



## Effect of aging on the NO<sub>x</sub> storage and regeneration characteristics of fully formulated lean NO<sub>x</sub> trap catalysts<sup>☆</sup>

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### ABSTRACT

In order to elucidate the effect of washcoat composition on lean NO<sub>x</sub> trap (LNT) aging characteristics, fully formulated monolithic LNT catalysts containing varying amounts of Pt, Rh and BaO were subjected to accelerated aging on a bench reactor. Subsequent catalyst evaluation revealed that in all cases aging resulted in deterioration of the NO<sub>x</sub> conversion as a consequence of impaired NO<sub>x</sub> storage and NO<sub>x</sub> reduction functions, while increased selectivity to NH<sub>3</sub> was observed in the temperature range 250–450 °C. Elemental analysis, H<sub>2</sub> chemisorption and TEM data revealed two main changes which account for the degradation in LNT performance. First, residual sulfur in the catalysts, associated with the Ba phase, decreased catalyst NO<sub>x</sub> storage capacity. Second, sintering of the precious metals in the washcoat occurred, resulting in decreased contact between the Pt and Ba, and hence in less efficient NO<sub>x</sub> spillover from Pt to Ba during NO<sub>x</sub> adsorption, as well as decreased rates of reductant spillover from Pt to Ba and reverse NO<sub>x</sub> spillover during catalyst regeneration. For the aged catalysts, halving the Pt loading from 100 to 50 g/ft<sup>3</sup> was found to result in a significant decrease in overall NO<sub>x</sub> conversion, while for catalysts with the same 100 g/ft<sup>3</sup> Pt loading, increasing the relative amount of Pt on the NO<sub>x</sub> storage components (BaO and La-stabilized CeO<sub>2</sub>), as opposed to an Al<sub>2</sub>O<sub>3</sub> support material (where it was co-located with Rh), was found to be beneficial. The effect of Rh loading on aged catalyst performance was found to be marginal within the range studied (10–20 g/ft<sup>3</sup>), as was the effect of BaO loading in the range 30–45 g/L.

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### 1. Introduction

Lean NO<sub>x</sub> traps (LNTs), also known as NO<sub>x</sub> storage–reduction catalysts, represent a promising technology for the abatement of NO<sub>x</sub> emissions from lean burn gasoline and diesel engines. LNT catalysts typically comprise precious metals (generally Pt and Rh) and an alkali or alkaline earth metal storage component (most com-

monly BaO) supported on a high surface area metal oxide such as γ-Al<sub>2</sub>O<sub>3</sub> [1]. LNT catalysts require cyclic operation between lean and rich conditions. Under lean conditions, NO is first oxidized to NO<sub>2</sub> over the precious metal, which is followed by NO<sub>x</sub> storage on the storage component as nitrates and nitrites. Stored NO<sub>x</sub> species are subsequently released and reduced to N<sub>2</sub> after switching to rich (i.e., net reducing) conditions. The trapping ability of the LNT catalysts is thus restored after a lean–rich cycle [2]. Although LNTs have been commercialized for some applications, the durability of LNT catalysts still remains problematic. Sulfur poisoning and thermal aging are recognized as two major causes of deactivation. The BaO NO<sub>x</sub> storage component of a LNT catalyst has a greater affinity for SO<sub>3</sub> than for NO<sub>2</sub>, and the resulting sulfate cannot be removed under typical rich purging conditions as for nitrates; hence sulfur accumulates on the catalyst and blocks the Ba sites with respect to further NO<sub>x</sub> storage [3–9]. Desulfation requires high temperature treatment under rich conditions [10–14], and such treatments give rise to deactivation mechanisms such as precious metal sintering, total surface area loss, and solid state reactions between the various oxides present in the washcoat.

The presence of Pt in LNT catalysts is required not only to facilitate NO<sub>x</sub> storage through spillover of NO<sub>2</sub> from Pt to the Ba

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phase (subsequent to NO oxidation on Pt) but also to facilitate NO<sub>x</sub> reduction during rich purging. Both functions are related to the proximity between the Pt and Ba phases, and both can be significantly deteriorated by Pt sintering which results in decreased interaction between the two phases. An early study by Mahzoul et al. [15] showed that only the Pt sites close to BaO crystallites are responsible for nitrate formation (i.e., NO<sub>x</sub> storage), although other Pt sites can act as centers for the oxidation of NO. Nova et al. [16] studied the role of the Pt–Ba interaction in the regeneration behavior of LNTs. A comparison between Pt/BaO/Al<sub>2</sub>O<sub>3</sub> and a Pt/Al<sub>2</sub>O<sub>3</sub>–BaO/Al<sub>2</sub>O<sub>3</sub> physical mixture showed that the promoting effect of Pt on the rate of nitrate reduction required Pt and Ba dispersed on the same support, this being in line with the role of the Pt–Ba interface in nitrate decomposition suggested by Coronado et al. [17] and the involvement of NO<sub>x</sub> spillover from Ba to its nearest Pt sites suggested by Olsson et al. [18]. Similarly, Cant and co-workers [19] inferred the occurrence of forward and reverse spillover of NO<sub>x</sub> during exchange between gaseous <sup>15</sup>N<sub>2</sub>O and stored NO<sub>x</sub>, these processes being five times faster when Pt and BaO were located on the same support.

In another study, Büchel et al. examined the influence of Pt location – on BaCO<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> – for Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by flame spray pyrolysis [20]. The benefit of a close interaction between Pt and Ba was confirmed for NO<sub>x</sub> storage, although Pt on Al<sub>2</sub>O<sub>3</sub> exhibited better NO oxidation activity which was limiting for NO<sub>x</sub> storage at low temperatures. During NO<sub>x</sub> reduction, Pt on Ba showed superior activity to Pt on Al<sub>2</sub>O<sub>3</sub>, which was attributed to the importance of reverse spillover and the promotional effect of Ba on the Pt reduction activity. A recent TAP reactor study by Kumar et al. has provided further evidence of the role of spillover processes and the importance of the Pt/Ba interface during NO<sub>x</sub> storage and reduction [21]. Their data suggests that NO<sub>x</sub> storage proceeds radially outward from the Pt sites and that the stored NO<sub>x</sub> possesses some degree of mobility. In essence, Pt acts as a conduit for spillover to and from the Ba phase, in addition to playing a key role in catalyzing the NO oxidation and reduction reactions themselves. In another recent study [22] concerned with fast NO<sub>x</sub> storage on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> (that is, the initial phase of storage when there is essentially no NO<sub>x</sub> slip from the LNT), it was concluded that the Pt–Ba interface plays a key role, associated with the spillover of dissociated oxygen atoms from Pt to Ba which participate in the adsorption of NO and NO<sub>2</sub> on the Ba sites via nitrite and nitrate formation. In summary, therefore, close proximity of Pt and Ba is required to achieve both efficient NO<sub>x</sub> storage and NO<sub>x</sub> reduction during lean–rich cycling.

Pt sintering mainly occurs under oxidizing conditions during thermal aging. Graham et al. compared the behavior of Pt under both reducing and oxidizing conditions [23], and found that the most significant Pt particle growth occurred under oxidizing conditions. A recent study by Dartye and co-workers supports the notion that Pt sintering in air results from the formation of volatile Pt oxide, PtO<sub>x</sub>, leading to enhanced interparticle transport and sintering via Ostwald ripening [24]. However, sintering was significantly inhibited in reducing atmospheres, probably due to the low vapor pressure of metallic Pt; consequently, particle migration and coalescence was suggested to be the major mechanism of Pt sintering under reducing conditions. Pt sintering has a permanent impact on catalyst performance due to its irreversibility and consequently it has been recognized as a key issue associated with thermal deactivation. Indeed, a number of studies have provided evidence that Pt sintering can result in decreased interaction between the Pt and Ba phases (i.e., phase segregation) which in turn leads to degraded NO<sub>x</sub> storage and regeneration behavior [25–31]. Fekete et al. [25] attributed the observed decrease in NO<sub>x</sub> storage capacity after aging to loss of contact between the precious metals and the storage material, in addition to the formation of mixed metal oxides

**Table 1**  
Composition of catalysts subjected to simulated road aging.

Component	Catalyst code/loading <sup>a</sup>			
	Pt-50	Pt-100	30-50	45-50
Pt (g/L) (g/cuft)	1.77 (50)	3.53 (100)	3.53 (100)	3.53 (100)
Rh (g/L) (g/cuft)	0.35 (10)	0.35 (10)	0.71 (20)	0.71 (20)
BaO (g/L)	30	30	30	45
CeO <sub>2</sub> <sup>b</sup> (g/L)	50	50	50	50
Al <sub>2</sub> O <sub>3</sub> <sup>c</sup> (g/L)	Balance	Balance	Balance	Balance

<sup>a</sup> Nominal loadings. Total washcoat loading = 260 g/L.

<sup>b</sup> Stabilized with 5 wt% La<sub>2</sub>O<sub>3</sub>.

<sup>c</sup> Stabilized with 3 wt% La<sub>2</sub>O<sub>3</sub>.

from unwanted side reactions between the storage material and the support. It was suggested that the diminished contact leads to a reduced spillover rate of NO<sub>2</sub> from the precious metal to the adsorbent, thereby decreasing NO<sub>x</sub> storage efficiency. Uy et al. [26] characterized fresh and aged Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalysts using in situ UV and visible Raman spectroscopy and found evidence for Ba particles “separating from” or behaving independently from the Pt/Al<sub>2</sub>O<sub>3</sub> in aged Pt/Ba/Al<sub>2</sub>O<sub>3</sub>.

Unwanted side reactions between Ba and the support is another effect associated with thermal aging, resulting in the formation of Ba aluminate, zirconate, cerate, etc., as applicable [31–39]. From studies with Pt–Ba/Al<sub>2</sub>O<sub>3</sub> catalysts, Jang et al. [32] emphasized the importance of Ba–Al mixed oxide formation as a cause of degraded NO<sub>x</sub> storage capacity. Upon heating Pt–Ba/Al<sub>2</sub>O<sub>3</sub> from 550 to 850 °C, they observed the gradual conversion of Ba/Al<sub>2</sub>O<sub>3</sub> to BaAl<sub>2</sub>O<sub>4</sub>. Several other authors have similarly found that BaAl<sub>2</sub>O<sub>4</sub> forms at about 850 °C [33–35] and concluded that the formation of such mixed oxides is a significant factor in thermal deactivation. However, recent studies have shown that the formation of BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub> is largely reversible in nature [34–39]. For example, Casapu et al. [34] studied LNT catalysts that contain CeO<sub>2</sub> as a support material and observed the formation of BaCeO<sub>3</sub> at 800 °C. Decomposition of BaCeO<sub>3</sub> was found to occur at 300–500 °C in the presence of NO<sub>2</sub>/H<sub>2</sub>O or CO<sub>2</sub> [34,35], resulting in an improvement in NO<sub>x</sub> storage capacity. Another recent report indicates that BaCeO<sub>3</sub> formation is inhibited in the presence of CO<sub>2</sub> at a concentration as low as 5% [39]. In comparison, BaAl<sub>2</sub>O<sub>4</sub> is much more stable under typical operating conditions but can be converted to BaCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> at room temperature in the presence of liquid water [36,37].

In a previous paper [40], we reported the results of a study into the effect of catalyst ceria content and type (La-stabilized CeO<sub>2</sub> or CeO<sub>2</sub>–ZrO<sub>2</sub>) on LNT aging characteristics. Two main causes of LNT aging were discerned, corresponding to (i) sintering of the precious metals present and (ii) the accumulation of sulfur in the washcoat as BaSO<sub>4</sub>. In addition, spectacular improvement in LNT durability was observed for catalysts containing CeO<sub>2</sub> or CeO<sub>2</sub>–ZrO<sub>2</sub> relative to a non-ceria containing analog. This was attributed to the ability of ceria to participate in NO<sub>x</sub> storage/reduction as a supplement to the main Ba NO<sub>x</sub> storage component, the fact that Pt and the CeO<sub>2</sub>–(ZrO<sub>2</sub>) support remain in intimate contact, and the ability of ceria to trap sulfur, resulting in decreased sulfur accumulation on the Ba component. In this paper, we report the results of a study aimed at investigating the effects of precious metal (Pt, Rh) loading and BaO loading on catalyst durability.

## 2. Experimental

### 2.1. Catalyst preparation

Four fully formulated Ba-based LNT catalysts were used in this study, the compositions of which are shown in Table 1. Details of the catalyst preparation have been described elsewhere [41]. Briefly,

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