

Impact of Dopants in Ba-based NO_x Storage Reduction (NSR) Catalysts on Sulfation, Desulfation and Performance

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Introduction

Lean-burn engines are being introduced into the US automobile market in order to increase fuel efficiency. A major challenge with these engines is the reduction of NO_x emissions in the lean exhaust. The NO_x storage-reduction (NSR) catalyst is a potential solution to NO_x abatement. It is formulated with a NO_x storage component, usually alkali or alkaline earth metal oxides such as Ba or K, and precious metals, such as Pt, dispersed over a high surface area γ -alumina washcoat. Unfortunately, fuel-borne sulfur is also trapped on the storage component in the form of sulfates, diminishing the storage capacity of the NSR catalyst. The sulfates must be removed through periodic high temperature excursions, which can have detrimental effects on catalyst surface area due to sintering.

The performance of an NSR catalyst is strongly dependent on the relative stabilities of nitrates and sulfates on the catalyst surface. This effort studies the effects of introducing La, Ca, and K dopants into the BaO lattice. The dopants were chosen with a range of properties (see Table 1) to affect the BaO lattice spacing and/or the number of oxygen vacancies. The resulting changes in the storage material should, in turn, impact the stability of stored nitrates and sulfates, as measured by NO_x conversions and desulfation temperatures.

Table 1. Storage material and dopant properties

| | Ba | Ca | K | La |
|---------------------|------|------|------|------|
| Covalent Radius (Å) | 1.98 | 1.74 | 2.03 | 1.69 |
| Valence | +2 | +2 | +1 | +3 |

Materials and Methods

The NSR catalysts were synthesized in a stepwise fashion. The Pt was dispersed on commercial-grade γ -Al₂O₃ using H₂PtCl₆ and the incipient wetness technique to obtain a 1.5%wt loading. Wet impregnation of nitrate salts was then used to add the adsorption phase, with 5%mol of the storage phase being substituted with Ca, K, or La. The specific final catalyst compositions along with BET surface areas are listed in Table 2.

Table 2. Catalyst composition, initial surface area, NO_x conversion and desulfation temperature

| Catalyst | Pt (wt %) | Ba (mol %) | Dopant (mol %) | Surface Area (m ² /g) | Initial NO _x conversion | | | Desulfation T | |
|-----------------------------------|-----------|------------|----------------|----------------------------------|------------------------------------|-------|-------|---------------|-------|
| | | | | | 200°C | 300°C | 400°C | onset | peak |
| Pt/Al ₂ O ₃ | 1.5% | - | - | 133 | - | - | - | - | - |
| Ba-only | 1.1% | 20% | 0% | 77 | 24% | 81% | 75% | 550°C | 700°C |
| Ca+Ba | 1.1% | 19% | 1% | 79 | 37% | 89% | 75% | 500°C | 790°C |
| K+Ba | 1.1% | 19% | 1% | 78 | 5% | 78% | 62% | 590°C | 760°C |
| La+Ba | 1.1% | 19% | 1% | 80 | 29% | 80% | 65% | 565°C | 740°C |

Results and Discussion

The impact of the dopants on NO_x conversion performance is shown in Table 2. The Ca-doped material shows a significant increase in performance at 200 and 300°C, while also maintaining high conversion at 400°C. Conversely, both the K- and La-doped NSR catalysts show moderate decreases in performance at 200 and 400°C while matching the Ba-only performance at 300°C.

Following the performance measurements, the samples are then sulfated to 5.5 mg S/g_{cat} and desulfated to 1000°C. Figure 1 shows the impact of the dopants on the desulfation behavior. The Ba, K+Ba, and La+Ba all show similar desulfation behavior, with moderate differences in desulfation onset and peak release temperatures (see Table 2) indicating that sulfates on the K+Ba and La+Ba are slightly more stable than those on the undoped Ba. The Ca+Ba catalyst, on the other hand, demonstrates a markedly different bimodal desulfation behavior with desulfation onset occurring 50°C before the undoped Ba catalyst. Although the peak release temperature is higher than the Ba-only sample, the significant amount of less stable sulfur released before 550°C is very beneficial to the overall desulfation behavior of an NSR-catalyst.

These results suggest that the electronic manipulation of the storage phase does not have a positive effect on the performance or desulfation characteristics of the NSR catalyst; however, introducing metals with the same valence but different radii can benefit both the NO_x performance and desulfation. Additional experimentation and characterization are performed on the fresh and desulfated NSR catalysts to understand the physical impact of the dopants on the BaO and their durability. Specifically, lattice spacing, surface area, pore size distributions, and elemental analysis are evaluated.

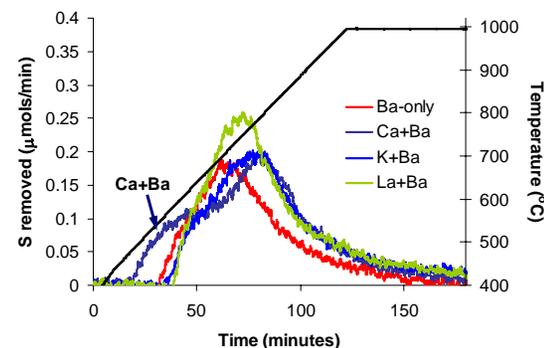


Figure 1. De-sulfation profiles for the series of NSR catalysts. Flow conditions: 40k h⁻¹, 0.7% H₂, 1.2% CO, 5% H₂O, 5% CO₂, in Ar.

Significance

This work demonstrates the impact of adding dopants into the storage phase of an NSR catalyst. The outcome of this research will guide catalyst manufacturers as they consider mixed oxide catalysts for second generation NSR catalysts that will be essential for improving the efficiency and durability of the lean exhaust emissions control system.