencon Easterling[a], Yaying Ji[a], Mark Crocker[a,*], Mark Dearth[b], Robert W. McCabe[b]

[a] *Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA*
[b] *Chemical Engineering Department, Ford Motor Co., Dearborn, MI 48124, USA*

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ABSTRACT

SpaciMS was employed to understand the factors influencing the selectivity of NO_x reduction in two fully formulated LNT catalysts, both degreened and thermally aged. Both catalysts contained Pt, Rh, BaO and Al_2O_3, while one of them also contained La-stabilized CeO_2. The amount of reductant required to fully regenerate each catalyst was first determined experimentally based on the OSC of the catalyst and the NO_x storage capacity (NSC). In this way a correction was made for the change in catalyst OSC and NSC after aging, thereby eliminating these as factors which could affect catalyst selectivity to NH_3. For both catalysts, aging resulted in an elongation of the NO_x storage–reduction (NSR) zone due to a decrease in the concentration of NO_x storage sites per unit catalyst length. In addition to decreased lean phase NO_x storage efficiency, stretching of the NSR zone affected catalyst regeneration. Three main effects were identified, the first being an increase of the NO_x "puff" that appeared during the onset of the rich front as it traversed the catalyst. Spatially, NO_x release tracked the NSR zone, with the result that the NO_x concentration peaked closer to the rear of the aged catalysts. Hence the probability that NO_x could re-adsorb downstream of the reduction front and subsequently undergo reduction by NH_3 (formed in the reduction front) was diminished, resulting in higher rich phase NO_x slip. Second, the stretching of the NSR zone resulted in increased selectivity to NH_3 due to the fact that less catalyst (corresponding to the OSC-only zone downstream of the NSR zone) was available to consume NH_3 by either the NH_3-NO_x SCR reaction or the NH_3-O_2 reaction. Third, the loss of OSC and NO_x storage sites, along with the decreased rate of NO_x diffusion to Pt/Rh sites (as a result of Pt/Rh–Ba phase segregation), led to an increase in the rate of propagation of the reductant front after aging. This in turn resulted in increased H_2:NO_x ratios at the Pt/Rh sites and consequently increased selectivity to NH_3.

1. Introduction

Recent years have witnessed concerted efforts to reduce NO_x emissions from mobile sources of lean exhaust gas using lean NO_x trap (LNT) or selective catalytic reduction (SCR) catalysts. Although both technologies have many positive features, each approach has drawbacks which have slowed their application to the automotive marketplace. For LNT catalysts, one of the main disadvantages is the cost associated with the use of platinum group metals (PGMs), while for SCR, the cost of the injection system and refilling of the NH_3 source adds to the consumer's costs. However, recent studies have shown that by combining LNT and SCR catalysts in series, these drawbacks can be lessened [1–5]. In this configuration the SCR catalyst functions in a passive or in situ mode, i.e., with the storage and utilization of NH_3 generated by the LNT during rich purge events. Given that the presence of the SCR catalyst relaxes the NO_x conversion requirements of the LNT catalyst, the volume of the LNT in the LNT–SCR system can, in principle, be lower than for an LNT-only system, thereby reducing the precious metal costs. Furthermore, the need for a urea injection system is eliminated.

To realize a LNT–SCR system capable of achieving these aims, an understanding is required of the interplay between system operating parameters and the underlying chemistry of NO_x reduction. Probably the most important aspects to be considered are the generation of NH_3 over the LNT, and its subsequent reaction with NO_x over the SCR catalyst. A potential problem in studying these processes in a LNT–SCR system is the integral nature of the catalysts. Reactants and products can react, adsorb, and desorb multiple times before exiting the system. This makes the study of LNT–SCR systems difficult using traditional laboratory techniques based on analysis of the reactor effluent.

To overcome these problems, spatially resolved capillary inlet mass spectrometry (spaciMS), developed at Oak Ridge National Laboratory, has been applied to monitor the composition of

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* Corresponding author. Tel.: +1 859 257 0295; fax: +1 859 257 0302.
E-mail address: mark.crocker@uky.edu (M. Crocker).

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simulated exhaust gas as it passes through LNT catalysts [6–14]. The key feature of a spaciMS system is the use of a capillary connected to the sample cell of a mass spectrometer. The capillary allows the internal gas stream to be analyzed at different points along the length of the LNT or SCR catalyst under study. Consequently, the gaseous components present can be monitored on both a spatial and temporal scale. Partridge et al. employed spaciMS to study NH_3 formation and utilization over a $Pt/Ba/Al_2O_3$ catalyst during regeneration with H_2 [10]. It was found that NH_3 was formed at the same time as the N_2 product inside the catalyst during regeneration, and was consumed as aggressively as the H_2 reductant along the catalyst. From this it was concluded that the intermediate NH_3 regeneration pathway plays an important role in LNT catalyst regeneration. The same research group also utilized this technique to study the effect of sulfur on the spatiotemporal distribution of NO_x storage and reduction [11]. Prior to sulfation, NO_x storage/reduction was found to be localized in the front portion of catalyst, whereas sulfation resulted in a shift of the NO_x storage/reduction (NSR) zone downstream, thereby decreasing the length of the downstream zone in which only oxygen was stored. These workers also reported an increase in selectivity to NH_3 after sulfation, and ascribed it to decreased oxidation of NH_3 slipping from the NSR zone by the oxygen stored downstream [11,12]. A more recent study by this group further demonstrated that NH_3 slip at the catalyst exit increased with sulfur loading due to its formation closer to the catalyst outlet and decreased NH_3 conversion by stored oxygen downstream of the NSR zone [13]. Moreover, during catalyst regeneration the extent of NO_x readsorption downstream of the NSR zone was found to diminish after sulfation, resulting in earlier and broader NO_x peaks at the catalyst outlet. The spaciMS technique was also applied in another recent LNT study by Luo et al. [14] in which catalyst desulfation was examined. For a partially sulfated commercial catalyst, the plug-like sulfur profile was redistributed after desulfation at 600 °C as a result of re-adsorption. The extent of re-adsorption was found to be determined by the catalyst formulation and sulfation degree.

We have previously investigated the effect of regeneration conditions on NH_3 formation in LNT catalysts [15]. One of the findings from these studies was that NH_3 selectivity is dependent on the local H_2:NO_x ratio at the precious metal sites. Increasing the regeneration time or reductant concentration fed to the catalyst increases this ratio and thereby increases the amount of NH_3 formed, as opposed to N_2. Conversely, increasing the amount of NO_x stored decreases the selectivity to NH_3. It was also observed that the addition of a ceria-based oxygen storage material to a $Pt/Rh/BaO/Al_2O_3$ catalyst caused a decrease in NH_3 selectivity [15–18], which was explained on the basis that consumption of reductant by stored oxygen results in decreased H_2:NO_x ratios during regeneration, which favors the formation of N_2 over NH_3. In addition, oxygen stored in the rear of the catalyst can consume NH_3 formed upstream via oxidation to produce N_2, NO, or N_2O. After aging, increased selectivity to NH_3 was observed, for both the ceria-containing and ceria-free catalyst. In principle, this increase in selectivity to NH_3 can be accounted for by any one of a number of factors [15]:

(i) Aging-induced Pt sintering, resulting in Pt–Ba phase segregation. Consequently, the rate of NO_x transport to the Pt sites during regeneration is decreased. As Harold and co-workers have pointed out [19], if this rate is slower than the H_2 feed rate, then H_2 will break through with substantially more NO_x remaining on the catalyst. Consequently, the Pt surface will be predominantly covered by hydrogen, and as the stored NO_x diffuses to the Pt particles, NH_3 will be formed with high selectivity. Modeling studies confirm this idea, i.e., that 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 [20].
(ii) For a fixed concentration of reductant, the decreased oxygen storage capacity (OSC) of the aged catalysts should result in higher effective H_2:NO_x ratios in the reduction front due to decreased reductant consumption by stored oxygen, thereby favoring NH_3 formation. Furthermore, there is less oxygen available downstream of the reductant front to react with formed NH_3.
(iii) After aging, there are fewer NO_x storage sites available per unit of catalyst length. This should result in higher effective H_2:NO_x ratios in the reductant front, again favoring NH_3 formation [15].
(iv) The length of the NO_x storage–reduction zone increases due to the decrease in NO_x storage capacity (NSC) as the catalyst ages [11,12,15]. More NH_3 slips from the LNT without being oxidized because the increased length of the NSR zone decreases the length of the downstream OSC-only zone.
(v) After aging, higher NH_3 emissions may result from decreases in the rates of NH_3 consumption via reaction with NO_x or O_2 stored downstream of the reaction front.

Table 1
Composition of catalysts used in this study.

Component	Catalyst code/nominal loading	
	B-225	BC-175
Pt (g/L)	3.05	2.38
Rh (g/L)	0.61	0.48
BaO[a] (g/L)	26	20
CeO_2[b] (g/L)	0	67
γ-Al_2O_3[c] (g/L)	Balance	Balance
Total washcoat (g/L)	225	175

[a] 21.5 wt% supported on γ-Al_2O_3.
[b] Stabilized with 5 wt% La_2O_3.
[c] Stabilized with 3 wt% La_2O_3.

From the foregoing, it is evident that NH_3 selectivity after aging is likely to be dependent – at least in part – on the residual OSC of the catalyst, as well as the amount of NO_x stored. In an effort to distinguish between the factors that can account for increased LNT selectivity to NH_3 after aging, in this study we adjusted the amount of reductant used to regenerate each catalyst (degreened and thermally aged) based on the OSC of the catalyst and the NO_x storage capacity (NSC). In this way we attempted to correct for the change in catalyst OSC and NSC after aging, thereby eliminating these as factors. SpaciMS was used to monitor the NO_x storage and reduction processes for degreened and aged catalysts in order to investigate the contribution of other factors to NO_x reduction selectivity.

2. Experimental

2.1. Catalyst preparation

Two fully formulated Ba-based LNT catalysts were used in this study, the compositions of which are shown in Table 1. For simplicity, the BaO-only formulation is denoted as B-225 (where 225 refers to the washcoat loading in g/L), while the catalyst containing both BaO and CeO_2 is denoted as BC-175 (containing a washcoat loading of 175 g/L). Details of the catalyst preparation have been described elsewhere [16,17]. In both cases, the washcoat was applied to a 4 in. × 6 in. cordierite monolith substrate, possessing a cell density of 400 cpsi and a wall thickness of 6.5 mil. The BaO component (21.5 wt %) was supported on γ-alumina, while bare alumina was also used as a balance to bring the total washcoat loadings to the values indicated in Table 1.