

Characteristics of Pt-BaO/CeO₂ lean NO_x trap catalysts: the role of the CeO₂ support in the desulfation process

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Introduction

Removal of harmful NO_x emissions from lean burn and diesel engines in the presence of excess oxygen presents a great challenge. Lean-NO_x traps (LNTs, aka NO_x storage/reduction (NSR) catalysts or NO_x adsorbers) are one of the promising technologies to remove NO_x effectively. 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], which are released from the active oxide catalyst component, and then reduced to N₂ on the precious metal component of the catalyst during a rich cycle. However, the stability of LNT materials against SO₂ poisoning remains a critical issue.

In a previous publication [2], our group reported the superior intrinsic NO_x uptake of Pt-BaO/CeO₂ sample over Pt-BaO/Al₂O₃ over typical operating temperature ranges. In addition, the ceria-supported sample showed significantly improved sulfur resistance than the latter. From a practical point of view for ceria supported samples, however, a question arises about its desulfation behavior compared with the alumina-supported sample reported previously [3]. In this contribution, we explore the characteristics of Pt-BaO/CeO₂ sample by focusing on the role of ceria in the desulfation, compared with that for the similarly prepared alumina supported one. For this purpose, we used temperature programmed reaction (H₂ TPRX), synchrotron time resolved x-ray diffraction (TR-XRD) and *in situ* sulfur K-edge x-ray absorption near-edge spectroscopy (XANES) techniques.

Materials and Methods

Pt/BaO(10 wt%)/CeO₂ and Pt-BaO(20wt%)/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 while ramping the temperature up to 1073 K to give information about phase changes, and the amount and chemical nature of residual sulfur, respectively.

Results and Discussion

From the H₂ TPRX experiments for sulfated Pt-BaO(20)/Al₂O₃ and Pt-BaO(10)/CeO₂, we find that the CeO₂-supported one hardly removes the sulfur species from the catalyst during the reductive treatment with hydrogen up to 1073 K, compared with alumina-supported one. Considering that the amounts of initial sulfur species on these two samples are nearly identical, it is quite evident that these two sulfate species have considerably different desulfation behavior depending on the support. In other words, it can be claimed that

the sulfur species deposited on the ceria supported sample are more resistant to removal as H₂S during reaction with hydrogen even up to 1073 K than the alumina-supported one.

Figure 1(a) shows TR-XRD patterns of ceria-supported samples during treatment up to 1073 K. The peak intensity of a BaS phase in Pt-BaO/CeO₂ is much less than that observed in a Pt-BaO/Al₂O₃ sample (not shown), implying that the tendency to form the large crystallites of BaS is significantly inhibited for the case of ceria-supported sample.

In situ sulfur K-edge XANES experiments were carried out to investigate changes of the residual sulfur species as a function of H₂ reduction temperature. We collected XANES spectra during H₂ treatment while ramping the temperature with the results shown in Figure 1(b). The spectrum taken at room temperature has a single peak at 2482 eV, which can be assigned to primarily sulfate species. As the temperature increases above 573 K, a couple of changes were observed including a gradual decrease in the sulfate peak and the subsequent increase in a broad peak around 2474 eV, which can be assigned to S¹⁺ or S²⁺ species based on previous assignments. These trends become more apparent above 650 K, as evidenced in the drastic decrease in the sulfate peak. Interestingly, the transition temperature where the sulfate peak decreases is much lower than the alumina-supported sample, implying that the ceria support plays a crucial role in reducing the sulfate at lower temperature. However, the reduction of sulfates with increasing temperature does not lead to the desorption of sulfur species from the catalyst, but to their transformation to other sulfur species on the catalyst, thus resulting in little, if any, removal of sulfur species arising from the reductive treatment, which is consistent with the H₂ TPRX results. The role of the ceria support in this desulfation behavior will be discussed based on the characterization results obtained in this study.

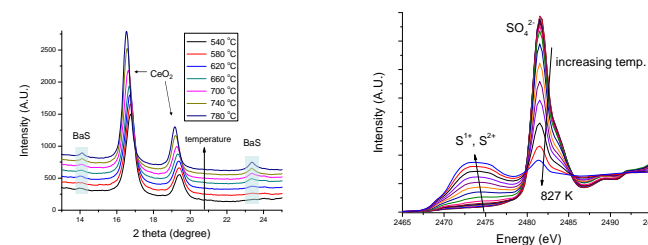


Figure 1. TR-XRD patterns (a) and Sulfur XANES spectra (b) of Pt-BaO/CeO₂ during treatment with H₂ for sulfated Pt-BaO(10)/CeO₂ with increasing temperature.

Significance

Understanding of the desulfation behavior for the ceria-supported LNT catalyst is expected to provide practical information for designing 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. Kwak, J.H., Kim, D.H., Szanyi, J., Peden, C.H.F., *Appl. Catal. B* **2008**, 84, 545.
3. Kim, D.H., Szanyi, J., Kwak, J.H., Szailer T., Hanson, J., Wang, C.M., Peden, C.H.F. *J. Phys. Chem. B* **2006**, 110, 10441.