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Investigations of sulphur deactivation of NO_x storage catalysts: influence of sulphur carrier and exposure conditions

Annika Amberntsson[a,b,*], Magnus Skoglundh[a,c], Martin Jonsson[a,c], Erik Fridell[a,b]

[a] *Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*
[b] *Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*
[c] *Department of Applied Surface Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

Abstract

The influence of SO_2, H_2S and COS in low concentrations on the deactivation of $Pt/Rh/BaO/Al_2O_3$ NO_x storage catalysts was investigated. Different samples of the catalyst were exposed to synthetic gas mixtures mimicking lean/rich engine cycling in a mixed lean application at 400 °C. The lean gas mixture contained 8 vol.% O_2, 500 vol-ppm C_3H_6 and 400 vol-ppm NO balanced to 100 vol.% with Ar. The rich excursions were performed by switching off the oxygen supply. Sulphur, 25 vol-ppm of either SO_2, H_2S or COS, was added to the gas flow either during the lean, the rich or both periods. This procedure aimed at investigating the influence of the exposure conditions and therefore the lean and rich periods were kept equally long (5 min). In addition, thermodynamical calculations for the prevailing conditions were performed.

It was concluded that all sulphur compounds investigated, i.e. SO_2, H_2S and COS, had similar, negative impact on the NO_x storage ability of the catalyst and that they all showed increased deactivation rates during rich exposure compared to lean. During lean exposure, all sulphur carriers showed similar behaviour, while H_2S and COS caused severe loss of noble metal activity during rich exposure. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulphur deactivation; NO_x storage catalysts; Sulphur carrier; H_2S; COS; Platinum; Rhodium

1. Introduction

Demands for more fuel effective combustion engines, both for environmental and economical reasons, have lead to increased interest in lean-burn and diesel technologies due to their, compared to stoichiometric combustion, higher fuel efficiency [1]. However, these engines work under excess oxygen and as a consequence produce oxygen rich exhausts. New techniques to treat these exhausts have been developed since the reduction of nitrogen oxides (NO_x) to harmless nitrogen in standard three way catalytic converters is obstructed by the large excess of oxygen. Several approaches have been suggested and one of them is the so-called NO_x storage concept [2–6]. Nitrogen oxides are here trapped during lean conditions by forming chemical compounds with a dedicated storage material in the converter. In order to regenerate the catalyst, the engine is tuned to rich conditions for short periods whereby the NO_x is released and reduced. The storage involves nitrate formation (e.g. barium nitrate), and normally this means that the storage compounds also show high affinity for sulphate formation. This will eventually deactivate the catalyst and high temperature sulphur regeneration has to be undertaken.

Several previous studies have dealt with SO_2 exposure of NO_x storage catalysts [7–12]. Engström

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* Corresponding author. Present address: Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. Fax: +46-31-772-2967.
E-mail address: amberntt@fy.chalmers.se (A. Amberntsson).

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et al. [7] suggested that the total sulphur dose is more important for the poisoning than the inlet SO_2 concentration. The exposure temperature, in the working interval of a NO_x storage catalyst, was also reported to be of minor importance [8]. Formation of sulphates on the catalyst surface and eventually in the bulk material occurs under oxygen rich conditions [7–10]. The NO_x conversion has been reported to decrease from 80 to 18% for a $Pt/BaO/Al_2O_3$ catalyst [10] and from 99% down to 30% for a $Pt/Rh/BaO/Al_2O_3$ catalyst [11]. However, the sulphates are reported to be, at least partly, removable under strongly reducing conditions under formation of, e.g. SO_2, H_2S and COS [12]. Recent FT-IR investigations showed that sulphation may occur also under rich conditions [13].

In this study, the importance of the deactivation of sulphur and the importance of different exposure conditions is investigated. The sulphur compounds investigated were chosen to be in line with detected sulphur regeneration products directly after the regeneration procedure. A model NO_x storage catalyst with noble metals (platinum and rhodium), a storage compound (barium oxide) and a support (γ-alumina) was used. The effect on the performance of the catalyst when adding 25 vol-ppm of either SO_2, H_2S or COS to a synthetic lean-burn exhaust, containing NO, C_3H_6, O_2 and Ar at 400 °C was investigated.

2. Experimental procedure

Six washcoated monoliths (75 mg BaO derived from $Ba(NO_3)_2$ from Aldrich on 500 mg γ-alumina from Condea) were prepared. The cordierite substrates (cylindrical, $Ø = 20$ mm, $L = 15$ mm, 400 cells per square inch) were then impregnated with solutions of the non-halide platinum and rhodium salts ($Pt(NO_3)_2$ from Hereaus and $Rh(NO_3)_2$ from Johnson Matthey) until the amount (based on the washcoat) of noble metal was 2 wt.% Pt and 1 wt.% Rh to provide both good oxidation and reduction activity by the samples and mimic a commercial NO_x storage catalyst [14]. The catalyst preparation route has been described in detail in the previous works [6,15]. The impregnated catalysts were then calcined in air at 600 °C for 90 min and subsequently reduced in 2 vol.% H_2 at 500 °C for 30 min.

Each sample was placed in a quartz tube flow reactor system described elsewhere [17] containing mass flow controllers, temperature control, detectors for NO, NO_2 (chemiluminescence) and N_2O (IR), and was exposed to synthetic gas mixtures, simulating NO_x storage/release cycles in a mixed lean application [2–6]. The NO, NO_2, N_2O and total NO_x traces were recorded making evaluation of NO_x storage, NO oxidation (lean phase) and NO_x reduction (rich phase) activities possible. The storage was performed in 8 vol.% O_2, 400 vol-ppm NO, 500 vol-ppm C_3H_6, and 25 vol-ppm of either SO_2, H_2S or COS, and balanced with Ar for 5 min. This time was sufficient to saturate the NO_x storage capacity of the samples. The NO_x regeneration was simulated by switching off the oxygen flow for another 5 min. This is not a realistic time scale for the rich periods in a real application, but since one of the objectives of the present study was to investigate the influence of sulphur exposure conditions, equally long periods for NO_x adsorption and regeneration were preferred. The total gas flow was 3000 ml/min, which corresponds to a space velocity of 38,000 h^{-1}. The temperature was chosen to 400 °C which is close to the temperature for maximum NO_x uptake for this type of catalyst [6,16] and results in 50% NO and 50% NO_2 at equilibrium under the given conditions, which were chosen to be as close to real conditions as possible and still provide an easily evaluated model system. Each experimental series contained four initial, sulphur free cycles to be used as reference followed by 15 cycles including sulphur either in the lean, in the rich or in both periods. Four experimental sequences starting with two continuous exposures followed by lean and finally rich exposure. In between each experimental series, a sulphur regeneration was done. The sulphur regeneration procedure consisted of heavy reduction in 2 vol.% H_2 at 750 °C for 30 min followed by oxidation in 10 vol.% O_2 at 400 °C for another 30 min and was sufficient to retain stable initial performance of the samples.

3. Thermodynamic calculation

The thermodynamically expected equilibrium compositions of solid platinum compounds were calculated using the commercial software HSC Chemistry® for two different gas mixtures; one lean containing

8 vol.% O_2, 0.5 vol.% C_3H_6 balanced with Ar and one rich with 0.1 vol.% O_2, 0.5 vol.% C_3H_6 also balanced with Ar to 100 vol.%. Addition of a small amount of oxygen (to replace oxygen present in NO which was excluded for simplification) to the rich mixture was necessary to allow formation of all compounds. The temperature interval (200–800 °C) was chosen to correspond to the interval of interest for the application. One volume percent of either SO_2, H_2S or COS was added giving mainly four different platinum compounds (Pt^0, PtO, PtO_2 and PtS). The relatively high concentration of sulphur compounds was chosen to make the formed species easily detectable in the complex mixture.

4. Results

Fig. 1 displays the outlet concentrations of NO and total NO_x during transient lean/rich conditions (see above) with continuous: (a) SO_2, (b) H_2S and (c) COS exposure of the Pt/Rh/BaO/Al_2O_3 samples. The figure shows that all samples initially store a considerable, almost equal amount of NO_x (the dashed areas in the first cycles, calculated by subtracting the integrated NO_x trace between $t = -10$ and -5 min from the integrated inlet concentration). This is indicated by the slow increase of the outlet NO_x concentration during the lean periods. Under sulphur exposure which starts at $t = 0$, however, the same behaviour as previously described by Engström et al. [7] for SO_2 occurs for H_2S and COS as well: the outlet traces of NO_x gradually assume the shape of the system response indicating that less and less NO_x is stored in the catalyst (compare the period between $t = -10$ and -5 min with the period between $t = 70$ and 75 min). For the fresh catalyst, and in the early stages of the sulphur exposure, NO release peaks arise when the conditions are switched from lean to rich, e.g. at $t = -5$ min. These peaks have previously been associated with NO adsorbed on the noble metals [6], decreased adsorption rate of NO_x in the absence of oxygen or remaining oxygen on the noble metals obstructing the reduction of the nitrogen oxides [11]. After a few minutes of sulphur exposure, and most rapidly for SO_2, these peaks disappear; indicating blocking of the noble metal sites, compare $t = -5$ and 65 min. Another type of NO release peak occurs when switching from rich to lean conditions after extended sulphur treatment, e.g. at $t = 60$ min. These peaks grow with sulphur exposure and are somewhat more pronounced under COS exposure.

Fig. 1 also shows a clear loss of reduction capacity during the rich excursions, indicated by the increase in the outlet NO signal during rich periods; compare

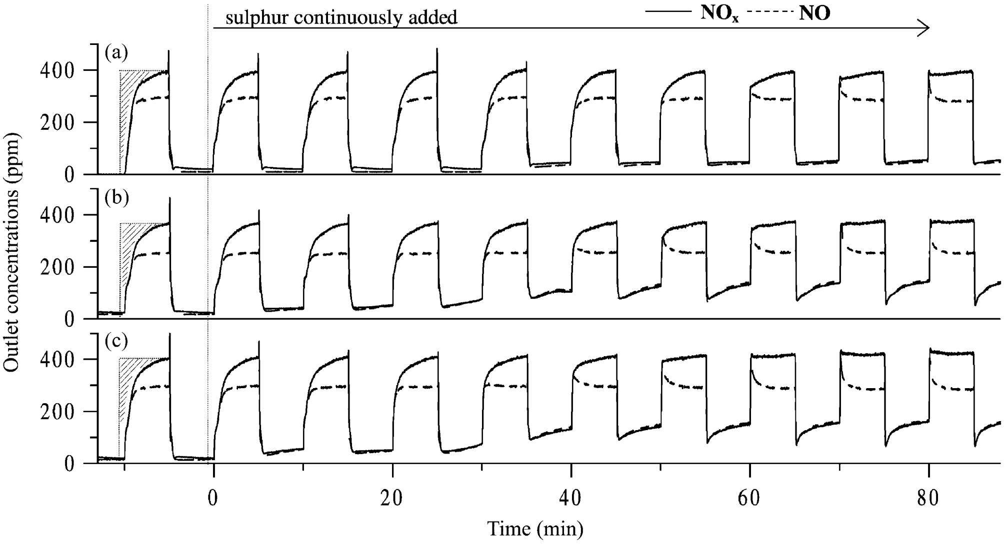

Fig. 1. Outlet traces of NO (dashed lines) and total NO_x (solid lines) for Pt/Rh/BaO/Al_2O_3 during lean/rich cycles with continuous exposure to 25 vol-ppm of: (a) SO_2, (b) H_2S and (c) COS at 400 °C.

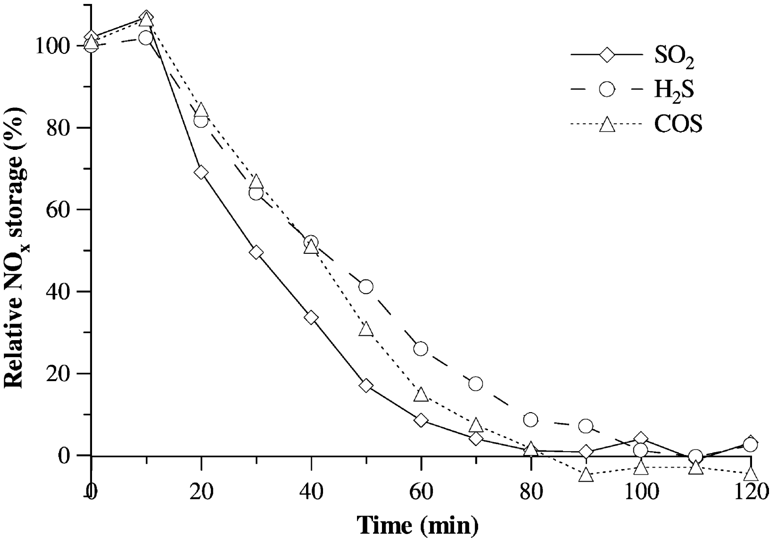

Fig. 2. NO$_x$ storage capacity, normalised to fresh catalyst, for Pt/Rh/BaO/Al$_2$O$_3$ for different sulphur compound during exposure to 25 vol-ppm of: SO$_2$ (◇); H$_2$S (○); or COS (△), as function of exposure time.

the period between $t = 5$ and 10 min with $t = 65$ to 70 min. The reduction activity is more suppressed during addition of H$_2$S and COS than for SO$_2$ and the NO$_x$ level during the rich periods increases with sulphur exposure to a fairly steady level. The oxidation activity, indicated by the NO$_2$ formation (not shown directly but is the difference between NO and total NO$_x$ since no other nitrogen containing species were detected), seems relatively unaffected by the sulphur exposure.

The amount of NO$_x$ stored during each lean period, normalised to the initial value for the fresh sample, as a function of sulphur exposure time at continuous exposure to 25 vol-ppm SO$_2$, H$_2$S or COS is displayed in Fig. 2. The figure mainly shows four features. First, the deactivation rate under SO$_2$ exposure seems to be somewhat higher than for H$_2$S and COS; 50% of the activity remains after 30 min of SO$_2$ exposure. The corresponding value for H$_2$S and for COS is about 40 min. Secondly, the deactivation caused by COS changes character after about 40 min of exposure. It starts off by being fairly similar to the deactivation caused by H$_2$S but the rate is then increased and the NO$_x$ storage capacity of the catalyst is completely eliminated in a time scale similar to what was found for SO$_2$. The third point is the apparent negative NO$_x$ storage in the case of COS exposure which is caused by release of adsorbed NO when the conditions are switched from reduction to trapping mode, see Fig. 1. The negative values are obtained since the integral of the NO$_x$ outlet trace during these storage periods ($t > 90$ min) becomes larger than the supplied amount of NO$_x$. This is related to NO$_x$ being adsorbed on the noble metal sites also during the rich period [18]. The last feature to note is the increased NO$_x$ storage occurring at the very beginning of the sulphur treatment (at $t = 10$ min).

In Fig. 3, the relative NO$_x$ storage is plotted vs. sulphur exposure time for repeated continuous, lean and rich exposures to 25 vol-ppm of either SO$_2$, H$_2$S or COS. In this figure, it can be observed that the deactivation is more rapid for rich exposure than for lean exposure for all three sulphur carriers. In all three cases, the rich exposure procedure causes a 60–80% loss of the initial NO$_x$ storage activity in less than 15 min. When the sulphur compound is added to the lean gas mixture, much longer times (between 25 min for COS and 40 min for SO$_2$) are observed to reach 70% deactivation for all three sulphur compounds.

Fig. 3 also shows that the deactivation rates for rich and continuous exposures are similar and much more rapid than for the lean conditions. This behaviour is

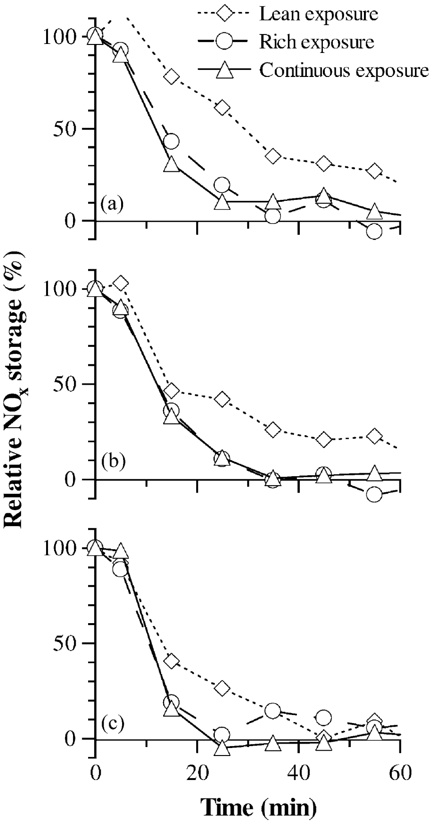

Fig. 3. Relative NO_x storage capacity vs. time under continuous (△), lean (◇), or rich (○) exposure of $Pt/Rh/BaO/Al_2O_3$ to 25 vol-ppm of: (a) SO_2, (b) H_2S and (c) COS.

found for all three sulphur compounds and indicates that the overall sulphur deactivation is dominated by the rich exposure periods. Note that the continuous exposure supplies twice the amount of sulphur between the measurement points compared to the discontinuous exposures (see Section 2).

In Fig. 3, the slight increase in NO_x storage capacity at the beginning of the sulphur exposure can be observed (compare with Fig. 2). It is clear that this behaviour only appears for lean sulphur exposure and for all three sulphur compounds. However, the effect seems to be somewhat larger for SO_2 than for H_2S or COS.

Fig. 4 shows the calculated equilibrium compositions of platinum species under either (a) lean or rich (b) exposure to SO_2, H_2S or COS. The solid lines correspond to the metallic state, dotted lines corresponds to oxidic states (PtO or PtO_2) and the dashed lines illustrate the sulphide expected (PtS). No other species were expected to be present. From this figure, it can be established that the equilibrium compositions of Pt species are clearly different under oxygen excess and deficit, respectively. Under excess oxygen (Fig. 4a), the formation of platinum oxide species (PtO_2 below 350 °C and PtO at higher temperatures) is favoured at temperatures below 450 °C. Only minor differences between the sulphur sources (i.e. SO_2, H_2S or COS) are obtained. By additional calculations, it was recognised that this behaviour is very similar to the sulphur free case. The formation of platinum oxides for the present type of samples has recently been observed by XPS after exposure to a gas mixture mimicking the lean period in a lean/rich cycle at 350 °C [19].

Under rich conditions, however, a completely different picture appears, see Fig. 4b. The formation of significant amounts of PtS (no other sulphide species were predicted) and minor quantities of Pt^0 are thermodynamically favoured in the presence of COS and especially, in the presence of H_2S. However, under SO_2 exposure platinum is most stable in its metallic form. Additionally, under COS exposure the formation of elementary carbon is strongly favoured (not shown).

Similar calculations were performed for Rh (not shown) and the main result from these was that under lean conditions the formation of RhO_2 is favoured at the temperatures of interest. Under rich conditions, several forms of rhodium sulphide ($RhS_{0.889}$, Rh_3S_4, Rh_2S_3) and Rh^0 are favoured.

5. Discussion

Previous studies dealing with the deactivation of NO_x storage catalysts in synthetic gas mixtures have all used SO_2 as the sulphur source and the main conclusion is that sulphates are formed with the storage material under lean sulphur exposure [2,4,7–10,20]. This study does not contradict that—deactivation does occur under lean SO_2 exposure probably due to formation of sulphates. However, the additional information collected in this work indicates that the sulphur regeneration products H_2S and COS are just as harmful, or under certain conditions even worse, for the function of the NO_x storage catalyst as SO_2. For the lean

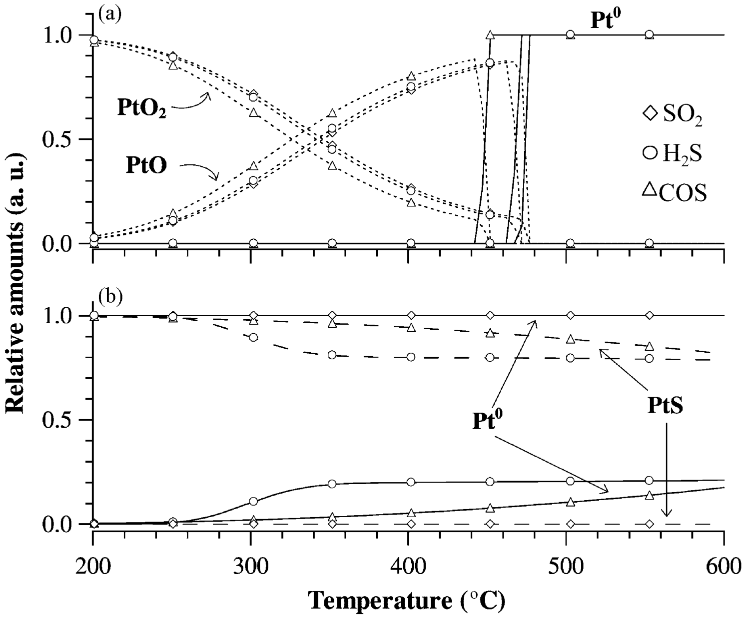

Fig. 4. Calculated thermodynamic equilibrium compositions of metallic (solid lines), oxidic (dotted lines) and sulphide (dashed lines) species when platinum is exposed to (◇) SO_2, (○) H_2S or (△) COS under (a) lean conditions (8 vol.% O_2, 0.5 vol.% C_3H_6 and 1 vol.% sulphur) or (b) rich conditions (0.1 vol.% O_2, 0.5 vol.% C_3H_6 and 1 vol.% sulphur).

conditions, this is reasonable since one can expect that H_2S and COS are oxidised into SO_2 when oxygen is in excess. This has been established both experimentally and from thermodynamic considerations.

All three sulphur compounds cause a more rapid deactivation of the Pt/Rh/BaO/Al_2O_3 catalyst under rich compared to lean exposure. This strongly implies that the deactivation is more complex than just sulphation of the NO_x storage sites. One may also note that the reduction of NO during the rich periods is strongly affected by prolonged sulphur exposure (see Fig. 1) especially during exposure to H_2S or COS. Thus it seems that the interaction between the sulphur compounds and the noble metal sites is of importance also for the deactivation of the NO_x storage function of the catalysts. This interaction seems to occur mainly during rich exposure. This is also what has been observed in a number of studies on the deactivation of alumina-supported noble metal catalysts by sulphur where it was found that for lean conditions, the sulphur is oxidised to SO_2 which show no large effect on the noble metals [21]. For rich conditions, however, reports of different sulphur deposits on the catalytic performance of the noble metals can be found. Both elementary sulphur and noble metal sulphides have previously been detected under similar conditions [22–25]. For example, PtS formation under H_2S exposure has been observed by Chang et al. [23] for Pt/Al_2O_3 catalysts for hydrogenation of aromatic compounds. The authors also found a severe agglomeration of the platinum clusters due to high mobility of the formed PtS species [23]. It is reasonable to expect that similar compounds may form in the presence of COS since both COS and H_2S strongly interact with the noble metals. However, loss in noble metal surface due to sintering is not supported by the present data since the activity is regained from high temperature reduction.

The formation of reduced sulphur compounds on the noble metals found in the previous studies [22–25] is in line with the observation (Fig. 3) that the deactivation during lean exposure to H_2S and COS is more rapid than for SO_2. One reason for this may be that sulphur deposits may form on the noble metals even during lean conditions for H_2S and COS. The latter might be a result of blocking of active surface by chemisorbed H_2S or COS, or species derived from these compounds. If the sulphur form compounds with the noble metals, the activity of these are also expected to be lower than for the clean metals. Formation of sulphide species is, as seen in Fig. 4b, thermodynamically favourable under hydrocarbon rich conditions in the presence of these compounds.

Blocking of noble metal sites was previously discussed by Engström et al. [7] and was then suggested to be a reason for the growth of NO breakthrough peaks when the conditions are switched from rich to lean. These NO breakthrough peaks indicate that NO can adsorb on the noble metals even when sulphur adsorbates are present. It does thus seem that the adsorption of propene is more strongly suppressed. In this work, these NO peaks indicated in Fig. 1, are shown to grow larger under COS exposure than for SO_2 and H_2S. This may possibly be due to deposition of carbonaceous residues on the noble metal sites. The thermodynamic calculations suggested formation of considerable amounts of elementary carbon under rich conditions. This, however, has not been investigated in the present work and should therefore be considered as pure speculation.

The observation of an increased NO_x storage ability during the initial state of lean sulphur exposure, displayed in Figs. 2 and 3, is probably connected with the characteristic of SO_2. This assumption agrees with that the increase only occurs under lean conditions where H_2S and COS will be oxidised to SO_2. SO_2 has previously been reported to enhance the oxidation activity of saturated hydrocarbons for Pt/Al_2O_3 [26]. Additionally, SO_2 may initially reduce platinum oxides to metallic platinum [27] while forming sulphite or sulphate species. The formation of NO_2 will then increase since platinum is suggested to be more active for NO oxidation than PtO_x [19]. The increased NO_2 production would then lead to a larger NO_x storage capacity. However, after some time, sulphation of NO_x storage sites will be dominant and the NO_x storage capacity will decrease with sulphur exposure.

To summarise, the deposition of sulphur (chemisorbed, elementary or compounds) on the noble metals will affect the NO_x storage capacity since the formation of NO_2 will be suppressed and the nitrate decomposition will be slower. Both of these aspects have been suggested as crucial steps in the NO_x storage and reduction mechanism for noble metal–barium oxide type NO_x storage catalysts [6,28]. A third important step in the NO_x storage mechanism is the spillover of formed NO_2 from the noble metal to the storage site [28]. This step is dependent on the available contact area between the noble metal and the storage compound. When the oxygen is switched back on, the sulphur deposits will be oxidised into SO_2 [22]. The formed SO_2 may spillover and form sulphates at sites close to the noble metal particles and thus block the NO_x storage sites expected to be the most important ones [28]. This will not only decrease the available number of NO_x storage sites close to the noble metal but also obstruct the spillover of NO_2 from the noble metal (sites) to the barium oxide since the available contact area between the storage compound and the noble metal will be decreased.

6. Conclusions

This work showed that all the prepared $Pt/Rh/BaO/Al_2O_3$ catalysts exhibit NO_x storage activity, NO oxidation and reduction included. They are also, in agreement with previous studies [7–10], sensitive to sulphur exposure.

Additionally, this study showed that catalyst deactivation occurs when sulphur is present in the feed under lean as well as under rich conditions. The rich exposure even showed to be more severe than the lean exposure. These behaviours were observed for SO_2 as well as the sulphur regeneration products H_2S and COS implying that sulphur deactivation of NO_x storage catalyst occurs independently of the sulphur source.

Finally, it is concluded from this work that sulphur exposure, especially H_2S and COS, strongly affects the noble metal activities of the catalyst. The NO reduction activity was more affected than the activity for NO oxidation.

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