Leaching of Ba^{2+} in NO_x traps

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It has been found that crystalline $BaCO_3$ replaces crystalline $BaAl_2O_4$ in prototypical NO_x traps upon exposure to liquid water. This phenomenon can be understood in terms of acid–base chemistry, where Ba^{2+} is leached from the aluminate, precipitating as a carbonate, under the influence of weak carbonic acid naturally present due to the equilibrium between CO_2 in the air and the water. Consequences of such a redistribution of Ba^{2+} in a NO_x trap could include a decrease in surface area of the trapping material and a loss of contact between the trapping material and the catalytic components, such as Pt. Indeed, preliminary testing has shown that exposure of fully formulated NO_x traps to liquid water results in the loss of approximately half of the initial trapping capacity.

KEY WORDS: NO_x trap; automotive-exhaust catalyst; barium carbonate; barium aluminate.

1. Introduction

The NO_x trap, introduced several years ago by Toyota [1], is generally regarded as one of the leading technologies for the control of NO emissions from vehicles powered by lean-operating gasoline and diesel engines. The prototypical trap, comprised of Pt supported together with BaO on high-surface-area Al_2O_3, works on a lean-rich cycle. According to the simplified version of operation, incoming NO becomes oxidized and reacts with BaO to form $Ba(NO_3)_2$ during the lean portion of the cycle, and the nitrate subsequently undergoes reduction to form N_2 during the rich portion. In reality, the trapping medium is $BaCO_3$, thermodynamically favored over BaO under realistic conditions, but still less stable than $Ba(NO_3)_2$.

Although NO_x traps are in limited use, obstacles to widespread application remain. One is the problem of sulfur poisoning, where SO_2 from the combustion of fuel sulfur follows a parallel reaction path under lean conditions, producing $BaSO_4$, effectively blocking the trapping of NO_x since reduction of the sulfate requires higher temperatures than the nitrate [2]. Another is the problem of Pt particle coarsening, which decreases the rate of the catalytic steps, such as NO oxidation (G.W. Graham *et al.*, submitted for publication). Yet another is the problem of the loss of trapping capacity that has generally been associated with loss of BaO (or $BaCO_3$) surface area. Of these three problems, the last is possibly the least understood and thus the most resistant, so far, to mitigation.

In this study, we present observations that suggest a mechanism for the loss of trapping capacity, thereby leading to a conceptual framework within which improvements may be sought. It is perhaps significant that the mechanism is non-thermal in nature, whereas the aforementioned problems have been studied almost exclusively from the standpoint of thermal durability and temperature management in NO_x traps.

2. Experimental procedures and observations

Two model NO_x traps and a related commercial material, together with two fully formulated traps, were examined in this study. The model traps were made with γ-Al_2O_3 from Alfa-Aesar and W.R. Grace (MI-307), using an aqueous solution of $Ba(NO_3)_2$ to impregnate the aluminas (with excess solution removed in a rotary evaporator) to a level equivalent to the composition $BaO \cdot 6Al_2O_3$. The materials were then calcined at 750 °C before impregnation with Pt (2 wt%), by the incipient wetness method, from an aqueous solution of H_2PtCl_6. The model traps were finally calcined at 350 °C and reduced at 500 °C in a N_2 stream containing 1% H_2 and 10% H_2O. In the course of their characterization (which is the subject of G.W. Graham *et al.*, submitted for publication), it was noticed that strong, sharp peaks, arising from $BaAl_2O_4$, in the powder X-ray diffraction (XRD) patterns taken from both materials before impregnation with Pt were not present after the reduction step. Further investigation revealed that crystalline $BaAl_2O_4$, formed during calcination, is transformed into crystalline $BaCO_3$ upon exposure of the materials to liquid water. This process is illustrated by the XRD patterns obtained from the material made with the W.R. Grace alumina (170 m^2/g BET surface area), shown in figure 1. A slower, partial conversion of $BaAl_2O_4$ to $BaCO_3$ was also found to proceed in powders stored under air. Re-formation of the $BaAl_2O_4$, through reaction of $BaCO_3$ and γ-Al_2O_3, was observed above ~600 °C in air. (Similar observations were also made in

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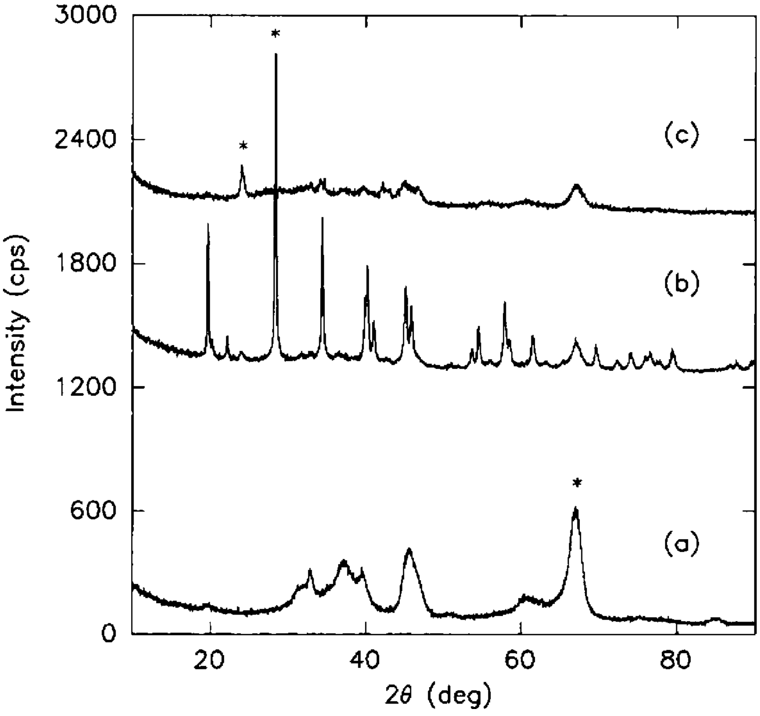

Figure 1. Powder XRD patterns obtained from W.R. Grace alumina (a), the $Ba(NO_3)_2$-impregnated alumina after calcination at 750 °C (b), and the same sample, following exposure to liquid water, after drying (c). The asterisks mark the strongest peak of γ-Al_2O_3, $BaAl_2O_4$, and $BaCO_3$ in each of the patterns, (a), (b), and (c), respectively.

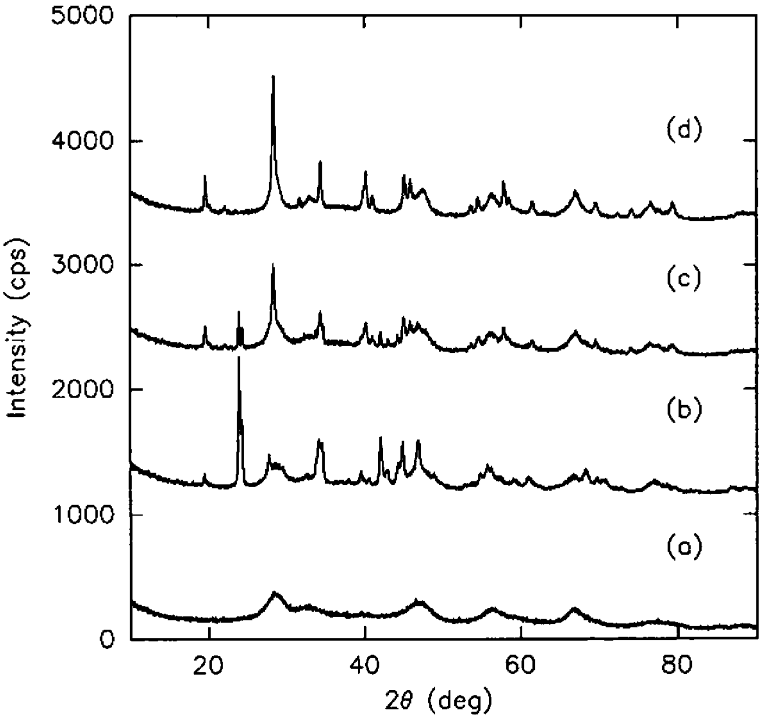

Figure 2. Powder XRD patterns obtained sequentially from ANTech CeO_2-BHA after initial calcination at 750 °C (a), exposure to liquid water, then dried (b), re-calcination at 750 °C (c), and final calcination at 850 °C (d). The sharp peaks in (b) are from $BaCO_3$ whereas those in (d) are from $BaAl_2O_4$.

the case of commercial three-way catalysts containing substantial levels of Ba.)

Formation of $BaCO_3$ upon exposure of the model traps to liquid water probably promotes the

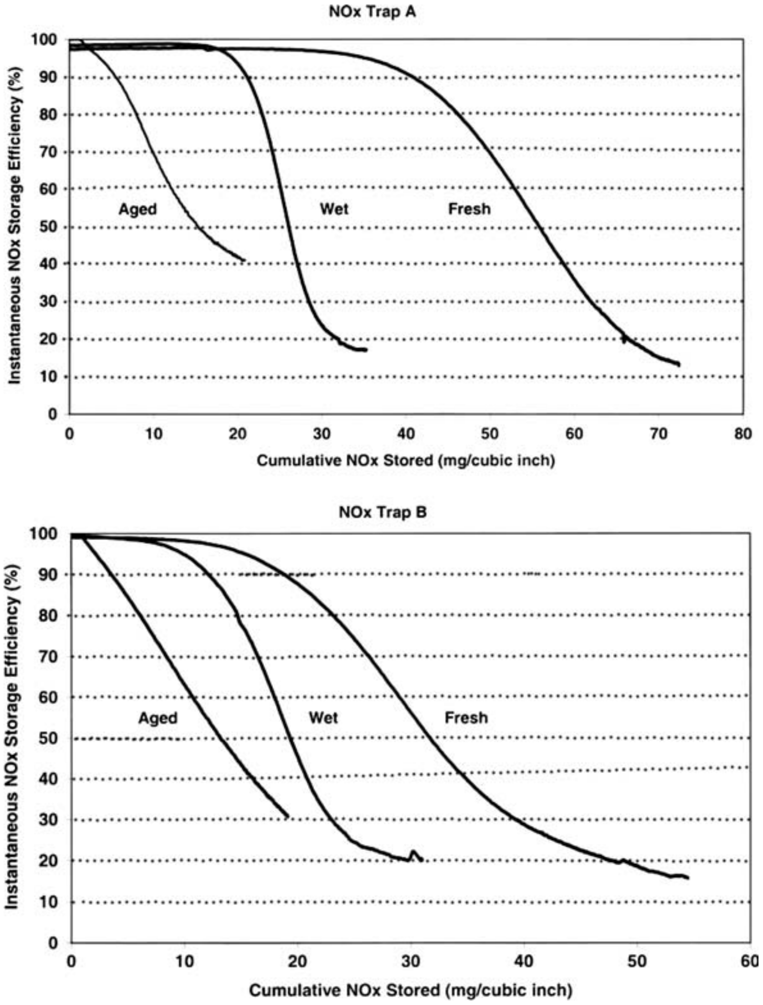

Figure 3. Storage efficiencies of two fully formulated Ba-containing NO_x traps, A and B, obtained following exposure to liquid water (wet). For comparison, the efficiencies following exposure to a representative accelerated aging cycle (aged) are also shown, together with the initial efficiencies (fresh).

concentration of Ba. This is clearly true in the case of the commercial material, ceria-doped barium hexaluminate (CeO_2-BHA), from ANTech. In this high-surface area (220 m^2/g BET) material, Ba^{2+} is apparently well dispersed throughout its alumina host since, unlike the $Ba(NO_3)_2$-impregnated aluminas described above, the powder XRD pattern obtained after calcination at 750 °C (and 850 °C) shows no sign of any crystalline phase (aside from the CeO_2). Upon exposure to liquid water, however, strong $BaCO_3$ diffraction peaks appear, as shown in figure 2. Subsequent calcination leads to formation of highly crystalline $BaAl_2O_4$, a reaction now made possible by the Ba-enriched domains of $BaCO_3$.

To see whether this phenomenon has any effect on NO_x trapping, the performance of two different fully formulated Ba-containing traps was evaluated in a laboratory test of capacity, following well-established procedures [3]. Briefly, samples of the traps were first stabilized by heating at 600 °C in a flowing stream of N_2 containing 10% H_2O, 10% CO_2, 1.2% CO, 0.4% H_2, and 500 ppm NO for 10 min. The samples were then cooled to 400 °C, both CO and H_2 were removed at the same time that 5% O_2 was added to the gas stream, and the NO concentration was monitored until the traps became saturated with NO_x, allowing the instantaneous NO_x storage efficiency to be determined as a function of the cumulative NO_x stored. After purging the stored NO_x, the samples were immersed in water for several hours, allowed to dry, and the test was repeated. As shown in figure 3, both traps lost about 50% of their initial capacity upon exposure to liquid water. Such a loss in capacity is judged to be significant, by comparison to the losses produced through a high-temperature (1000 °C peak) accelerated aging cycle (lasting 50 h), as also shown in figure 3.

3. Discussion

The behavior revealed by the XRD results above is entirely consistent with the well-known characteristics of NO_x traps and can be understood in terms of the same acid–base chemistry: the driving force for reaction between the basic oxide, BaO, and an acidic oxide increases with increasing acidity. Thus, BaO reacts more strongly with oxides of sulfur than oxides of nitrogen, which react more strongly than oxides of carbon, which in turn react more strongly than oxides of aluminum. The reaction in the present case begins with the leaching of Ba^{2+} from the aluminate under the influence of weak carbonic acid, naturally present in water exposed to air, and ends with the precipitation of $BaCO_3$.

Though simple, this particular chemistry has apparently not been considered before in connection with NO_x traps, and its implications have thus not been recognized. The rather significant effect that the exposure to water was found to have on the storage capacity of the fully formulated NO_x traps may, in fact, be attributable to a redistribution of Ba^{2+} caused by leaching and precipitation. This scenario is certainly not remote, since water condensation often occurs in exhaust systems during start-up and shut-down of the engine.

Further consideration of the acid–base chemistry suggests an approach for stabilizing the dispersion of Ba^{2+} in a NO_x trap. By employing as a support material, an oxide more acidic than oxides of carbon but less acidic than oxides of nitrogen, leaching of Ba^{2+} by carbonic acid could be avoided while retaining the necessary ability to trap NO_x. On the other hand, the driving force for reaction between Ba^{2+} directly bound to this support (representing a new trapping medium) and oxides of nitrogen would be smaller than for Ba^{2+} in a carbonate, possibly offsetting any gain in retention of trapping surface area. The investigation of such non-alumina support materials is currently under way in our laboratory.

Acknowledgment

Justin Ura performed the measurements of NO_x trap performance.

References

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