

Peculiar Changes in Pt Accessibility and Morphology for Pt/BaO-Al₂O₃ Lean NO_x Trap Catalysts with Varying Sulfation Levels

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Introduction

Lean NO_x trap (LNT) catalysts composed of Pt/BaO-Al₂O₃ represent a viable approach to meet the stringent NO_x emission standards being imposed on diesel engines [1]. However, poisoning of LNTs by SO₂ represents a particularly challenging issue for this technology [1]; thus, it is important to develop more sulfur-durable LNT catalysts. As part of such an effort, we have been studying the effects of sulfation and desulfation on Pt accessibility and morphology changes in Pt/BaO-Al₂O₃ model catalysts. In this work, a series of Pt/BaO-Al₂O₃ catalysts with three different sulfation levels (non-sulfated, partially-sulfated, and fully-sulfated) were prepared. Pt accessibility after successive reductions in H₂ at elevated temperatures was measured by an irreversible volumetric H₂ chemisorption method. Moreover, the morphology of the sample after reduction at 800°C was characterized by HRTEM and XRD techniques.

Materials and Methods

Materials preparation. One typical LNT catalyst containing 1.5wt% Pt and 14 wt.% BaO was supplied by Johnson Matthey (Wayne, PA). This sample was calcined at 500°C, then sulfated with SO₂ and O₂ (1:1) at 300°C. We prepared the samples with the different sulfation levels by varying the sulfation process time. In this work, three different sulfation levels, zero sulfation (labeled as 0gS), partial sulfation (3gS) and complete sulfation (10gS), were investigated. Their platinum accessibility and morphology changes were studied as a function of reduction temperatures in order to decouple the thermal degradation from sulfur poisoning.

Characterization methods. Platinum accessibility was evaluated with the number of hydrogen atoms per Pt (H/Pt) determined from irreversible H₂ chemisorption uptake measurements obtained after the sample was first reduced at varying temperatures. The morphologies of both the freshly sulfated samples and the samples after the chemisorption measurements at 800°C were characterized with high resolution TEM (HRTEM). The composition of the particles was analyzed by energy-dispersive X-ray spectroscopy (EDS). In order to understand the desulfation process, sulfur K absorption edge XAFS spectra were collected *in-situ* during the reduction of the catalysts in a flow of a 5% H₂ and 95% He gas mixture (~40 mL/min) at beamline X19A, and Pt L₃-edge EXAFS spectra were collected in air at room temperature at beamline X18B of the NSLS at BNL.

Results and Discussion

H/Pt values determined from H₂ chemisorption experiments is a common way to measure the number of active sites and Pt accessibility for many supported Pt catalysts. Fig. 1 shows the H/Pt values obtained as a function of reduction temperature for the fresh (0gS), partially sulfated (3gS), and heavily sulfated (10gS) samples. We observed that Pt accessibility and

morphology changes have a complex dependence on the levels of sulfation. The H/Pt ratio decreased uniformly as a function of reduction temperature for the non-sulfated sample. Compared to this one, the partially-sulfated sample instead displayed an optimum H/Pt value at 500°C, and then a slight increase in Pt particle sizes after thermal aging at 800°C. Still different behavior was observed for the fully sulfated sample which gave very low H/Pt ratios for all reduction temperatures, indicating essentially complete poisoning by SO₂.

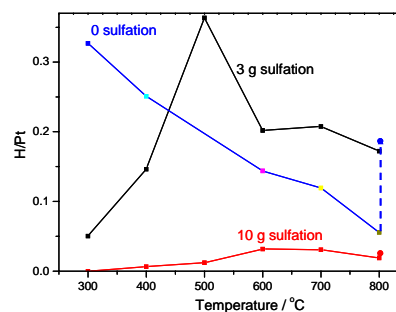


Fig.1. Pt dispersion (H/Pt) as a function of reduction temperature in H₂.

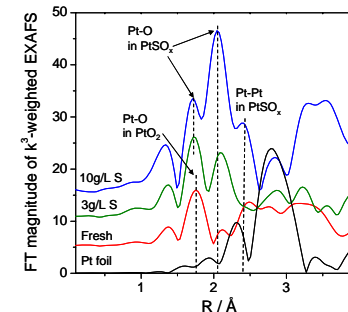


Fig.2. Pt L₃-edge EXAFS spectra for the variously sulfated catalysts and Pt foil.

Fig.2 compares the Fourier transformed Pt L₃-edge EXAFS spectra. The non-sulfated sample (0gS) primarily showed features similar to those of PtO₂ [2], while the fully sulfated sample (10gS) had features matching Pt sulfate clusters [3]. The partially sulfated sample (3gS) seems to have a pattern similar to that of 0gS sample, but the relative intensities of the two main peaks was different. With a simple linear fitting of the spectrum from the 3gS sample using those for the non-sulfated and fully sulfated samples, we estimate that there was around 20% Pt in the Pt sulfate cluster form in this 3gS sample. The EXAFS results were consistent with the initial Pt accessibility measurements in Fig. 1 and provided information regarding the reduction mechanism of the sulfated Pt/BaO/Al₂O₃ LNT catalysts. Over partially sulfated sample, in particular, S spillover from Pt to Ba occurred gradually and H/Pt was a combined effect of PtS(PtSO₄) reduction and Pt sintering. For the fully saturated sample, Pt sintering was facilitated by mobile PtS thereby slowing S spill over to Ba from PtS.

Significance

This work shows that S levels in LNTs have a significant effect on Pt accessibility and morphology, and they can alter the reduction mechanism. The results aid in decoupling the effects of thermal degradation from sulfur poisoning for the deactivation of LNT samples.

References

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