Combined XPS and TPR study of sulfur removal from a Pt/BaO/Al₂O₃ NOₓ storage reduction catalyst


*Zelinsky Institute of Organic Chemistry, Leninsky Pr. 47, Moscow, 119991 Russia
bHaldor Topsoe A/S, P.O. Box 213, Nymollevje 55, Lyngby, DK-2800 Denmark

Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts (1 wt% Pt, 10 wt% BaO) were sulfated under conditions simulating a real NSR catalyst operation. Comparative TPR and XPS studies of sulfur removal from Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts indicate that the sulfur removal from Al₂O₃ surface precedes reductive decomposition of BaSO₄ (250–400 °C). Barium sulfate decomposition started with further increase in desulfation temperature at the point of surface atomic ratio Ba:S = 1 (~450°). Simultaneously, an intensive formation of sulfide species on the catalyst surface was observed. Thermodynamic analysis of the desulfation process allows us to hypothesize that barium sulfide formation may hinder sulfur removal under reducing conditions.

KEY WORDS: NOₓ storage catalysts; sulfur deactivation; Pt; BaO; Al₂O₃; SO₂; BaS, BaSO₄; barium sulfate decomposition.

1. Introduction

A promising strategy in developing catalytic converters for NOₓ removal under oxidizing conditions (e.g. from exhaust gases of lean-burn and diesel engines) is based on NOₓ storage-reduction concept developed in 1990s by Toyota [1]. Typically, NSR systems contain: (i) a high surface area support (e.g. Al₂O₃); (ii) a storage material (alkaline or alkaline earth oxides e.g. BaO) and (iii) a component for NOₓ oxidation/reduction (precious metals, e.g. Pt) [1–3].

Unfortunately, the NOₓ storage component of these converters (alkaline-earth oxide) is highly susceptible with respect to sulfur poisoning by SO₂ in exhaust gases. Therefore, the development of an effective approach for desulfation of poisoned NOₓ trap catalysts is of primary importance for their practical implementation. Fundamental understanding of a surface chemistry of processes occurring upon desulfation of deactivated catalyst is a prerequisite of this development. This research was targeted toward a detailed study of sulfur removal under reducing conditions from the surface of a semi-model Pt/BaO/Al₂O₃ by combination of TPR and XPS techniques.

2. Experimental

2.1. Catalyst preparation

1 wt% Pt/Al₂O₃ and 1 wt%Pt/10 wt% BaO/Al₂O₃ catalysts were prepared by incipient wetness impregnation of γ-Al₂O₃ (180 m²/g) with water solutions containing appropriate amounts of H₂PtCl₆ and Ba(NO₃)₂. Pt and Ba were loaded simultaneously by impregnation with a solution containing both components. The resulting material was dried in ambient air overnight and calcined at 600 °C in air and reduced in an H₂ flow at 400 °C for 1 h. It is noteworthy that the following XPS analysis indicates that Cl content on the catalyst surface is below detecting limits of XPS, suggesting that the most of chloride was removed and it is unlikely to have affected catalytic performance. These data are in a good agreement with the results reported by Yu Su and M. Amiridis [4].

2.2. Catalytic tests

The sulfation was performed under conditions simulating an “on-engine” catalyst performance at 370 °C using alternating feed supply. In order to accelerate catalyst sulfation SO₂ content was increased as compared to real conditions to 150 ppm. During NOₓ storage stage (100 s) the feed gas containing 440 ppm NOₓ, 150 ppm SO₂, 10% CO₂, 4% O₂, 3.2% H₂O, balanced with N₂ was fed on the catalyst. After NOₓ storage stage the catalyst was regenerated for 10 s by a “rich” feed containing 440 ppm NOₓ, 150 ppm SO₂, 2200 ppm C₃H₈, 10 vol% CO₂, and 3.2 vol% H₂O, balanced with N₂. GHSV was maintained at a level of 36 000 h⁻¹ during both stages. Reaction products were analyzed by an ECO PHYSICS CLD 70 S chemiluminescence’s gas analyzer and gas chromatography.

It is noteworthy that the sulfur concentration in the feed gas is significantly higher as compared to real conditions (150 ppm versus ∼2–10 ppm respectively). However, our separate experiments with lower sulfur content (20–100 ppm) indicated that observed deactivation is
proportional to the overall exposure of SO₂. These data are also in a good agreement with the results reported previously by A. Amberntsson et al. [5]. Therefore we assume that the results obtained under conditions of accelerated sulfation are representative for a catalyst sulfated under realistic conditions after exposure to an equal amount of SO₂ (~0.1 g SO₂/g cat).

2.3. Temperature-programmed reduction

Prior the TPR measurements, the catalyst (40 mg) was calcined in situ in 2% O₂/Ar mixture at 400 °C for 30 min and cooled to room temperature. After flushing with argon, the reduction was carried out from room temperature to 800 °C using a 5%H₂/Ar mixture at 5 °C min⁻¹ heating rate. The sample was maintained at 800 °C for 30 min before cooling under argon. Hydrogen consumption was monitored by a thermal conductivity detector (TCD).

2.4. XPS study

X-ray photoelectron spectra of Al 2p, Ti 2p, Ba 3d₅/₂, and S 2p regions were obtained using an XSAM-800 spectrometer (Kratos) with Al Kα₁,₂ radiation for spectra excitation. Binding energies of the peaks were corrected with account of sample charging by referencing to the C 1s peak at 285.0 eV. Ba/Al and S/Al surface atomic ratio was calculated from integral intensities of XPS peaks using Scofield’s photoionization cross-sections for Al Kα₁,₂ excitation [6]. Reductive treatment of the catalysts were performed using a homemade reactor attached to the spectrometer [7] in 5%H₂/Ar flow at atmospheric pressure. The reactor enables the sample treatment in different gases followed by the transfer of the sample into a spectrometer without exposing to air.

3. Results and discussion

3.1. Catalytic data

Variations of NOₓ conversion over three samples studied with time on stream in SO₂-containing feed gas are displayed in figure 1. Parent alumina is not active in NOₓ conversion, while Pt/Al₂O₃ demonstrates an appreciable NOₓ conversion of ~35%. However more detailed analysis of exhaust gases indicated that a selectivity toward N₂ is low (>20%), and the main reaction product is N₂O. It is noteworthy that Pt/Al₂O₃ did not reveal a pronounced deactivation upon exposing to a feed gas containing 150 ppm SO₂. Presumably the catalyst operation upon conditions of lean-rich cycling prevents a formation of Pt sulfide formation observed under fuel rich conditions [8] due to oxidation of sulfide to SO₂ during lean conditions. Unlike Pt/Al₂O₃, the catalyst containing NOₓ storage component demonstrated high NOₓ conversion to N₂ (selectivity >90%) at the beginning of the test and a prompt deactivation during first 2–3 h of the experiment. After 4 h “on-stream” the performance of Pt/BaO/Al₂O₃ resembled the performance of Pt/Al₂O₃: overall NOₓ conversion decreases to ~30%, selectivity to N₂ decreases to ~30%, and a significant amount of N₂O was detected in the reaction products. These results imply that after 3–4 h NOₓ storage component seems to be completely deactivated, while Pt active sites retain their activity.

3.2. TPR data

TPR profiles of the sulfated samples are compared in figure 2. The single peak at ~650 °C observed over sulfated Al₂O₃ can be attributed to a formation of surface aluminum sulfates, which is in a agreement with the data reported previously by Elbouazzaoui et al. [9].

Loading of the parent Al₂O₃ with 1% Pt significantly enhanced sulfur deposition as evidenced by an increase in TPR profile area. On the other hand the main peak of