

NO_x Storage-Reduction Characteristics of Ba-Based Lean NO_x Trap Catalysts Subjected to Simulated Road Aging

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Introduction

Although Lean NO_x Trap (LNT) catalyst technology has made significant strides in recent years, LNT durability still remains problematic due to the occurrence of sulfur poisoning. Periodic desulfation at high temperature is required in order to restore catalyst activity, and over time the resulting thermal aging leads to catalyst deactivation. For Ba-based LNTs, this is principally associated with sintering of the precious metal and Ba phases. On the other hand, incomplete removal of sulfur during desulfation can result in decreased NO_x storage capacity and hence lower NO_x conversion. Following on from our previous research concerning the effect of ceria addition on LNT performance [1], in this study we focus on the role of ceria in ameliorating the deterioration of Ba-based LNT catalysts during aging.

Materials and Methods

Fully formulated monolithic catalysts were prepared containing varying amounts of La-stabilized CeO₂ (5 wt% La₂O₃) and CeO₂-ZrO₂ mixed oxide (Ce:Zr = 70:30), at fixed loadings of Pt (3.5 g/L), Rh (0.7 g/L) and BaO (30 g/L). The BaO phase was supported on alumina. Details of the catalyst preparation have been given previously [1]. Core samples, 62 cells/cm², 2.2 cm (d) x 7.62 cm (l), were used for aging and evaluation on a bench reactor. Catalyst aging consisted of (i) sulfating the catalyst at 350 °C to an equivalent loading of 1 g S/L, (ii) desulfation at 700 °C for 10 min under cycling (5 s lean/15 s rich at λ= 0.90), and (iii) holding at 650 °C for 30 min under lean conditions (to simulate DPF regeneration). Together, these three conditions constituted one aging cycle. Each catalyst was aged for 50 cycles, equivalent to ca. 75,000 miles of road aging. After aging, the catalysts were exposed to rich conditions at 750 °C for 10 min to remove residual sulfur. In addition to evaluation on a bench reactor, the aged samples were also characterized using a variety of physico-chemical techniques for comparison with the fresh catalysts.

Results and Discussion

Representative cycle averaged NO_x conversion and N₂ selectivity data for the aged catalysts are shown in Table 1, together with oxygen storage capacity (OSC) data obtained at 350 °C. For comparison purposes, data for the fresh (degreened) catalysts are included. Considering the NO_x conversion data, it is apparent that the performance of catalyst 30-0, containing no ceria, was severely degraded after aging. In comparison, catalyst 30-100, containing 100 g/L of ceria, continued to show high levels of NO_x conversion at 250-350 °C, while catalyst 30-100Z, containing 100 g/L of CeO₂-ZrO₂, retained the highest degree of

activity; indeed, NO_x conversion levels for the aged catalyst were only slightly lower than for the fresh state. Analysis of data (not shown) pertaining to the lean phase NO_x storage efficiency and rich-phase NO_x release characteristics of the three catalysts indicates that the decreased NO_x conversion after aging mainly results from degradation of the lean-phase NO_x storage efficiency (NSE) under cycling. Significantly, lean phase NO₂ slip was consistently observed for the catalysts (at all temperatures), indicating that NO oxidation is not the limiting factor; rather, it is the inability of the catalyst to store NO₂ that limits the storage efficiency. To provide further insights into the origin of the NSE degradation, the NSE measured during the first lean cycle after complete catalyst regeneration was compared with the NSE measured under steady state cycling. Catalyst 30-0 exhibited a large difference between the two NSE values, implying that its NO_x storage efficiency was significantly limited by its inability to be completely regenerated during rich purging. However, a small difference between these two NSE values for catalysts 30-100 and 30-100Z indicated that these two catalysts retained their good regeneration characteristics.

From Table 1 it is apparent that after aging, all of the catalysts showed decreased selectivity to N₂ during NO_x reduction; this results from their increased selectivity to NH₃. Simultaneously, in each case the catalysts exhibited decreased OSC after aging. This suggests that the decreases in N₂ selectivity and OSC may be related, an idea which can be rationalized on the basis that: 1) a reduction in stored oxygen should result in an increased reductant concentration in the gas front, favoring the formation of NH₃ over N₂; 2) less stored oxygen will be available in the rear of the catalyst to react with initially formed NH₃ to give N₂.

Table 1. Comparison of OSC, cycle averaged NO_x conversion and N₂ selectivity before and after catalyst aging

Catalyst	Temp (°C)	OSC (mmol/L)		NO _x conversion (%)		N ₂ selectivity (%)	
		Fresh	Aged	Fresh	Aged	Fresh	Aged
30-0	250	--	--	94.3	39.7	31.7	41.7
	350	10.8	6.2	95.9	40.0	66.4	23.5
30-100	250	--	--	98.7	87.7	76.8	57.8
	350	28.0	18.5	98.7	91.1	95.9	88.3
30-100z	250	--	--	97.2	92.0	79.5	15.8
	350	36.6	34.1	98.0	93.4	97.0	89.2

Conditions: Lean: 300 ppm NO, 10% O₂, 5% CO₂, 5% H₂O in N₂ (60 s); Rich: 1.575% H₂, 2.625% CO, 5% CO₂, 5% H₂O in N₂ (5 s); GHSV = 30,000 h⁻¹.

Significance

This study shows the spectacular improvement in LNT durability which can be achieved through the incorporation of CeO₂ and CeO₂-ZrO₂ (particularly the latter). Insights into the mechanisms by which CeO₂-ZrO₂ improves LNT durability should be useful in aiding the design of more robust and cost-efficient LNT systems.

References

1. Ji, Y., Choi, J.-S., Toops, T.J., Crocker, M., and Naseri, M., *Catal. Today* 136, 146 (2008).