



Sulfate storage and stability on representative commercial lean NO_x trap components

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ABSTRACT

Components found in a commercial lean NO_x trap have been studied in order to determine their impact on sulfate storage and release. A micro-reactor and a diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) were used to compare components MgAl₂O₄, Pt/MgAl₂O₄, Pt/Al₂O₃, Pt/Ba/Al₂O₃, Pt/CeO₂–ZrO₂, and Pt/Ba/CeO₂–ZrO₂, as well as physical mixtures of Pt/Al₂O₃ + MgAl₂O₄ and Pt/Ba/CeO₂–ZrO₂ + MgAl₂O₄. Desulfation temperature profiles as well as DRIFTS NO_x and SO_x storage spectra are presented for all components. This systematic approach highlighted the ability of the underlying support to impact sulfate stability, in particular when Ba was supported on ceria–zirconia rather than alumina the desulfation temperature decreased by 60–120 °C. A conceptual model of sulfation progression on the ceria–zirconia support is proposed that explains the high uptake of sulfur and low temperature release when it is employed. It was also determined that the close proximity of platinum is not necessary for much of the sulfation and desulfation chemistry that occurs, as physical mixtures with platinum dispersed on only one phase displayed similar behavior to samples with platinum dispersed on both phases.

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1. Introduction

Growing concern about the consequences of global warming and the obvious economic advantages of higher efficiency engines continue to increase interest in lean-burn automobiles. So far, though, their widespread introduction into the marketplace has been limited by the difficulty of meeting emissions restrictions due to ineffective catalytic reduction of tail-pipe NO_x emissions. Though several possible solutions to this problem are being explored, one option that has been extensively studied is the lean NO_x trap (LNT), also known as a NO_x adsorber or NO_x storage reduction (NSR) catalyst. The details of LNT functionality, i.e. cyclical lean/rich operation, dependence on platinum-group metals (PGM), such as Pt, Pd, and Rh, and dependence on alkali/alkaline earth metals, such as Ca, Ba, K, and Na, has been established and well documented [1,2], and thus the details will not be repeated here.

Because of their ability to achieve high NO_x conversions over a range of temperatures without the need for additional on-board reductants such as urea, LNTs are attractive as NO_x reduction catalysts [3,4]. However, in the presence of sulfur, performance is impacted as NO_x storage sites are blocked by sulfur. This impact can alter both performance and selectivity to N₂ or NH₃. How the

impact is manifested will depend on the components within the complex LNT catalyst and which one is being affected by sulfur. Using a commercial catalyst, Choi et al. [5–7] have shown that sulfation to 3.4 g S/g_{cat} can reduce NO_x conversion by 40% at 325 and 400 °C as well as increase NH₃ yield at the same temperatures. The authors found that sulfur is stored on Ba, Ce, Mg, and Al phases depending on the dose of sulfur introduced. Additionally, Choi et al. [8,9] have found that desulfation results in a complex desulfation profile which cannot be adequately explained with the present knowledge of LNT sulfur storage and release characteristics. In other studies, Rohr et al. [10] sulfated a Pt/Pd/Rh/Ba/CeO₂/Al₂O₃ LNT to 1.3 g S/L_{cat} and found that while Ba was significantly sulfated, Ce and Al₂O₃ did not store sulfur at this level of sulfation. Other studies have shown that sulfur is stored on a variety of LNT components including Ba [5–17], γ-Al₂O₃ [5–24], MgAl₂O₄ [24–30], and Ce–Zr mixed oxides [5–7,31–33]. These studies serve to demonstrate that sulfur may be deposited on all of these components found in LNTs, but it is difficult to extract the individual roles of the components in these mixtures.

From this pertinent literature, it was determined that a deeper understanding of the sulfation and desulfation behavior of common LNT components was necessary. This effort aims to improve the understanding of the role of components that exist in this commercial LNT catalyst, a reference catalyst selected by the CLEERS LNT focus group was the emphasis of this study. This catalyst is known to contain Pt, Pd, Rh, Ba, Ce, Zr, Mg, and Al [7], and it was determined that this catalyst fundamentally differs from the typical model

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Table 1
Component contributions by mass percent.

	Pt	Ba	Al ₂ O ₃	MgAl ₂ O ₄	CeO ₂ -ZrO ₂
MgAl ₂ O ₄	–	–	–	100	–
Pt/MgAl ₂ O ₄	1.0	–	–	99	–
Pt/Al ₂ O ₃	1.5	–	98.5	–	–
Pt/Ba/Al ₂ O ₃	0.8	20	79.2	–	–
Pt/CeO ₂ -ZrO ₂	1.0	–	–	–	99
Pt/Ba/CeO ₂ -ZrO ₂	0.8	20	–	–	79.2

catalysts being studied in several ways. The first key difference is that the Ba storage phase is almost entirely supported on ceria-zirconia rather than γ -Al₂O₃. This Ba/ceria-zirconia phase also contains a significant amount of Pt/Pd, but not Rh. A second key difference is that there is a significant fraction of MgAl₂O₄ in the commercial LNT. This phase generally contains little PGM, but does comprise up to 40 wt% of the washcoat. While there have been some reports as to the potential of MgAl₂O₄ in LNT chemistry [24–30] the role here is examined with and without precious metal in direct contact with the material to ascertain the potential of PGM in neighboring oxides to benefit the oxides with low PGM content. Micro-reactor sulfation experiments were employed in order to quantify the affinity of specific LNT components for SO₂ during typical, cyclic operating conditions. After sulfating, the stability of stored SO₂ was probed with desulfation experiments. A diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) was also used to probe the effect that sulfation and mild desulfations have on the NO_x storage and NO_x stability of the LNT components.

2. Experimental

2.1. Components

The components studied fit into two groups: those prepared by wet impregnation and physical mixtures. A full list of the catalysts prepared as well as their formulations is found in Table 1. Physicochemical properties of the studied catalysts including surface area and SO₂ storage capacity are shown in Table 2. T₂₀ and T₉₀, the temperatures necessary for 20% and 90% removal of stored sulfur, are also shown in Table 2, and will be used later to describe the stability of sulfur on the studied components.

- MgAl₂O₄ (MA) was used directly from the supplier, 99.985% pure from Alfa-Aesar.
- Pt/MgAl₂O₄ (PMA) was prepared by the wet impregnation of hydrogen hexachloroplatinate (IV) onto the MgAl₂O₄ support described above.
- Pt/Al₂O₃ (PA) was prepared by the wet impregnation of hydrogen hexachloroplatinate (IV) onto commercial grade γ -Al₂O₃ provide by EmeraChem, LLC. The sample was then calcined at 500 °C for 2 h.
- Pt/CeO₂-ZrO₂ (PCZ) was prepared by the wet impregnation of Pt (as Pt(NH₃)₄(NO₃)₂) onto CeO₂-ZrO₂ (Rhodia, Ce/Zr = 70/30, surface area = 114 m²/g). The sample was then calcined in air at 550 °C for 2 h.²
- Pt/Ba/Al₂O₃ (PBA) and Pt/Ba/CeO₂-ZrO₂ (PBCZ) were both prepared by the wet impregnation of aqueous barium acetate (Ba(C₂H₃O₂)₂H₂O) onto Pt/Al₂O₃ and Pt/CeO₂-ZrO₂, respectively. The samples were then air dried and calcined at 550 °C overnight.

- Physical mixtures of Pt/Al₂O₃ + MgAl₂O₄ (PA+MA) and Pt/Ba/CeO₂-ZrO₂ + MgAl₂O₄ (PBCZ+MA) were created by mixing equal parts by mass of the two catalysts. The PBCZ+MA catalyst is most representative of the commercial catalyst.

2.2. Instrumentation

The micro-reactor used in this study has previously been described in great detail [33,34]. It consists of lean and rich gas banks controlled by a 4-way valve, a bypass line for flow equilibration and calibration, a mass spectrometer (SRS RGA100), and a sulfur analyzer (API Model 100A UV fluorescence SO₂ analyzer). In addition to the main reactor, an oxidation reactor (oxycat) is used to oxidize H₂S to SO₂ because the sulfur analyzer detects only SO₂, and the mass spec is more sensitive to SO₂ than H₂S. The oxycat used was a Pt/Al₂O₃ catalyst coarsely crushed to minimize pressure drop and maintained at 1000 °C in order to prevent SO₂ adsorption. A constant supply of O₂ (7.5 sccm) was fed directly to the oxycat to maintain an oxidizing environment. A similar setup for monitoring SO₂ has been used by Kylhammar et al. [19] and McLaughlin et al. [35], and their protocol was used to account for SO₂ to SO₃ oxidation.

The DRIFTS apparatus has also been previously described [36]. It consists of a MIDAC M2500 spectrometer coupled to a Harrick barrel ellipse diffuse reflectance attachment and an integrated heated stainless steel reaction cell. The reaction cell is capable of achieving sample temperatures of 550 °C and is operated at a pressure of 500 Torr in order to prevent gas stagnation and maintain a seal between the reaction cell and the hemispherical zinc selenide (ZnSe) dome. Mass flow controllers metered the flows of inlet gases. All spectra are presented in absorbance units, and consist of one hundred scans taken at a resolution of 2 cm⁻¹. The background spectra varied for each experiment and are detailed in Section 3. The gases used in DRIFTS experiments were from Air Liquide® and originated from the same cylinders as those used in micro-reactor experiments.

2.3. Characterization

Sulfation and desulfation experiments were performed in a micro-reactor. Samples were ground into a powder, and 75 mg of each catalyst sample was mixed with an equal amount of quartz wool in order to minimize pressure drop across the catalyst bed. In the case of the physical mixtures, 37.5 mg of each catalyst was mixed together and then added to 75 mg quartz wool. The samples were positioned between two plugs of quartz wool in a U tube reactor. Prior to experiments, the catalysts were pretreated for 8 h at 700 °C while cycling 127 s lean and 17 s rich. Lean gases consisted of NO, O₂, CO₂, H₂O, and Ar bal., while rich gases were made up of H₂, CO, CO₂, H₂O, and Ar bal. Specific gas compositions used for pretreatment, sulfation, and desulfation experiments are shown in Table 3.

A total flow rate of 120 sccm (GHSV ~ 30,000 h⁻¹) was used, and SO₂ was introduced at 30 ppm during sulfation experiments. Gas bottles used for experiments were from Air Liquide®, and had the following purities: Ar (99.999%), 10% H₂ (99.999%) in Ar (99.999%), 10% CO (99.97%) in Ar (99.999%), 1% NO (99%) in Ar (99.999%), O₂ (99.9995%), CO₂ (99.997%), and 1000 ppm SO₂ (99.9%) in Ar (99.999%). CO₂, O₂, and H₂O traps removed impurities from Ar lines, and mass flow controllers were used for gas metering.

Three sulfation and desulfation experiments were performed on each catalyst to achieve an equilibrated sulfur state. Sulfation experiments were performed at 400 °C while cycling 127 s lean and 17 s rich. SO₂ was fed at 30 ppm and for long enough to achieve an estimated loading of 5.5 mg S/g_{cat}; actual loading is typically less than this due to sulfur slip. After each sulfation, all weakly bound

² Sample prepared by Yaying Ji at the Center for Applied Energy Research in Lexington, Kentucky.

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