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A NO_x trap for low-temperature lean-burn-engine applications

Lifeng Xu,* George Graham, and Robert McCabe

Chemical Engineering Department, Ford Research and Innovation Center, Dearborn, MI 48121, USA

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A NO_x trap that uses only high-surface-area alumina as the NOx-storage material appears to provide significant advantages over the conventional baria-based trap for exhaust-gas after-treatment in low-temperature exhaust (~250 °C) characteristic of light-duty diesel-powered vehicles operating at low speed/load conditions. In particular, an alumina trap provides better low-temperature NO_x conversion and also allows more efficient de-sulfurization than a baria-based trap in laboratory evaluations. Both of these features are ascribed to the difference in basicity of the NO_x-storage materials, which leads to thermally less stable nitrate (nitrite) and sulfate compounds in the case of alumina compared to conventional traps with high levels of alkali or alkaline-earth metal oxides. Further studies, extending the laboratory experiments to engine and vehicle evaluations, are still needed, however, in order to fully assess the true potential of the alumina trap.

KEY WORDS: LNT; alumina based LNT; lean burn; diesel exhaust; de-SO_x.

1. Introduction

Government emissions regulations, created in response to environmental and health concerns, have necessitated the treatment of exhaust gas from vehicle engines in order to reduce the level of certain combustion by-products, including carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x). In conventional gasoline engines (i.e., engines that operate a majority of the time at a stoichiometric air-to-fuel ratio), such treatment generally includes the use of a three-way catalyst (TWC). However, lean-burn engines such as diesel engines, which offer 10–30% better fuel economy than conventional gasoline engines, are challenged to meet increasingly stringent NOx requirements and require special treatment since a TWC cannot effectively reduce the level of NO_x under the oxidizing atmosphere present in the exhaust gas of such engines, which are operated under fuel-lean conditions ($\lambda > 1$, where λ represents the air-to-fuel ratio divided by the stoichiometric air-to-fuel ratio).

A potential solution to this problem is the use of a lean NO_x trap (LNT) [1–5], which conventionally includes a catalyst comprising one or more precious metals and an alkali or alkaline-earth metal oxide supported on a high-surface-area material such as alumina. The LNT is capable of absorbing NO_x from the exhaust gas and storing it during fuel-lean operation of the engine, then releasing and converting it to nitrogen gas when the engine operation changes to stoichiometric or rich ($\lambda < 1$).

However, the LNT has not been widely used in diesel-engine-powered vehicles since the exhaust-gas temperature is usually somewhat lower than the operating temperature window normally provided by the trap. For example, the exhaust-gas temperature of a light-duty diesel vehicle driving under the Federal Test Procedure (FTP) is typically less than 200 °C, while the temperature window of operation of a conventional LNT ranges from 200 to 500 °C.

Additionally, the LNT is not very durable, suffering loss of both catalyst activity (e.g., through thermally activated coarsening of precious-metal particles [6]) and NO_x storage capacity (e.g., through aqueous-based leaching of the alkaline-earth metal oxide [7]). Thermal deactivation is further aggravated because of the need to periodically purge the trap of stored SO_x, which blocks the storage of NO_x. The SO_x accumulates on the LNT due to the combustion of fuel sulfur (and some lubricating oil). It is generally necessary to perform an occasional (every 5,000 miles of low-sulfur fuel used) desulfurization (de-SO_x) treatment at relatively high temperatures (650–800 °C) for relatively long times (5–10 min). In addition, fuel-rich operation ($\lambda = 0.9$) is typically required for the de-SO_x treatment, which takes away some of the efficiency provided by diesel engine operation.

It may be surmised that the severity of these problems can be reduced, however, by using a less basic oxide than baria as the primary NO_x-storage material. In this work, we thus consider an LNT that uses alumina alone (i.e., without any added alkali or alkaline-earth metal oxide) as the NO_x-storage material. Although the overall storage capacity is somewhat less, especially at high temperature, alumina is known to store significant

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*To whom correspondence should be addressed.
E-mail: lxu1@ford.com

amounts of NO_x [8,9]. As described below, such an LNT provides high NO_x conversion efficiency at relatively low temperature (150–300 °C) and also allows for a much more efficient de-SO_x process: 1–2 min at relatively mild temperatures (550–650 °C) under only slightly rich conditions ($\lambda = 0.98$–0.99). There is thus relatively little activity loss due to thermal damage from the de-SO_x process and only a small fuel economy penalty.

2. Experimental details

The experiments were run on a synthetic gas bench where bottled gases are blended to make a desired gas composition. A schematic of the lab is shown in figure 1. All lines are heated stainless steel, with 30 mm outer diameter quartz tubes used to hold the catalyst samples in ovens. The gas mixture can be passed over the catalyst or bypassed. Instrumentation is as follows:

- V&F Airsense chemical ionization mass spectrometer.
- Horiba Mexa 9100 Hegr–Bench analyzers

  - Chemiluminescent analyzer (NO_x, NO);
  - Flame ionization / Magneto-pneumatic analyzer (THC and O_2);
  - Infrared analyzer (CO and CO_2);

Gas to the mass spectrometer and analyzers are diluted by N_2 in a ratio of about 1:2. Therefore, no water condensation problem exists with only 5% water in the reaction gas and less than 2% after the dilution. The outlet gas is sent to analyzers and the sample line is heated before the dilution. Catalyst temperatures are measured at the inlet (1/4 inch in front of the sample), middle (middle of the one inch sample core), and the outlet (1/4 inch after the sample). Catalyst activities are plotted as a function of inlet temperature.

For the majority of testing, standard gas compositions are used, as shown in table 1. The gas flow is set to the lean composition for a period of time, then switches to the rich composition for a different period of time, and this cycle repeats. Typical times are 84 s lean and 6 s rich (84/6) or 24 s lean and 6 s rich (24/6). Thus, 84/6 might be representative of a control strategy for moderate NO_x conversion at a small fuel economy penalty, while 24/6 might be a typical of a strategy for higher NO_x efficiency with a larger fuel economy penalty. These gas compositions are not entirely representative of diesel exhaust. The NO_x level, for example, is rather high for a part-load operating mode, but it is chosen to place a high stress on the catalyst to help differentiate between better and worse. Also, we use a 3:1 ratio of CO:H_2 whereas recent data from other experimenters suggests that 2:1 may be more representative for rich operating conditions. Propylene (C_3H_6) is a lighter HC than typical of diesel exhaust, but it avoids problems of deposition in test lines and instrumentation. Unless otherwise stated,

- The input NO_x is in the form of NO
- Gas flow is adjusted to the catalyst size such that the space velocity is 30 K h^{-1}
- Catalysts tested are 25 mm diameter by 25 mm long cores cut from larger monoliths
- Substrates are cordierite (400 cells per square inch, 6.5 mil wall thickness).

NO_x conversion is reported as "Gross NO_x" conversion – that is, disappearance of NO and NO_2. For the sulfur poisoning and de-SO_x study, sulfur was loaded onto the LNT under lean conditions using an SO_2

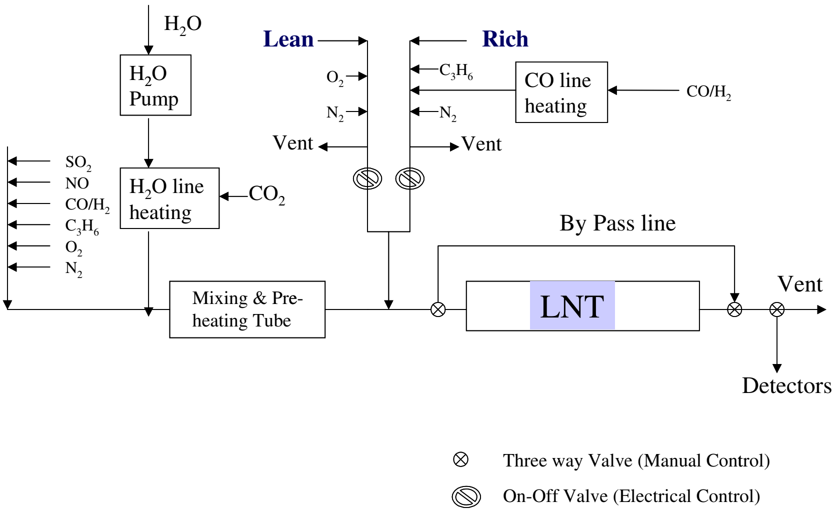

Figure 1. Schematic of the lab flow reactor.

Table 1

Standard gas compositions. (does not include S02, which is listed in the experimental set-up below)

Gas	Lean	Rich
CO	500 ppm	4%
H_2	167 ppm	1.33%
C_3H_6	300 ppmC_1	5000 ppmC_1
NO_x	500 ppm	500 ppm
O_2	10%	1%
CO_2	5%	5%
H_2O	5%	5%
	$\lambda = 1.96$	$\lambda = 0.90$

concentration of 30ppm in the feed-gas, with temperatures ranging from 250 to 650 °C for different lengths of time. De-SOx process for alumina based LNT was operated at 650 °C under a slightly rich condition ($\lambda = 0.98 \sim 0.99$).

An alumina-only LNT was prepared by simply adding Pt and Rh (at loadings of about 100 g-Pt/ft^3 and 20 g-Rh/ft^3), through sequential impregnations, to an alumina pre-coated (2.4 g/in^3) monolith. In order to observe the effect of very low loadings (of order one tenth that used in a conventional LNT) of alkaline-earth metal oxide, some of the alumina-only LNTs were modified by adding 1–3 wt% (relative to the alumina) of these oxides before impregnation of the precious metals; these LNTs are termed alumina-based. Results were also obtained from a commercially-feasible conventional (baria-based) LNT with the same precious metal loadings. This LNT is designated BT.

3. Results and discussion

Figure 2 compares the NO_x conversion efficiency of the alumina-only LNT with that of an alumina-based LNT containing less than 2 wt% calcia under lean/rich cycles of 24/6 and 16/4. The temperature window of active NO_x conversion is clearly shifted up by adding a very small amount of calcia to the washcoat. In particular, NO_x reduction activity at low temperatures is lower than without calcia (e.g., at 150 °C, NO_x conversion efficiency decreases from about 90–70% under 16/4) but higher at high temperature (e.g., at 300 °C, NO_x conversion efficiency increases from about 50–80%). The impact of adding small amounts (2–3 wt%) of other alkaline-earth metal oxides, such as baria, magnesia, or strontia, to the NOx conversion activity of an alumina-only LNT were found to be similar to that of calcia.

Figure 3 compares the NO_x conversion efficiency of an alumina-based LNT (containing about 2 wt% calcia) under varying lean/rich cycle times, such as 84/6, 24/6 16/4 and 8/2, with that of a conventional LNT (labeled BT) under both 24/6 and 84/6 cycles. Significantly, the conventional LNT has zero activity at 150 °C, whereas the alumina-based LNT exhibits greater than 50% conversion efficiency. (The alumina-only is even higher, as shown in figure 2.) Note that the NO_x conversion efficiency of the alumina-based LNT exhibits better efficiency at low temperature (150 °C) with a shorter cycle time (8/2) than with the longer cycle times (24/6, and 16/4). Although not shown, shorter lean/rich cycle times had no effect on the NO_x conversion efficiency of the conventional LNT. The low NOx conversion efficiencies of the alumina-based LNT under 84/6 is very likely due to its low NOx storage capacity, associated with its low alumina loading. Except for 84/6, the alumina-based LNT exhibits better NO_x conversion efficiency than the conventional LNT at temperatures below 200 °C. Clearly, however, lean-burn applications such as gasoline and medium- or heavy-duty diesel, which operate above 200 °C, would require the conventional LNT in place of, or in combination with, the alumina-based LNT.

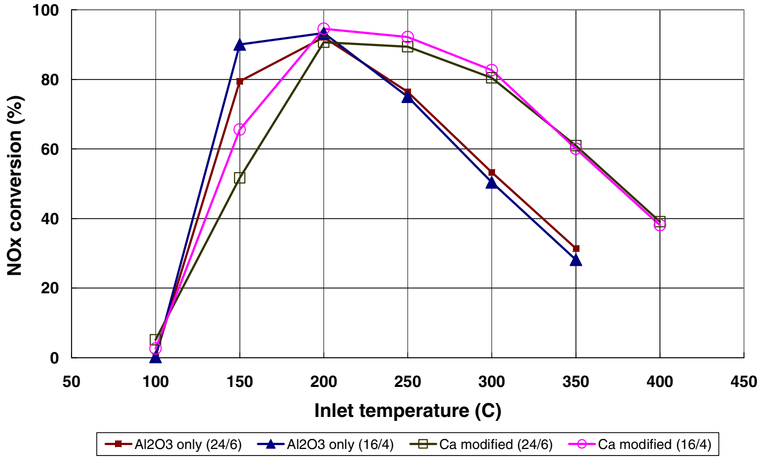

Figure 2. The NO_x conversion efficiency of the alumina-only LNT compared with that of an alumina-based LNT (containing about 2 wt% calcia, relative to the alumina) under lean/rich cycles of 24/6 and 16/4.

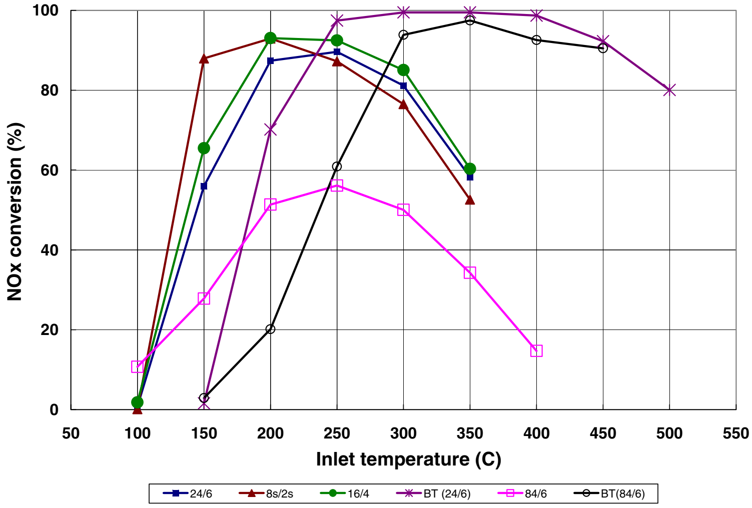

Figure 3. The NO_x conversion efficiency of an alumina-based LNT (containing about 2 wt% calcia, relative to the alumina) under varying lean/rich cycle times, such as 84/6, 24/6 16/4 and 8/2, compared with that of a conventional LNT under a 24/6 cycle.

In separate experiments, the N_2O formation of the alumina-based LNT was also measured over a wide temperature range by FTIR. Only small amounts of N_2O were formed during NO_x reduction at low temperature (<200 °C): the peak of N_2O formation was at about 150 °C, and about 15% of NO_x reduced was converted to N_2O (i.e., the N_2O concentration in the outlet was about 8% of NO_x in the feedgas). This is better than in the conventional LNT, which converts about 25% of the NO_x to N_2O at the same temperature.

The de-SO_x process of the alumina-only LNT was found to be very interesting. In particular, a sulfur-poisoned alumina-only LNT can be de-SOxed very quickly (1–2 min) at temperatures of 500–650 °C under only slightly rich conditions ($\lambda = 0.98$–0.99). As mentioned above, the poisoning was accomplished by exposing the LNT to 30 ppm SO_2 (at a space velocity of 30k/hr) at 200–450 °C with $\lambda = 2.0$ for 3200 s. (The sulfur loading was about 1.14 g/L of catalyst.) The de-SO_x treatment was then performed at 650 °C under slightly rich conditions ($\lambda = 0.987$). Figure 4 shows the gas composition measured after the catalyst during this de-SO_x treatment. Desulfurization started at $t = 5500$ s, and more than 95 wt% of the sulfur was released in about 60 s as SO_2.

Similarly efficient desulfurization was also found for the alumina-based LNT, modified by the addition of less than 3 wt% of alkaline-earth metal oxide. After 20 cycles of loading sulfur and de-SO_x in this manner, the alumina-based LNT was crushed and prepared for XRF analysis. The XRF results showed only little sulfur left in the catalyst, which indicated that sulfur was thoroughly cleaned out of the LNT during each de-SO_x process.

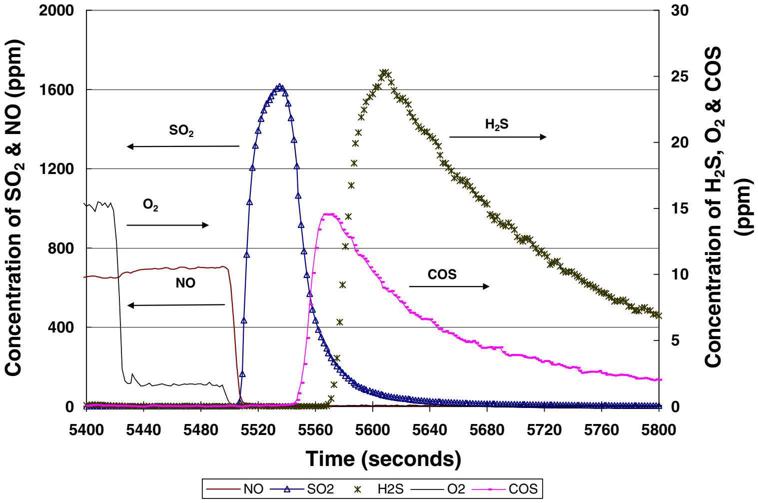

Figure 4. The gas composition measured after the alumina-only LNT during the de-SO_x treatment at 650 °C under slightly rich conditions ($\lambda = 0.987$).

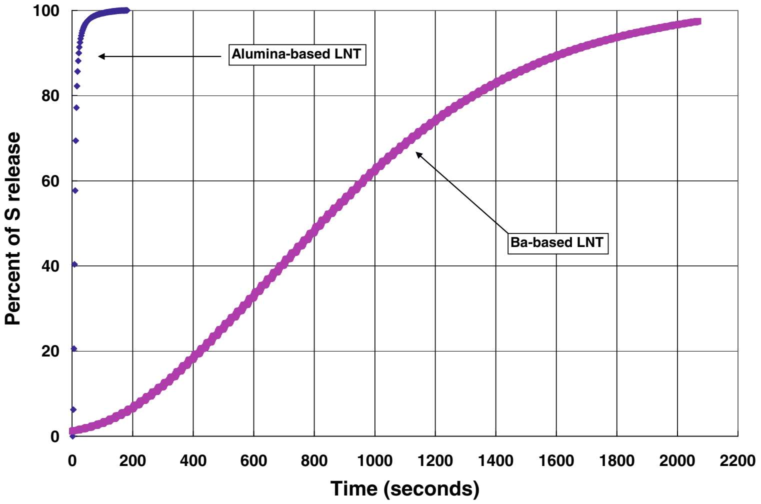

Figure 5. The comparison of the de-SO_x performances of an alumina-based LNT and a conventional LNT with similar sulfur loadings (1.14 g/L). The conventional LNT was heated from 650 to 850 °C at 5 °C/min. with a 5s/15s lean/rich cycle (λ of 2.0/0.9) and the de-SO_x of alumina-based LNT was performed at 650 °C under slightly rich conditions ($\lambda = 0.987$).

Figure 5 compares the de-SO_x performance of the alumina-based LNT with a conventional LNT for similar sulfur loadings (1.14 g/L). The conventional (Ba-based) LNT was heated from 650 to 850 °C at 5 °C/min. with a 5s/15s lean/rich cycle (λ of 2.0/0.9) and the de-SOx of alumina-based LNT was performed at 650 °C under slightly rich conditions ($\lambda = 0.987$). It is clear that desulfurization of the alumina-based LNT is much more efficient (95 wt% S released in about 60 s) than that of the conventional LNT (95 wt% S release in more than 20 min). The alumina-based LNT thus provides significant advantages in terms of both minimum thermal exposure and fuel penalty during desulfurization over the conventional LNT. In fact, the desulfurization process of the alumina-based LNT causes almost no deactivation. Moreover, the main S-containing product from the alumina-based LNT during its de-SO_x process is SO_2, whereas that from the conventional LNT during its de-SO_x process is mainly H_2S, which has an objectionable smell.

The NO_x conversion efficiency of the alumina-based LNT was quite stable after one sulfur loading and de-SO_x at 650 °C, and it remained almost unchanged after about 40 h at 650 °C lean conditions and 20 de-SO_x cycles. (Thus, one cycle of loading with sulfur and de-SO_x was actually used as a de-greening process, applied prior to obtaining the data shown in figures 2 and 3.)

4. Summary

The alumina-only LNT was found to provide higher NO_x conversion efficiency at low temperature (150 °C) than the conventional (baria-based) LNT, and it also was found to undergo desulfurization much more efficiently, with production of relatively little H_2S and COS. These features are most likely a consequence of the fact that alumina has a lower basicity than baria. Although not tested, other less basic oxides might also be expected to perform similarly.

The relatively narrow temperature window of operation of the alumina-only LNT can be extended slightly by addition of small amounts of alkaline-earth metal oxides (at an order-of-magnitude lower loading than in the conventional baria-based LNT) without degrading the characteristics of the alumina-only LNT by very much, but an alternative solution would be to simply combine multiple alumina-only LNTs in series along an exhaust system, taking advantage of the natural gradient in temperature.

The alumina-based LNT thus appears to be well matched to low-temperature lean-burn-engine applications, like the light-duty diesel vehicle, and hopefully it will prove to be useful in practice.

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References

[1] W. Bogner, M. Kramer, B. Krutzsch, S. Pischinger, D. Voigtlander, G. Wenninger, F. Wirbeleit, M.S. Brogan, R.J. Brisley and D.E. Webster, Appl. Catal. B: Environ. 7 (1995) 153.
[2] N. Takahashi, H. Shinjoh, T. Iijima, T. Suziki, K. Yamazaki, K. Yokota, H. Suzuki, N. Niyoshi, S. Matsumoto, S. Tanizawa, S. Tanaka, T. Tateishi and K. Kashara, Catal. Today 27 (1996) 63.
[3] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier and J.E. Parks, Catal. Rev. Sci. Eng. 46 (2004) 163.
[4] D. Tomazic, M.M. Tatur and M.J. Thornton, SAE 2004-01-0581.

[5] K. Nakatani, S. Hirota, S. Takeshima, K. Itoh and T. Tanaka, SAE 2002-01-0957.
[6] G.W. Graham, H.-W. Jen, W. Chun, H.P. Sun, X.Q. Pan and R.W. McCabe, Catal. Lett. 93 (2004) 29.
[7] G.W. Graham, H.-W. Jen, R. Theis J. and R.W. McCabe, Catal. Lett. 93 (2004) 3.
[8] L. Castoldi, I. Nova, L. Lietti and P. Forzatti, Catal. Today 96 (2004) 43.
[9] T. Szailer, J.H. Kwak, D.H. Kim, J. Szanyi, C. Wang and C.H.F. Peden, Catal. Today 114 (2006) 86.