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Studies on the deactivation of NO_x storage-reduction catalysts by sulfur dioxide

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Abstract

The interaction of sulfur dioxide with a commercial NO_x storage-reduction catalyst (NSR) has been investigated using in situ IR and X-ray absorption spectroscopy. Two pathways of catalyst deactivation by SO_2 were identified. Under lean conditions (exposure to SO_2 and O_2) at 350 °C the storage component forms barium sulfates, which transform from surface to hardly reducible bulk sulfate species. The irreversible blocking of the Ba sites led to a decrease in NO_x storage capacity. Under fuel rich conditions (SO_2/C_3H_6) at 350–500 °C evidence for the formation of sulfides on the oxidation/reduction component (Pt) of the catalyst was found, which blocks the metal surface and thus hinders the further reduction of the sulfides. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lean-burn gasoline and diesel engines offer substantial reductions in fuel consumption and, hence, lead to lower CO_2 emissions when compared to traditional gasoline engines. The crucial difference between these engines and traditional gasoline engines is the high concentration of O_2 ($\lambda > 1$) in the exhaust gas [1], which does not allow the use of conventional three-way catalysts (TWCs) for the removal of NO_x.

A promising strategy in developing catalytic devices to convert NO_x under oxidizing conditions for lean-burn and diesel engines is based on the concept of NO_x storage-reduction (NSR) [2,3]. This concept utilizes a catalyst with dual functionality: (i) a storage function, typically Ba-oxides and (ii) a NO_x reduction/oxidation component, typically Pt. During lean operation conditions (i.e., oxidizing atmosphere) NO is oxidized to NO_2 and stored on the barium component as nitrate. When a switch is made to fuel-rich conditions (i.e., reducing atmosphere) NO_2 is released from the storage component and converted to N_2 over the noble metal component of the catalyst. The major drawback of these catalysts at present is their high susceptibility to sulfur poisoning by competitive sorption of SO_2/SO_3, which lowers the capacity of the catalyst to store and reduce NO_x [4,5].

In the present study the deactivation processes of a commercial NSR catalyst by sulfur components under lean and rich periods was investigated by in situ IR and X-ray absorption spectroscopy. The interaction of SO_x with barium (storage component) and Pt (oxidation/reduction component) was examined in detail regarding the formation and stability/reducibility of the sulfur species formed.

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2. Experimental

The catalyst investigated was a typical NSR material supplied in powdered form by Johnson Matthey, Royston, UK, containing Pt as part of the oxidation/reduction components and BaO/$BaCO_3$ as storage component on Al_2O_3 as support. The reference materials used for X-ray absorption spectroscopy (XAS) experiments were obtained by Aldrich Chemical (BaO 97%; $BaCO_3$ 99.98% and $BaSO_4$ 99%).

The nature of sulfur species was investigated by sorption experiments carried out in an in situ IR-cell, which allows the simultaneous and controlled admission of reaction gases. The catalyst powder was pressed into self-supporting wafers and analyzed in situ during all treatments by transmission IR-spectroscopy (resolution 4 cm^{-1}). The adsorption experiments were carried out at temperatures between 350 and 500 °C. Activated catalysts were investigated using a gas stream (25 ml/min) containing 400 ppm SO_2 in helium, 5% O_2 or 2000 ppm C_3H_6 in helium.

The structural and chemical properties of barium and platinum were investigated by XAS. The materials were activated at 450 °C in He for 60 min. To investigate the sulfur poisoning of barium under lean conditions, the activated catalyst was treated with 400 ppm SO_2 and 5% O_2 at 350 °C in a total gas flow of 100 ml/min for 2 h. XAS spectra were recorded at the Ba-L_{III} edge (5247 eV) in situ before and after the treatment.

To study the oxidation state of platinum, the catalyst was pretreated: (a) under lean (400 ppm SO_2/5% O_2), (b) under rich conditions (400 ppm SO_2/2000 ppm C_3H_6) and (c) cycling lean (100 s) and rich (20 s) conditions at 350 and 500 °C. All samples were pretreated for 5 h under the conditions described. XANES was used to probe the reducibility of Pt on the pretreated catalysts. Spectra were recorded every 50 °C during temperature programmed reduction (TPR) in H_2 with a temperature increment of 10 °C/min up to 450 °C. For analysis of the XANES, the scattering background was subtracted using a second order polynomial function and the position of the edge was calibrated using the spectra of a simultaneously measured Pt foil. The area of the peak above the Pt-L_{III} edge (11 564 eV), which can be related to the oxidation state of the Pt, was integrated numerically. For qualitative comparison of the EXAFS, the oscillations were extracted from the background using a third order polynomial function and after weighting with k^2, Fourier transformed in the range between 2.1 and 8 $Å^{-1}$. The program WINXAS 97 (version 1.3) was used to extract the EXAFS from the measured absorption and to analyze the data.

3. Results

3.1. Interaction of SO_x with the storage component (Ba)

Time resolved in situ IR-spectra during adsorption of 400 ppm SO_2 and 5% O_2 on the catalyst at 350 °C are presented in Fig. 1. In the activated sample a broad absorption band at 1460 cm^{-1} was observed before SO_2 exposure, which is attributed to barium carbonate species [6]. During contact with SO_2 and O_2 this band decreased indicating the progressive removal and partial substitution of the carbonate by sulfates. After 1 min of adsorption two small bands appeared at 1120 and 1060 cm^{-1}, which increased in intensity with exposure time. Bands at 1248, and 1155 cm^{-1} and in the region of 1060–1000 cm^{-1} appeared after 5 min of SO_2/O_2 adsorption. The bands at 1120 and 1060 cm^{-1} are characteristic for the S–O stretching vibrations of bidentate sulfates located on the surface of an alkaline earth metal [7,8], while the bands at 1248 and 1155 cm^{-1} were attributed to bulk barium sulfate species [9]. Additionally bands at 1350 and 1040 cm^{-1} were observed, which correspond to the ν(S=O) vibration and to the ν(S–O) vibration of tri-coordinated sulfate species on the Al_2O_3 support [10]. The IR spectrum remained almost unchanged when the SO_2/O_2 exposure was stopped and the catalyst was treated in He flow only at 350 °C. After exposing the catalyst for 20 min at 350 °C to 2000 ppm C_3H_6 in He (simulate a reducing/rich atmosphere), significant differences in the band intensities were not observed, also confirming the high stability of the sulfates formed on barium.

To investigate the SO_x formation on the material under reducing conditions the fresh catalyst was activated and subsequently exposed to 400 ppm SO_2 and 2000 ppm C_3H_6 in He at 350 °C. The corresponding IR-spectra are shown in Fig. 2. Besides the already described disappearance of the carbonate species (band at 1460 cm^{-1}), no additional bands were observed

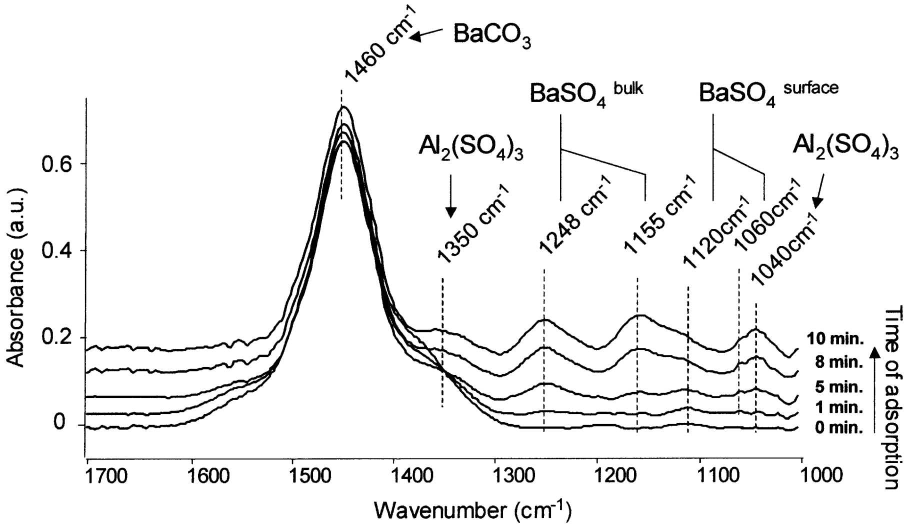

Fig. 1. IR-spectra during adsorption of 400 ppm SO_2 and 5% O_2 at 350 °C for 10 min.

between 1350 and 1000 cm^{-1}, the region characteristic for the formation of sulfate species on the storage function.

The effect of SO_2/O_2 treatment on the local environment of the barium component was studied by in situ XAS of the Ba-L_{III} edge. Fourier transformed oscillations of the catalyst before and after 2 h treatment with 400 ppm SO_2 and 5% O_2 at 350 °C are compared with the reference materials of BaO, $BaCO_3$ and $BaSO_4$ in Fig. 3. The longer Ba–O distances of the catalyst observed after SO_2/O_2 treatment indicated changes in the local environment of Ba. The comparison of the Ba–O distances in the fresh catalyst and the reference samples indicated that barium exists as a mixture of

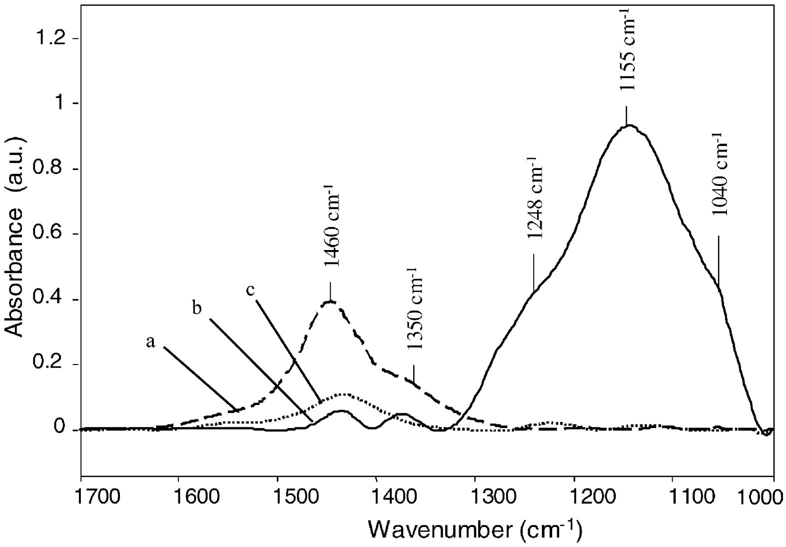

Fig. 2. IR-spectra of: (a) the activated catalyst, after exposure (b) to 400 ppm SO_2 and 5% O_2 at 350 °C for 30 min and (c) to 400 ppm SO_2 and 2000 ppm C_3H_6 at 350 °C for 30 min.

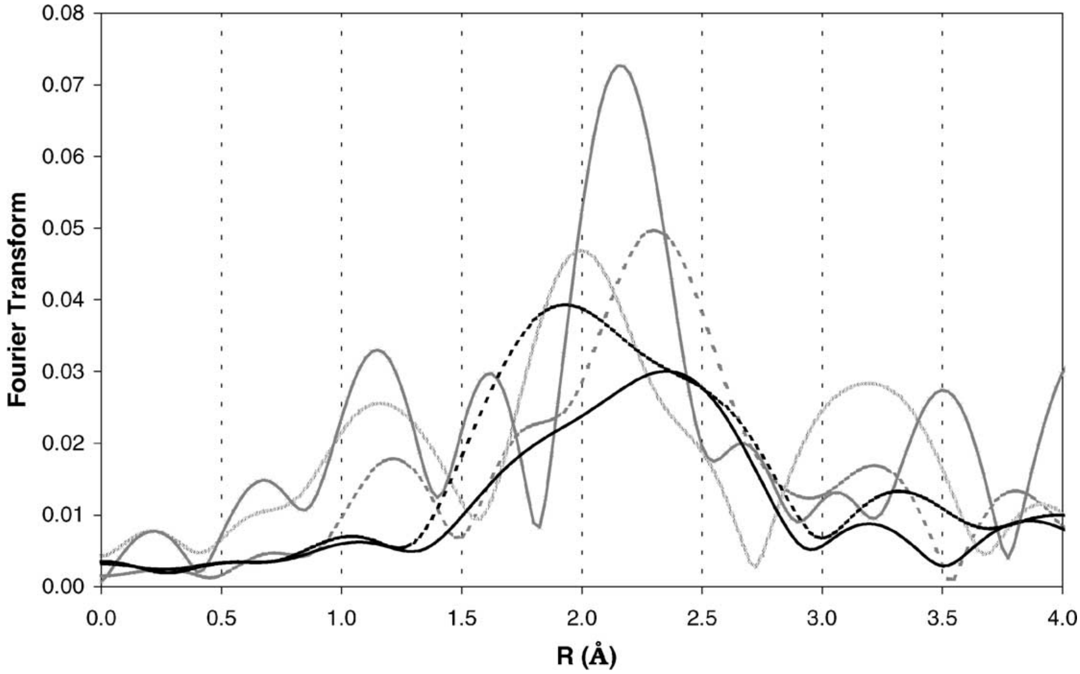

Fig. 3. Fourier transformed EXAFS at the Ba-L_{III} edge of the catalyst before and after exposure to SO_2/O_2: (- -) NSR catalyst before exposure, (—) NSR catalyst after exposure, (▬) BaO, (┈) $BaCO_3$, (- - -) $BaSO_4$.

BaO and $BaCO_3$ species. After exposure to SO_2 and O_2 the Ba–O distance of the catalyst is similar to the distance obtained for the $BaSO_4$ sample.

3.2. Interaction of SO_x with the oxidation/reduction function (Pt)

The oxidation state and the reducibility of Pt in the catalyst after treatment under lean and rich gas atmospheres were investigated by XANES and EXAFS at the Pt-L_{III} edge. XANES was used to examine the reducibility of Pt by H_2 for the variously pretreated catalysts. Note that this technique allows to specifically follow the reduction of Pt, while other techniques will lead to an integral signal, where other reducible components of the catalyst might contribute. The area of the peak above the Pt-L_{III} edge as a function of the temperature was used to describe the reduction of Pt with H_2 (Fig. 4). In the fresh material Pt was reduced by H_2 between 150 and 200 °C. A similar reduction behavior was observed for the catalyst pretreated under lean conditions (SO_2/O_2) at 350 °C. For the material pretreated under lean conditions at 500 °C, the cyclic pretreated material (SO_2/O_2, SO_2/C_3H_6) and the fuel-rich pretreated material (SO_2/C_3H_6) at 350 °C, a shift to higher reduction temperatures (from 230 to 280 °C up to 340 °C) was observed. In contrast to the other samples investigated the rich pretreated material at 350 °C was less reduced at the final temperature, while the fuel-rich pretreated material at 500 °C was hardly reducible in hydrogen up to 450 °C.

The local environment of Pt in the differently pretreated samples of the catalyst before TPR in H_2 was investigated by EXAFS to gain a better understanding of the sulfur species formed. The distance between Pt and its first neighbor (Fig. 5) in the fresh, lean and cyclic pretreated materials was 2 Å. Note that these distances are not corrected for the phase shift and, thus, are shifted to lower values. Distances above 2 Å were found in both samples pretreated in SO_2/C_3H_6 at 350 and 500 °C, which indicated structural changes in the neighborhood of the Pt atoms in presence of sulfur during fuel-rich conditions.

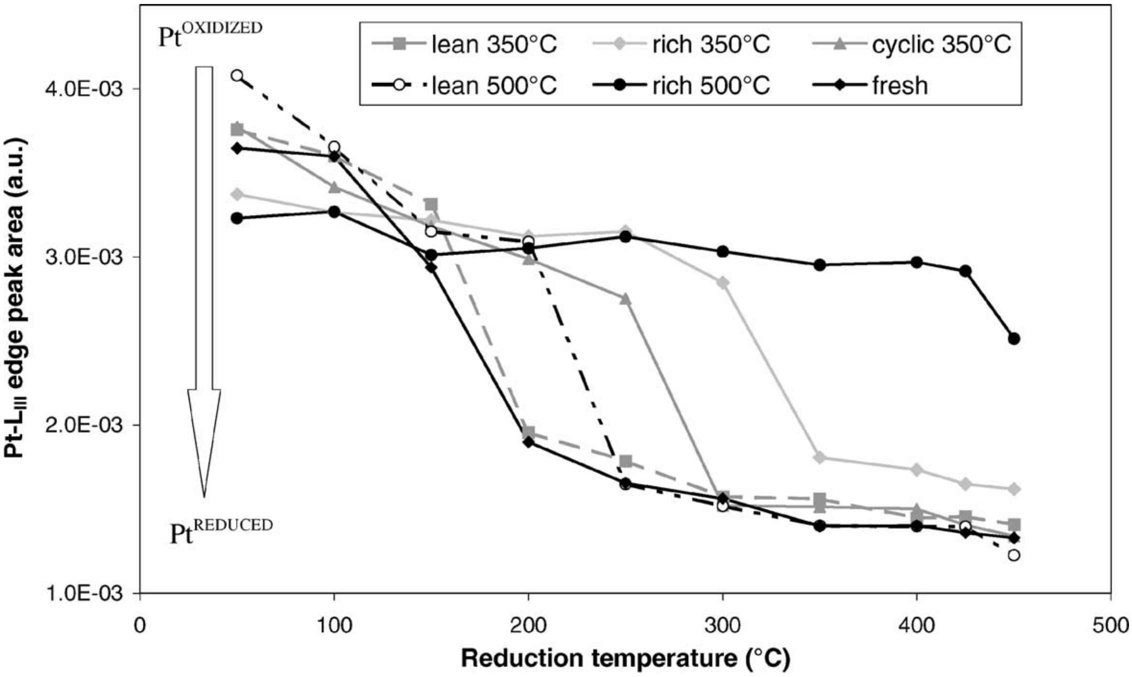

Fig. 4. Area of the peak above the Pt-L$_{\mathrm{III}}$ edge during TPR in H_2 after different pretreatments.

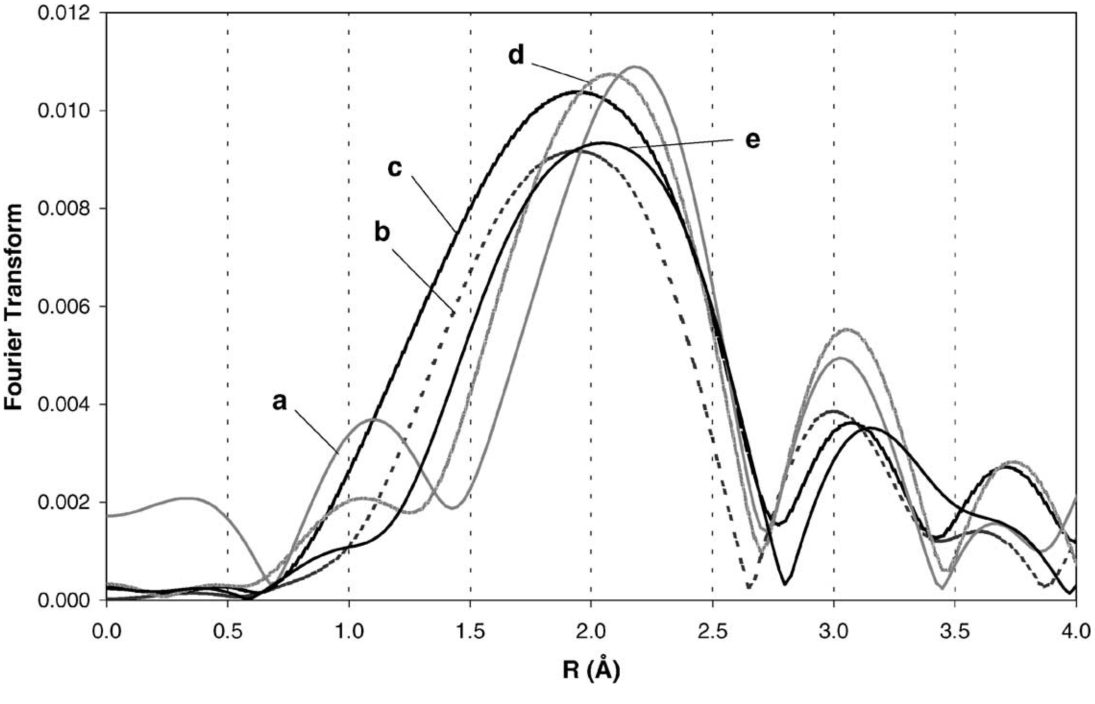

Fig. 5. Fourier transformed EXAFS at the Pt-L$_{\mathrm{III}}$ edge of the catalyst before TPR: (a) Pt-foil (reference), (b) untreated catalyst, (c) after SO_2/O_2 pretreatment at 350 °C, (d) after SO_2/C_3H_6 pretreatment at 350 °C, (e) after SO_2/C_3H_6 pretreatment at 500 °C.

4. Discussion

The results give a clear evidence for two possible pathways for the deactivation of NSR catalysts by sulfur. IR studies of the catalyst treated under lean conditions (400 ppm SO_2/5% O_2) at 350 °C mainly showed sulfur species adsorbed on the support and on the storage component. Initially, bands for sulfates on the surface of barium were observed, while after further SO_2/O_2 exposure, bulk barium sulfates and aluminum sulfates were detected, which clearly indicated the migration and transformation of the surface sulfates into bulk sulfates. After regeneration of the catalyst with C_3H_6 (2000 ppm) at 350 °C for 20 min significant changes in the intensities of the characteristic sulfate bands were not observed, which revealed that bulk sulfates were stable during the reduction in propene. Exposure of the fresh catalyst to rich conditions (SO_2/C_3H_6) showed only a negligible formation of sulfur species on the support and on the storage component, therefore the deactivation of the storage component occurred mainly under lean reaction conditions. The comparison of the distance between Ba and the next neighbor (oxygen) in the reference materials and the catalyst treated under lean conditions confirmed the formation of $BaSO_4$ on the catalyst after treatment with SO_2 under oxidizing conditions.

The distance between Pt and its first neighbor in the untreated, oxidized and cyclic pretreated materials was found to be less than or equal to 2 Å (all the distances were not corrected for the phase shift), while distances above 2 Å were found after pretreatment in SO_2/C_3H_6 at 350 and 500 °C. The increasing distances clearly revealed the formation of Pt sulfide species [11,12] during treatment under reducing conditions. Note that in order to obtain a sufficient time resolution during the TPR experiments, the XAS were measured only up to 8 $Å^{-1}$, which does not allow a detailed structural analysis of the Pt particles from the oscillations. XANES recorded during hydrogen TPR confirmed the lower reducibility of these platinum sulfide species as temperatures up to 450 °C were necessary to (partly) reduce the poisoned metal particles under H_2 atmosphere. Sulfur species permanently deactivating the Pt were not formed under lean condition, where the reduction behavior was comparable to that of the untreated material.

The differences in the reduction of the two fuel-rich pretreated materials clearly revealed a temperature dependency of the deactivation by sulfur. At 350 °C mainly surface Pt–S species were formed, which could be removed during fuel-rich reaction conditions. The temperature increase to 500 °C seems to accelerate the migration of the surface Pt–S into the bulk phase. As the catalyst could be regenerated under cyclic reaction conditions, sintering of the Pt particles and masking of the Pt surface with mobile sulfate species seem to be only minor effects in the deactivation of the Pt component.

5. Conclusions

The results clearly reveal the existence of two pathways for deactivation of NSR. Under lean conditions (exposure to SO_2 and O_2) surface sulfates are formed on the storage component barium, which subsequently migrate into the bulk phase. These species are hardly reducible by C_3H_6 up to 550 °C and block permanently Ba sites, which in turn leads to a decrease of NO_x storage capacity during successive cyclic treatments. A second pathway of deactivation by sulfur species occurs during fuel-rich (reducing) conditions. Sulfides seem to be formed on the platinum particles, which block the metal surface and, thus, hinder the further reduction function of the metal as revealed by the lower reducibility (higher hydrogen reduction temperature) of the noble metal.

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