

Barium loading effect on the Desulfation of Pt/BaO/Al₂O₃ Lean NO_x Trap Catalysts: *in situ* Sulfur XANES and TR-XRD study

Do Heui Kim^{1,*}, Ja Hun Kwak¹, János Szanyi¹, Xianqin Wang¹, Jonathan C. Hanson², Charles H.F. Peden¹

¹Institute for Interfacial Catalysis, Pacific Northwest Nat. Lab., Richland, WA 99354 (USA)

²Chemistry Department, Brookhaven Nat. Lab., Upton, NY 11973 (USA)

*do.kim@pnl.gov

Introduction

Internal combustion engines operating under lean-burn conditions, such as diesel engines, exhibit high fuel efficiency. Removal of harmful NO_x gases from their exhaust in the presence of excess oxygen, however, presents a great challenge. Among the approaches for NO_x reduction from internal combustion engines operating under lean-burn conditions, lean-NO_x traps (LNTs, aka NO_x storage/reduction (NSR) catalysts or NO_x adsorbers) are one of the promising technologies. In the LNT technology, an active (alkali and/or alkaline earth) oxide material takes up NO_x under lean engine operation conditions and stores them as nitrates [1]. In a brief rich cycle, these nitrates are released from the active oxide catalyst component, and then reduced to N₂ on the precious metal component of the catalyst. Although continuing research regarding NO_x storage and regeneration steps is providing for a good understanding of LNT performance, the stability of the material against SO₂ poisoning remains a critical issue. We have shown that NO_x adsorption/desorption chemistry is strongly dependent on the loading of barium based on Fourier Transform Infrared Spectroscopy (FTIR) and NO₂ temperature programmed desorption (TPD) [2]. By analogy to this, we have been addressing an important question about how the desulfation chemistry varies as a function of barium content in the LNT formulation by using H₂ temperature programmed reaction (H₂ TPRX), synchrotron time resolved x-ray diffraction (TR-XRD), *in situ* sulfur K-edge x-ray absorption near-edge spectroscopy (XANES), and transmission electron microscopy (TEM).

Materials and Methods

Pt/BaO(x, x = 8, 20 wt%)/Al₂O₃ samples were prepared by using conventional impregnation methods. The as-calcined samples were pre-sulfated by exposing them to a gas mixture of SO₂ and O₂. H₂ TPRX was carried out to investigate the desulfation behavior with temperature. TR-XRD and *in situ* sulfur XANES experiments, using procedures that simulate H₂ TPRX conditions, were performed under H₂ flowing conditions while ramping the temperature up to 800°C to give information about phase changes and sulfur oxidation state, respectively.

Results and Discussion

From the H₂ TPRX experiments for sulfated Pt-BaO(8)/Al₂O₃ and Pt-BaO(20)/Al₂O₃, it was found that H₂S is formed at higher temperature for the sample with higher barium loading, implying that the type of barium sulfate species formed upon the uptake of SO₂ is different depending on the loading of barium species (surface or bulk), resulting in markedly different desulfation behavior. In addition, the amount of H₂S produced over

Pt-BaO(8)/Al₂O₃ is two times larger than that of the sample with higher barium loading, indicating a more facile desulfation of the surface barium sulfates.

In situ sulfur K-edge XANES experiments were carried out to investigate changes in the oxidation states of sulfur as a function of H₂ reduction temperature. We collected XANES spectra during H₂ treatment while ramping the sample temperature up to 700°C. As shown in Figure 1(a), the sulfated sample contains a large peak at 2482 eV, which can be assigned to a sulfate (SO₄²⁻) species. As the temperature increases, a sulfide-like (S²⁻) species is formed above 400°C, while the main sulfate (SO₄²⁻) peak decreases significantly, especially after 600°C. However, compared with the sample with higher barium loading, the Pt-BaO(8)/Al₂O₃ catalyst contains a significantly lower amount of residual sulfur species of all types after H₂ TPRX up to 700°C, consistent with the H₂ TPRX results.

Figure 1(b) shows a series of XRD patterns collected during treatment with H₂ of the sulfated Pt-BaO(8)/Al₂O₃ sample. The room temperature XRD pattern contains peaks assigned to BaSO₄. Up to about 500°C, the BaSO₄ phase is unchanged. However, above 550°C, diffraction peaks associated with formation of a BaS phase appear and continue to grow with increasing temperature, along with a corresponding drop in the intensities of BaSO₄ peaks. Compared with the Pt-BaO(20)/Al₂O₃ sample (results not shown), the Pt-BaO(8)/Al₂O₃ catalyst contains a much smaller amount of BaS, leading to the conclusion that residual sulfur species were present at much lower concentrations for the lower barium loading sample after desulfation with H₂ based on the combination of characterization results.

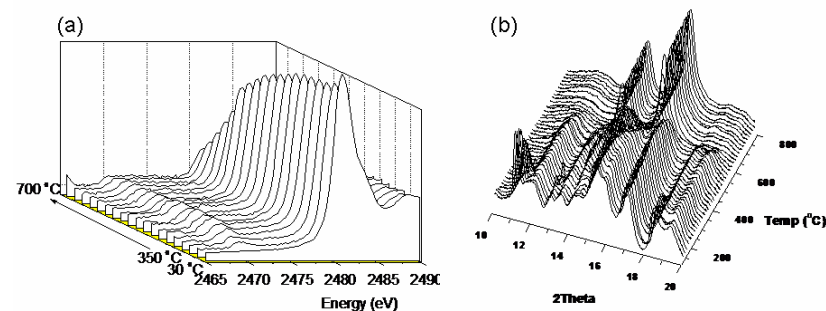


Figure 1. *In situ* Sulfur K-edge XANES spectra (a) and TR-XRD patterns (b) collected during desulfation with H₂ for sulfated Pt-BaO(8)/Al₂O₃ with increasing temperature.

Significance

Understanding of the desulfation behavior is expected to provide important information for the development of more sulfur resistant LNT catalyst systems.

References

1. Epling, W.S., Campbell, L.E., Yezerets, A., Currier, N.W., Parks II, J.E., *Cat. Rev.-Sci. Eng.* **2004**, *46*, 163.
2. Szanyi, J., Kwak, J.H., Kim, D.H., Burton, S.D., Peden, C.H.F. *J. Phys. Chem. B* **2005**, *109*, 27.