Sulfation and Desulfation Studies of Model Lean NO_x Traps

Todd J. Toops* and Josh Pihl
Fuels, Engines and Emissions Research Center, Oak Ridge National Laboratory,
2360 Cherahala Blvd., Knoxville, TN 37923 (USA)
**Corresponding author:* toopstj@ornl.gov

Introduction

Diesel powered vehicles will require catalytic systems to meet stringent emissions regulations beginning in 2010. A possible candidate for mitigating the NO_x portion of diesel emissions is the Lean NOx Trap (LNT). With careful engine control the LNT is able to meet the stringent regulations requirements; however, over the lifetime of the vehicle, fuel-borne sulfur and its high temperature removal currently limit LNT implementation. Understanding how sulfur impacts performance and how its impact depends on temperature will be critical to developing engine control strategies that minimize the fuel penalty associated with LNT regeneration and desulfation.

Materials and Methods

A powder-based microreactor equipped with a quadrupole mass spectrometer was used to evaluate reactivity of both Ba- and K-based model LNTs (20%BaO/1%Pt/Al_2O_3 and 8% K_2CO_3/1% Pt/Al_2O_3) while incrementally introducing 15 ppm of SO_2 during both the lean and rich phases. Sulfation and NO_x reduction efficiency were performed at 200, 300, and 400°C while operating at a space velocity of 30,000 h^{-1}. The cycling conditions are listed in Table 1. Following sulfation a temperature programmed reduction (TPR) was performed up to 800°C, and H_2S and SO_2 were measured with mass spectrometry. To complement the microreactor experiments and evaluate sulfur's impact on surface chemistry, an *in-situ* Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) reactor was also employed. This reactor was operated under similar sulfation and evaluation conditions, but desulfation was not possible due to reactor limitations.

Table 1. Reactor conditions used to evaluate both Ba- and K-based LNTs.

	Time (s)	NO (ppm)	O_2	CO (ppm)	H_2 (ppm)	CO_2	H_2O
Lean	390	300	10%	-	-	5%	5%
Rich	60	-	-	5625	3375	5%	5%

Results and Discussion

Our microreactor experiments have demonstrated that there is a period at the beginning of sulfation where the NO_x reduction efficiency is relatively unaffected, followed by a decrease in activity as shown in Figure 1. During the first four hours of SO_2 exposure, the NO_x conversion efficiency remains fairly constant at all three temperatures. This suggests that the sulfur initially blocks sites that are not critical to regeneration. As sulfation proceeds past this initial four hour period, NOx conversion decreases in a nearly linear fashion as the active storage sites and rate of NO reduction are both diminished. The general rate of deactivation increases with increasing temperature. Also evident in this study is the impact of sulfur on the characteristic NO_x profile during lean-rich cycling. During the first hours of sulfation, the characteristic NO_x puff that is evident upon switching from lean to rich diminishes significantly.

SO_2 and H_2S measurements during TPR desulfation experiments showed more sulfur was stored at 300°C compared to 200 or 400°C. The peak of maximum release, 780°C, did not vary significantly with respect to sulfation temperature. Low levels of sulfation (~3h), resulted in desulfation products primarily associated with highly stable sites; however, extended sulfation exposures demonstrated desulfation products at lower temperatures, ~500 and 700°C. This observation suggests that sulfates will preferentially block the most stable storage sites.

DRIFTS analysis detected three distinct sulfate forms on both Ba- and K-based LNTs (listed in order of increasing stability): ionic sulfate, monodentate sulfate and bidentate sulfate. The relative intensity of these peaks changed while switching from lean to rich, and upon mild reduction up to 500°C, the less stable forms would diminish in intensity while the more stable bidentate form would increase. This transformation of sulfur forms demonstrates the mobility of sulfur on LNTs, and suggests under the right conditions it may be possible to remove them before they transform to the "permanent" bidentate sulfate. Quantified DRIFT spectroscopy was employed on the K-based LNT to measure the impact of SO_2 on overall nitrate storage sites and active storage sites during lean rich cycling. It was determined that for the same sulfation time, SO_2 affects more storage sites at 300°C (210 μmols/g_{cat}) than at either 200 or 400°C (170 or 190 μmols/g_{cat} respectively). This temperature dependence for identical sulfation times illustrates that sulfur trapping efficiency changes with exposure temperature. The trend is similar to the one noted in the microreactor desulfation experiments where the maximum sulfur released during TPR experiments occurred after sulfating at 300°C.

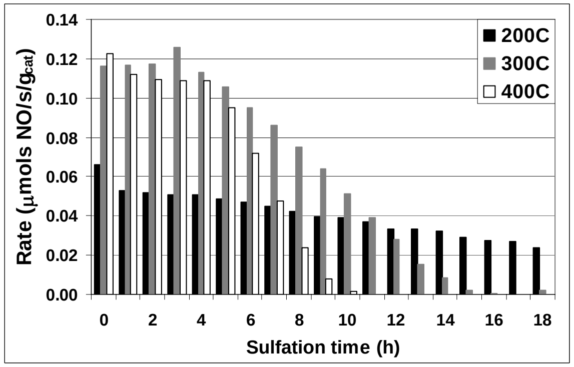

Figure 1. Impact of 15 ppm SO_2 on the cycle average NO_x reduction rate at 200, 300, and 400°C. Rate measured over the course of one complete lean to rich cycle.

Significance

The findings in this study can aid catalyst manufacturers' understanding of the mechanism of sulfate formation and help to determine desulfation frequency and consequently LNT lifetime.