

## BEAMLINES

X7B, X19A

## PUBLICATION

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## FOR MORE INFORMATION

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## Sulfur K-Edge XANES and TR-XRD Studies of Pt-BaO/Al<sub>2</sub>O<sub>3</sub> Lean NO<sub>x</sub> Trap Catalysts: Effects of Barium Loading on Desulfation

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*Sulfur K-edge X-ray absorption near-edge spectroscopy (XANES) and in situ time-resolved X-ray diffraction (TR-XRD) are used to show that the removal of sulfur (in the form of BaSO<sub>4</sub>) from Pt-BaO(x)/Al<sub>2</sub>O<sub>3</sub> (x = wt% BaO) catalysts is strongly dependant on barium loading. Sulfated Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub>, consisting predominantly of monolayer BaO/BaCO<sub>3</sub> species, displays more facile desulfation by H<sub>2</sub> at lower temperatures than sulfated Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub>, a material containing primarily particulate BaO/BaCO<sub>3</sub> species. This suggests that the initial morphology differences between the two samples play a crucial role in determining the extent of desulfation and the temperature at which it occurs, a result that may be important in developing more sulfur resistant LNT catalyst systems.*

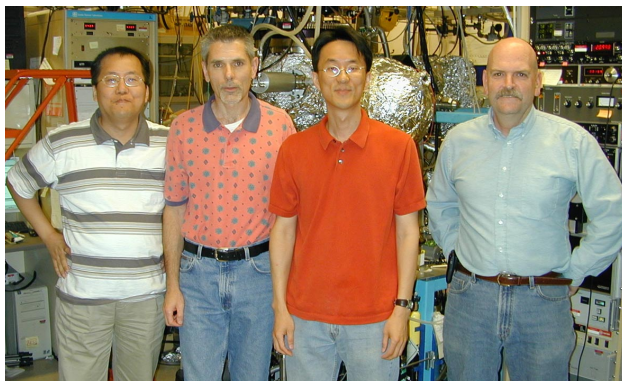
Internal combustion engines operating under lean-burn conditions, such as diesel engines, exhibit high fuel efficiency. Removal of harmful NO<sub>x</sub> emissions from the exhaust in the presence of excess oxygen, however, presents a great challenge to the catalysis community because traditional three-way catalysts are ineffective under these conditions. Among the approaches being considered, urea and hydrocarbon selective catalytic reduction (SCR), and lean-NO<sub>x</sub> traps (LNTs, aka NO<sub>x</sub> storage/reduction (NSR) catalysts or NO<sub>x</sub> adsorbers) are promising technologies. In the LNT technology, an active oxide (alkali and/or alkaline earth) material takes up NO<sub>x</sub> under lean engine operation conditions and stores them as nitrates. In a brief rich cycle, these nitrates are released from the active oxide catalyst component, and reduced to N<sub>2</sub> on the precious metal component of the catalyst.

Because even low concentrations of SO<sub>2</sub> in the emission gradually reduces the ability of the active phase to store NO<sub>x</sub>, the

resistance of the material to SO<sub>2</sub> poisoning remains a critical issue. Meanwhile, since we have shown that NO<sub>x</sub> adsorption/desorption chemistry is strongly dependent on the loading of barium, an important question concerns the variation of the desulfation chemistry as a function of barium content in the LNT formulation. As such, we performed a multi-spectroscopy study to understand desulfation processes on Pt-BaO/Al<sub>2</sub>O<sub>3</sub> LNT materials with varying barium loadings. In particular, we investigated the desulfation behavior of pre-sulfated Pt-BaO(8 or 20 wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts using H<sub>2</sub> temperature pro-

grammed reaction (TPRx). These two BaO loadings were chosen because we have previously shown that the Ba-phase morphologies are significantly different; notably, BaO consists of a monolayer 'coating' on the alumina surface in Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub>, while this monolayer phase coexists with a 'particulate' or bulk-like BaO phase in the Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub> sample. Thus, we also followed the changes in catalyst morphology and sulfur oxidation states during desulfation processes using synchrotron time resolved x-ray diffraction (TR-XRD) and sulfur K-edge x-ray absorption near-edge spectroscopy (XANES), which were performed on the X7B and X19A beamlines at NSLS, respectively.

**Figure 1** shows the H<sub>2</sub> TPRx spectra of sulfated Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub> and Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub> samples, obtained by ramping the temperature of these samples in a H<sub>2</sub>/He flow while continually monitoring the product gases with a mass spectrometer. H<sub>2</sub>S is the primary product of the reaction between H<sub>2</sub> and



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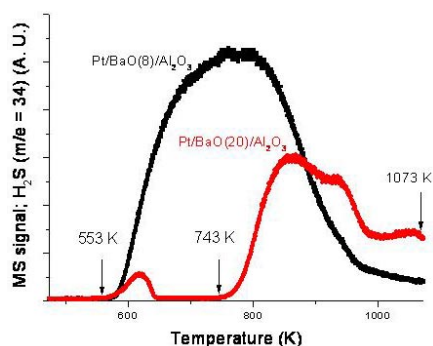
sulfur species on the sample.  $\text{H}_2\text{S}$  is formed at higher temperature for the sample with higher barium loading, implying that the type of barium sulfate species formed upon uptake of  $\text{SO}_2$  is different depending on the loading of barium species – surface or ‘monolayer’ sulfates for Pt-BaO(8)/ $\text{Al}_2\text{O}_3$ , and ‘bulk’  $\text{BaSO}_4$  for the Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample. In addition, the amount of  $\text{H}_2\text{S}$  produced over Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  is two times larger than that of the sample with higher barium loadings, which suggests a more facile desulfation of ‘monolayer’  $\text{BaSO}_4$ .

Sulfur K-edge XANES experiments were carried out to investigate changes in the oxidation states of sulfur as a function of  $\text{H}_2$  reduction temperature. We collected samples after  $\text{H}_2$  TPRx up to 553 K, 743 K, 1073 K

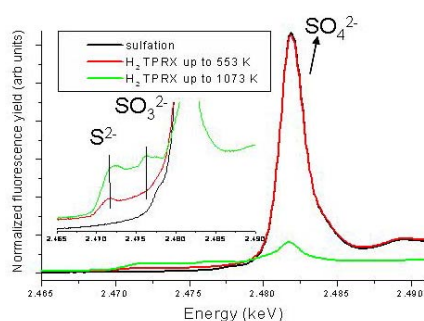
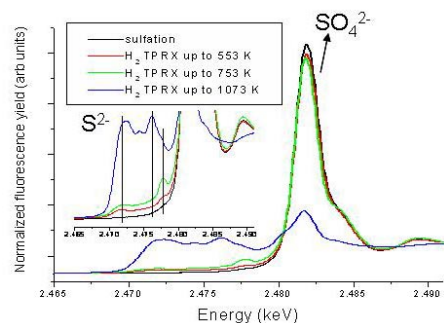
and 1073 K (see arrows in **Figure 1**). After  $\text{H}_2$  TPRx up to 553 K for the sulfated Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  sample, the spectrum in **Figure 2(a)** contains a small peak at 2472 eV, which can be assigned to a sulfide-like ( $\text{S}^{2-}$ ) species, while the main sulfate ( $\text{SO}_4^{2-}$ ) peak is unchanged. After  $\text{H}_2$  TPRx up to 1073 K, the sulfate peaks nearly disappears, while there is an increase in features from lower oxidation state sulfur species (sulfide-like and sulfite-like ( $\text{SO}_3^{2-}$ )). The sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample shows qualitatively similar behavior as shown in **Figure 2(b)**. However, compared with the sample with lower barium loading, Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  contains a significantly larger amount of residual sulfur species of all types after  $\text{H}_2$  TPRx up to 1073 K, which is consistent with the  $\text{H}_2$

TPRx results.

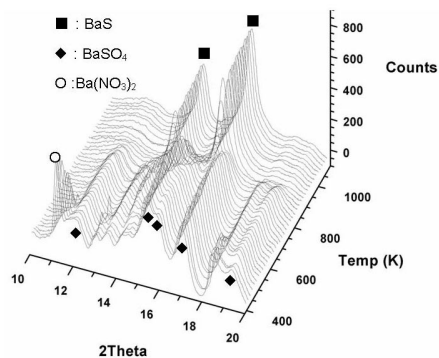
**Figure 3** shows a series of XRD patterns obtained during  $\text{H}_2$  TPRx for the sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample. The room temperature XRD contains peaks assigned to  $\text{BaSO}_4$ . Up to about 773 K, the  $\text{BaSO}_4$  phase is unchanged. However, above 773 K, diffraction peaks associated with BaS appear and continue to grow with increasing temperature, along with a corresponding drop in the intensities of the  $\text{BaSO}_4$  peaks. Compared with the Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample, Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  contains much smaller amounts of BaS, confirming that residual sulfur species were present at much lower concentrations for the lower barium loading sample.



**Figure 1.**  $\text{H}_2$  TPRx spectra for sulfated Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  and Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  samples.



**Figure 2.** Sulfur K-edge XANES spectra of (A) sulfated Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  and (B) sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  samples.



**Figure 3.** TR-XRD patterns collected during  $\text{H}_2$  TPRx from a sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample.