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A study of the deactivation by sulfur and regeneration of a model NSR Pt/Ba/Al₂O₃ catalyst

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Abstract

The deactivation by sulfur and regeneration of a model Pt/Ba/Al₂O₃ NO_x trap catalyst is studied by hydrogen temperature programmed reduction (TPR), X-ray diffraction (XRD), and NO_x storage capacity measurements. The TPR profile of the sulfated catalyst in lean conditions at 400°C reveals three main peaks corresponding to aluminum sulfates (~550°C), “surface” barium sulfates (~650°C) and “bulk” barium sulfates (~750°C). Platinum plays a role in the reduction of the two former types of sulfates while the reduction of “bulk” barium sulfates is not influenced by the metallic phase. The thermal treatment of the sulfated catalyst in oxidizing conditions until 800°C leads to a stabilization of sulfates which become less reducible. Stable barium sulfides are formed during the regeneration under hydrogen at 800°C. However, the presence of carbon dioxide and water in the rich mixture allows eliminating more or less sulfides and sulfates, depending on the temperature and time. The regeneration in the former mixture at 650°C leads to the total recovery of the NO_x storage capacity even if “bulk” barium sulfates are still present on the catalyst.

1 Introduction

To meet the Kyoto protocol regarding CO₂ emissions (greenhouse effect gas), a promising way is the development of gasoline engines working in lean mixture, with an excess of oxygen. Compared to common gasoline engines, they present a lower fuel consumption (20-30% less). However, in lean-burn conditions, the common three-way catalysts are unable to efficiently reduce the nitrogen oxides (NO_x) from the exhaust gas. To overcome this problem, different concepts have been proposed. One of them is the NO_x storage-reduction technique (NSR) developed in the 1990s by Toyota [1]. This system is working in transient conditions. During the lean periods, nearly one minute, NO_x is oxidized in NO₂ over precious metals and trapped by a storage material, mainly as nitrates. Then, the engine works in rich conditions (excess of hydrocarbons, HC) for a short period of few seconds. The stored NO_x are released and reduced over precious metals with HC, CO and H₂. 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 NO_x oxidation/reduction (precious metals e.g Pt) [1, 2, 3].

One of the major problems of the NSR catalyst is the high affinity of the storage material with SO₂ present in the exhaust gas, because it leads to the formation of stable sulfates during the lean periods [3, 4-15]. Sulfates are adsorbed preferentially on barium component but adsorption on alumina support is also possible with a slower rate [4-6]. Moreover, Limousy et al. have shown that sulfur species on support material can migrate on barium sites giving stable S-bound species [7]. Two types of barium sulfates are widely proposed in the literature: surface and bulk barium sulfates [4, 8-12]. Sedlimer et al. suggest that bulk sulfates are formed by migration and transformation of surface sulfates [11]. Unfortunately, sulfates are thermodynamically more stable than nitrates and the regeneration of a sulfated catalyst requires high temperatures (750-800°C) that may induce a thermal ageing of the catalyst (sintering and phase transformation) [6, 9, 10, 16-19]. The regeneration process of the storage component also depends on time [10] and on the nature of the reductant. Hydrogen is more effective than carbon monoxide which is itself more effective than hydrocarbons [4, 20]. However, only few authors have studied the influence of the regeneration gas composition upon storage material [6, 20]. During lean conditions, no poisoning of platinum by sulfur has been reported, while during rich phases sulfur species sorb on Pt with formation of PtS species [11, 13, 15]. These species inhibit the oxidation capacity of platinum [11, 13]. Thus the NO₂ formation, which is crucial for nitrate formation [14, 15], can be limited at the beginning of the lean phase until sulfides are removed. Moreover, the removal of the sulfides species in lean conditions leads to SO_x formation, which

can be trapped as sulfates in the vicinity of Pt particles, deactivating the most active sites for NO_x storage [12, 14, 21].

In this work, we investigate the deactivation of a Pt/Ba/Al₂O₃ model catalyst by SO₂ and the regeneration of the sulfated catalyst under hydrogen containing mixtures. After different treatments, the catalyst was characterized by XRD, TEM, H₂ temperature programmed reduction (TPR) and NO_x storage capacity measurements.

2 Experimental

2.1 Catalyst preparation, sulfation and regeneration

The Pt/Ba/Al₂O₃ catalyst was prepared using the following method. A γ -alumina powder (BET surface area 102 m².g⁻¹) was impregnated with a barium nitrate solution, in order to obtain a 10 wt % or 20 wt % BaO content. After drying, the support was calcined at 600°C (heating rate 2°C/min) under air for 4h. The resulting barium-alumina support was then impregnated with a dinitro-diamino platinum solution in order to obtain a 1 wt % Pt catalyst. After drying, the catalyst was calcined at 450°C under air, reduced at 500°C under pure H₂ for 4h (heating rate: 2°C/min), and then activated at 600°C for 6h under a mixture of 10%O₂, 10%H₂O, 10%CO₂ and N₂. Catalysts are denoted Pt/10Ba/Al and Pt/20Ba/Al depending of the BaO content, 10 wt % and 20 wt % respectively.

In the sulfation process, the catalyst sample was exposed to a 100ppm SO₂, 10%O₂, 10%H₂O and N₂ mixture at 400°C for 5h. The quantity of SO₂ introduced during the sulfation treatment corresponds to a 2.0 wt % S content if all the sulfur is stored on the catalyst. Then, the sample was treated at 400°C under 10%O₂, 10%H₂O and N₂ mixture for 2 h. These sulfated catalysts are denoted Pt/xBa/Al +S. Also, the effect of a thermal treatment at 500°C, 600°C and 800°C after sulfation has been studied. The catalysts are then denoted Pt/xBa/Al +S+Ty (y: temperature of the thermal treatment).

The regeneration of the sulfated catalysts was done with a rich mixture, with two different protocols. One is a reduction under 1%H₂/Ar until 800°C corresponding to a "temperature programmed reduction" treatment, as described below. The second one is using a more complex and more representative mixture containing 2.5%H₂, 10%CO₂, 10%H₂O and N₂. The catalyst is heated under this mixture from the room temperature up to the regeneration temperature (550°C, 600°C, 650°C, 700°C and 800°C, heating rate: 10°C.min⁻¹) and maintained at this temperature for 30 min before cooling under N₂.

2.2 Experimental techniques

NO_x storage capacity measurement

Before the NO_x storage capacity measurement, the sample (60mg) was pretreated *in situ* at 400°C for 30 min under a 10% O₂, 10% H₂O, 10% CO₂ and N₂ mixture (total flow rate: 10 L.h⁻¹). After flushing under N₂ at the same temperature, the sample was submitted to a 600ppm NO, 10% O₂, 10% H₂O, 10% CO₂ and N₂ mixture (total flow rate: 10 L.h⁻¹) at 400°C. The gas flow was introduced using mass-flow controllers, except for H₂O which was introduced using a saturator. Both NO and NO_x concentrations (NO+NO₂) were followed by chemiluminescence. H₂O was removed prior to NO_x analysis with a membrane dryer. The NO_x storage capacity was estimated by integration of the recorded profile after subtraction of the contribution of the apparatus (dead volume) measured from a test without catalyst.

Temperature programmed reduction (TPR)

Prior to the TPR, the catalyst (50 mg) was first pretreated *in situ* under oxygen at 400°C for 30 min and cooled to room temperature. After flushing under argon for 45 min, the reduction was carried out from room temperature up to 800°C under a 1% H₂/Ar mixture, using a 5°C min⁻¹ heating rate. The sample was maintained at 800°C for 30 min before cooling under argon. Hydrogen consumption was followed by thermal conductivity.

X-ray diffraction

X-ray powder diffraction was performed at room temperature with a Bruker D5005 using a K α Cu radiation ($\lambda=1.54056 \text{ \AA}$). The powder was deposited on a silicon monocrystal sample holder. The crystalline phases are identified by comparison to the ICDD database files. The in-situ XRD measurements at different temperatures were carried out with a Siemens D500 powder diffractometer using the K α Cu radiation ($\lambda=1.54056 \text{ \AA}$) coupled with an electrical furnace HTK16.

Specific surface measurement

The BET surface areas were deduced from N₂ adsorption at -196°C carried out with a Micromeritics apparatus. Prior to the measurement, the samples were treated at 250°C under vacuum for 8 h to eliminate the adsorbed species.

Electron microscopy (TEM + EDX)

Transmission electron microscopy (TEM) images were obtained with a Philips CM 120 microscope, equipped with an energy-dispersive X-ray detector. The sample was suspended in ethanol and spread onto a copper grid converted with an amorphous carbon film.

3 Results and discussion

3.1 Catalyst deactivation by SO₂

The TPR profile of the Pt/20Ba/Al catalyst sulfated at 400°C is shown in Figure 1 trace a. Three main peaks of hydrogen consumption are observed. In a previous work [18], the first peak near 500°C was attributed to the reduction of surface aluminum sulfates, while the two other peaks around 650°C and 750°C were ascribed to the reduction of surface barium sulfates and bulk barium sulfates, respectively. In order to determinate the role of platinum in the reduction process of sulfates, a 20Ba/Al sample was sulfated with SO₂ under oxidizing conditions. A 1wt%Pt/SiO₂ catalyst was placed upstream in order to ensure the oxidation of SO₂ towards SO₃. As it can be seen from Figure 1 and Table 1, the total hydrogen consumptions are quite similar for the reduction of the Pt/20Ba/Al+S and 20Ba/Al+S catalysts, which means that the same amount of sulfur is deposited on both samples (Table 1). On the other hand, the TPR profiles are different. The reduction of aluminum sulfates on the 20Ba/Al+S sample (Figure 1 trace b) appears with a maximum at 550°C comparing to 500°C on the Pt/20Ba/Al+S catalyst (Figure 1 trace a). Moreover, the amount of aluminum sulfates is smaller in the absence of platinum. This may result from a faster accumulation of sulfates at the sites proximal to platinum by surface diffusion from platinum in the case of the Pt/20Ba/Al+S catalyst [3].

The absence of the peak near 650°C for the 20Ba/Al+S sample tends to indicate that this hydrogen consumption on the Pt/20Ba/Al+S catalyst would correspond to the reduction of barium sulfates located in the neighborhood of platinum particles. Without platinum, the reduction of surface barium sulfates would appear as a shoulder feature at a temperature slightly above 700°C (Figure 1 trace b). On the contrary, the reduction of bulk barium sulfates seems to be not influenced by the presence of platinum since the maximum of the peak is around 750°C for both the Pt/20Ba/Al+S and the 20Ba/Al+S samples. To summarize, these results show that platinum promotes the reduction of surface aluminum and barium sulfates deposited in its vicinity.

The comparison of the results obtained in the present study and those published by Wei et al. [5] suggests that the type I BaSO₄ and type II BaSO₄ proposed by these authors correspond to the sulfates which we will call "surface barium sulfates" and "bulk barium sulfates", respectively. Wei and al. indicate that type I BaSO₄, which is reducible at lower temperature (650°C), has small crystallite size (smaller than 3 nm) and is proximal to platinum particles. The type II BaSO₄ has larger crystallite size and is reducible only at high temperature (750°C).

Table 1: Hydrogen consumptions from TPR of sulfated catalysts: Pt/20Ba/Al+S and 20Ba/Al+S.

Catalyst	H ₂ consumption ($\mu\text{mol.g}^{-1}$ cata)	S (%)
Pt/20Ba/Al	2520	2.0
20Ba/Al	2420	1.9

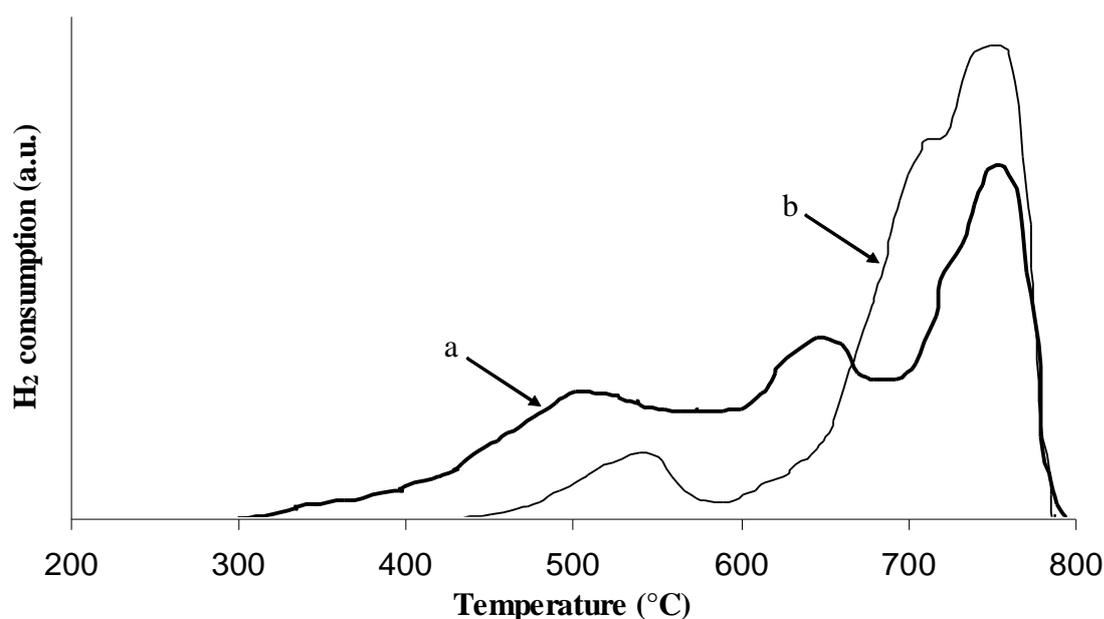


Figure 1: TPR profiles of sulfated catalysts: (a) Pt/20Ba/Al+S and (b) 20Ba/Al+S.

The characterization by electron microscopy (TEM associated with X-ray microanalysis) of the Pt/20Ba/Al catalyst prepared in the present work has shown effectively the presence of heterogeneous Ba particles with a particle size ranging from a few nm to few tens of nm (Figure 4a). On the other hand, in the case of the Pt/10Ba/Al catalyst, with a lower barium content, the Ba compound would be more dispersed since very few large Ba particles have been observed (results not shown). After sulfation at 400°C, Pt/10Ba/Al leads to the TPR profile reported in Figure 2 trace b. By comparison with the Pt/20Ba/Al+S catalyst (Figure 2 trace a), the main difference arises from the hydrogen consumption at high temperature, that is much lower in the case of Pt/10Ba/Al+S. That observation confirms the attribution of this peak to the reduction of large BaSO₄ crystallites. Thereafter, the sulfates close to platinum sites (peak near 650°C) will be called "surface" sulfates and surface and bulk sulfates that are not proximal to the platinum sites (peak near 750°C) "bulk" sulfates.

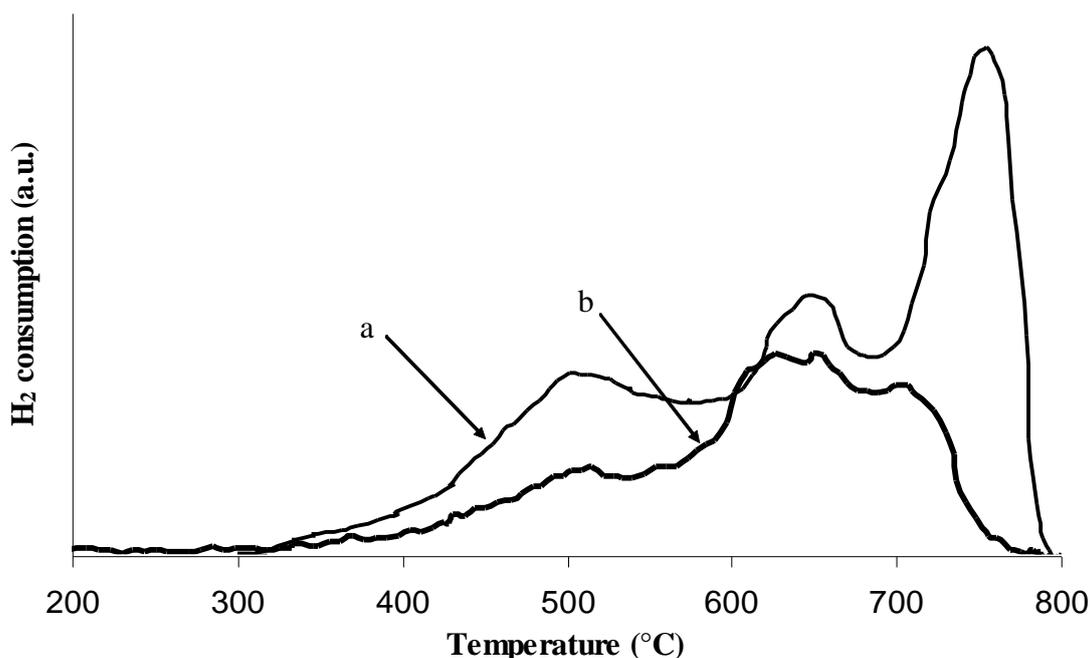


Figure 2: TPR profiles of sulfated catalysts: (a) Pt/20Ba/Al+S and (b) Pt/10Ba/Al+S.

3.2 Thermal ageing of sulfated catalyst under oxidizing conditions

The TPR profiles of the Pt/20Ba/Al+S catalyst treated in oxidizing conditions at different temperatures after sulfation are shown in Figure 3. An increase of the temperature from 400°C (trace a) to 600°C (trace c) leads to the disappearance of the hydrogen consumption corresponding to the reduction of aluminum sulfates, while the peaks attributed to "surface" sulfates and "bulk" sulfates increase. Moreover, the sulfur contents deduced from the hydrogen consumptions are quite similar whatever the temperature of the oxidizing treatment after sulfation (Table 2). These results can be explained by assuming that the SO_x species originating from the decomposition of aluminum sulfates at 600°C would readsorb on the barium sites and/or migrate to the surrounding barium particles [7]. The increase of the oxidizing temperature from 600°C to 800°C involves the disappearance of the peak ascribed to the reduction of "surface" barium sulfates and leads to the apparition of a shoulder near 680°C, just before the peak corresponding to the reduction of "bulk" barium sulfates. These results can be explained by the sintering of both the barium and platinum particles, which was observed by electron microscopy. Indeed, the micrographs of Figure 4 show mainly large barium and platinum crystallites after the thermal treatment at 800°C. Thus, the number of small sulfated barium particles and the catalytic role of platinum for their reduction are decreased.

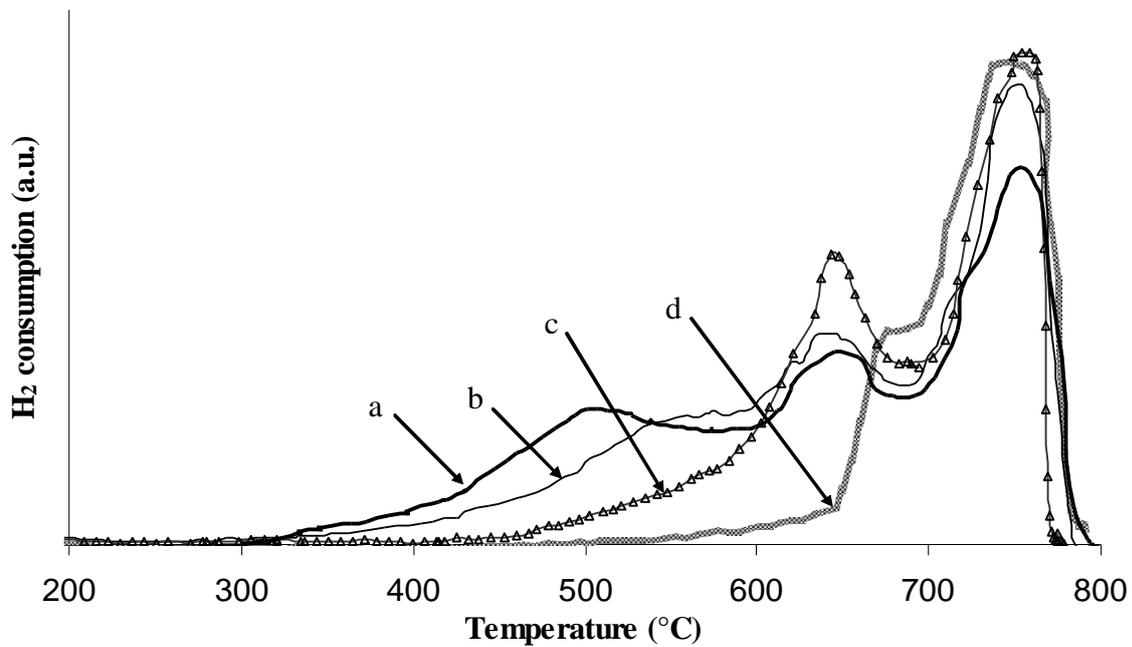


Figure 3: TPR profiles of the sulfated catalyst (Pt/20Ba/Al+S) treated in oxidizing conditions 2h at (a) 400°C, (b) 500°C, (c) 600°C and (d) 800°C.

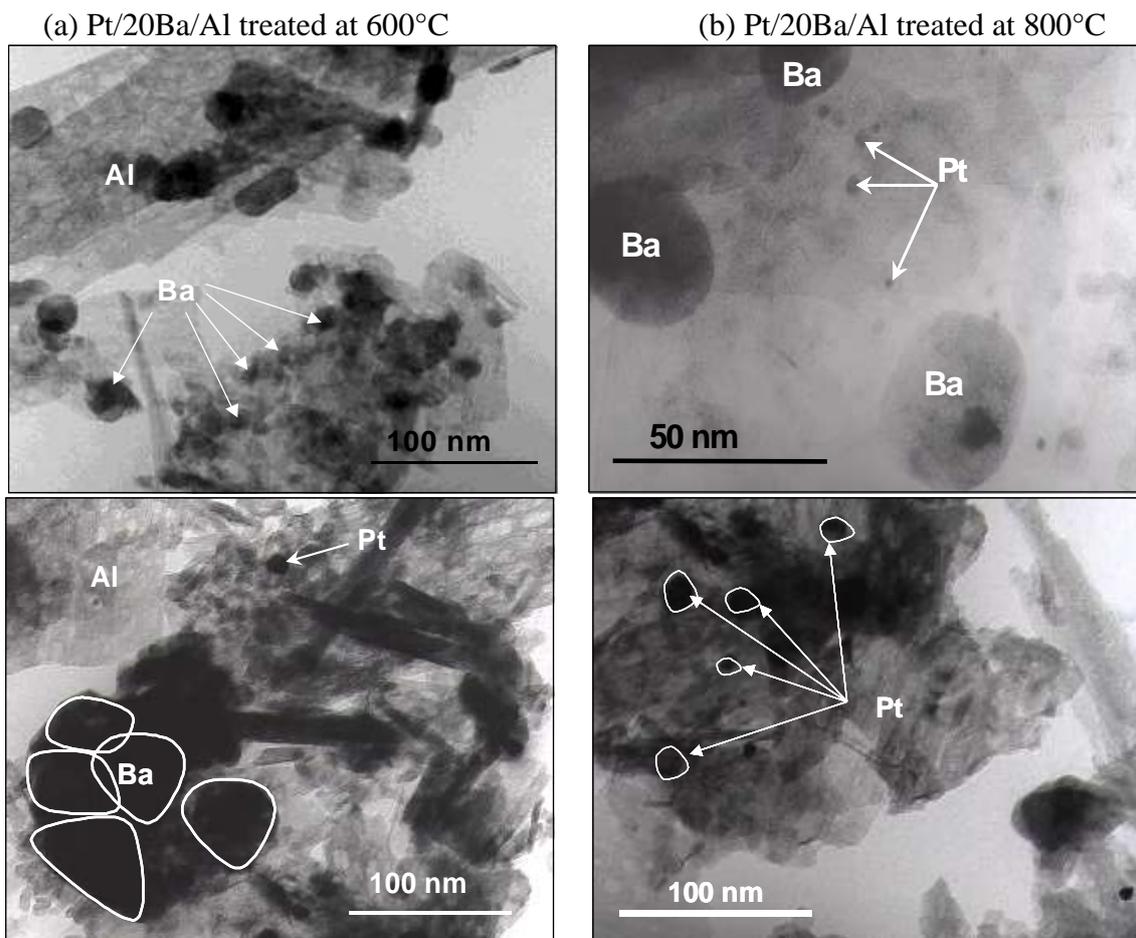


Figure 4: Micrographs of Pt/20Ba/Al (a) fresh and (b) aged at 800°C.

Table 2: Hydrogen consumptions from TPR of the sulfated catalyst (Pt/20Ba/Al+S) reoxidized at different temperatures.

Catalyst	H ₂ consumption ($\mu\text{mol.g}^{-1}$ cata.)	S(%)
Pt/20Ba/Al +S+T400	2520	2.0
Pt/20Ba/Al +S+T500	2581	2.0
Pt/20Ba/Al +S+T600	2530	2.0
Pt/20Ba/Al +S+T800	2400	1.9

The presence of crystallized barium sulfates was confirmed by XRD (barite $2\theta = 25.8$). Figure 5 shows *in situ* powder XRD patterns of the Pt/20Ba/Al+S catalyst heated at 600°C, 800°C and 1000°C. It can be seen that the surface area of the main peak corresponding to the BaSO₄ crystallized phase increases when the oxidation temperature rises from 600°C to 800°C indicating an enhancement of these species. Moreover, the barium sulfates are stable at 1000°C in accordance with the thermodynamic predictions [22]. XRD data also show the formation of a crystalline barium aluminate phase ($2\theta = 28.2$) on the sulfated catalyst treated at 800°C. Actually, the increase of the amount of crystallized barium sulfates and the formation of aluminates lead to a decrease of the specific area from 96 m² g⁻¹ for the fresh catalyst to 64 m² g⁻¹ for the sulfated catalyst treated in oxidizing conditions at 800°C.

In conclusion, the thermal treatment at 800°C under oxidizing atmosphere has a detrimental effect on a sulfated Pt/20Ba/Al+S catalyst with the stabilization of barium sulfates (bulk sulfates), the formation of barium aluminates and the sintering of platinum particles.

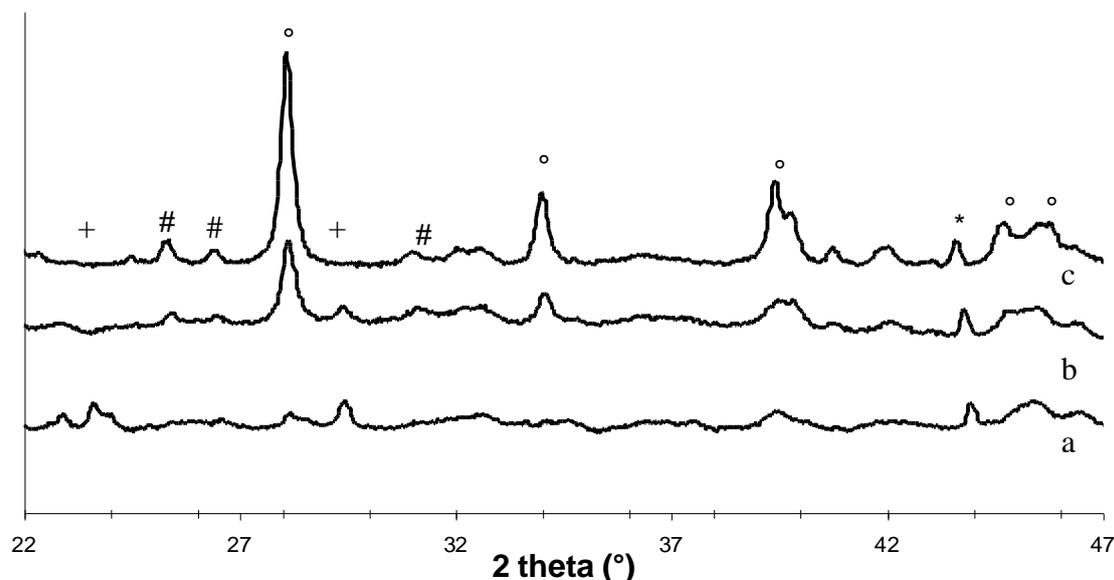


Figure 5: *In situ* powder XRD spectra of a Pt/20Ba/Al+S sample (sulfated at 400°C) and heated at: (a) 600°C, (b) 800°C, (c) 1000°C.

(#): BaSO₄, (°): BaAl₂O₄, (+): BaCO₃, (*): Al₂O₃ γ .

3.3 Regeneration of sulfated catalysts

In order to investigate the conditions for the regeneration of the sulfated Pt/20Ba/Al catalyst, we undertake several regeneration processes under different conditions, starting with regeneration under 1 % H₂/Ar up to 800°C to a more complex mixture, at different temperatures.

The TPR profiles of the Pt/20Ba/Al+S catalyst (Figure 6 trace a) and of the same sulfated catalyst regenerated at 800°C under 1 % H₂/Ar and reoxidized at 400°C are compared Figure 6 traces a and b. A H₂ consumption is still observed with the reoxidized catalyst, which shows that sulfur stored on the catalyst would be only partially eliminated by thermal treatment under hydrogen at 800°C, even though all sulfates were reduced.

In fact, in the presence of H₂, barium and aluminum sulfates can be reduced with the release of SO₂ and H₂S. The SO₂/H₂S ratio depends on the temperature and partial pressure of H₂. The presence of SO₂ and H₂S was observed by Poulston and Rajaram during a H₂-TPR of a sulfated Pt/Ba/Al catalyst under hydrogen [20]. In the present work, all the sulfates are probably reduced toward the sulfides since the amount of sulfur deduced from the hydrogen consumption (2.0 wt %) is equal to the quantity of sulfur introduced as SO₂ during the sulfation treatment (2.0 wt %). However, thermodynamic calculations show that BaS species can be formed either directly following reaction (1):



or by reaction between H₂S produced during the reduction ($\text{BaSO}_4 + 4\text{H}_2 \rightarrow \text{BaO} + \text{H}_2\text{S} + 3\text{H}_2\text{O}$) and BaO:



The presence of BaS crystallized in the cubic system ($2\theta = 27.9$) on Pt/20Ba/Al+S catalyst regenerated under 1 % H₂/Ar at 800°C was confirmed by XRD analysis (Figure 7), in accordance with the results of Poulston and Rajaram [20].

In order to determinate if all barium sulfides formed during the reducing treatment are reoxidized at 400°C, the catalyst reduced at 800°C under hydrogen was reoxidized 30 min under pure oxygen at different temperatures (600 and 800°C) and then tested again in TPR. The profiles of such samples are shown in Figure 6 (traces c and d). In accordance with hydrogen consumptions reported in Table 3, they put in evidence that the sulfides species formed by reduction under hydrogen are not fully reoxidized at 400°C. On the other hand, the comparable values of hydrogen consumptions for the samples reoxidized at 600°C (1654 $\mu\text{mol.g}^{-1}$) and 800°C (1703 $\mu\text{mol.g}^{-1}$) show that all barium sulfides are reoxidized at 600°C. It should be noticed that, for the samples reoxidized at 400°C or 600°C, the maximum of the TPR peak is

observed at an intermediary temperature between the reduction temperatures of "surface" barium sulfates and "bulk" barium sulfates (Figure 6). This result can be explained assuming that under rich conditions, sulfur is stored on barium sites which are different from that responsible for the deposition of sulfates under oxidizing atmosphere. Moreover, BaS and BaSO₄ have not the same crystal structure: BaS is cubic while BaSO₄ is orthorhombic, inducing a reorganization of the material. Nevertheless, the increase of the reoxidation temperature from 600°C to 800°C leads to the formation of "bulk" sulfates with a shift of the TPR peak to higher temperatures. This evolution results from the sintering of both platinum and the Ba component.

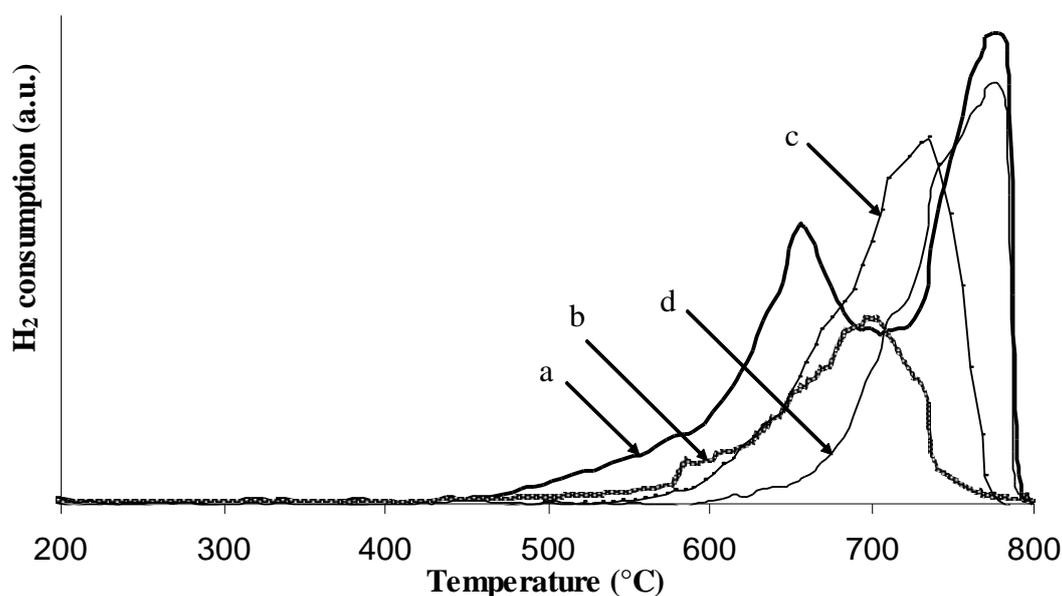


Figure 6: TPR profiles of (a): Pt/20Ba/Al+S+T600 ; (b): (a) reoxidized at 400°C ; (c): (a) reoxidized at 600°C ; (d): (a) reoxidized at 800°C.

Table 3: Hydrogen consumptions from TPR of the sulfated catalyst (Pt/20Ba/Al+S), same reduced at 800°C (TPR protocol) and reoxidized at different temperatures 30 min under pure oxygen.

Catalyst	H ₂ consumption ($\mu\text{mol.g}^{-1}$ cata)
TPR (a) : Pt/20Ba/Al T600 +S	2520
TPR (b) : TPR (a) + reoxidized 400°C	906
TPR (c) : TPR (a) + reoxidized 600°C	1654
TPR (d) : TPR (a) + reoxidized 800°C	1703

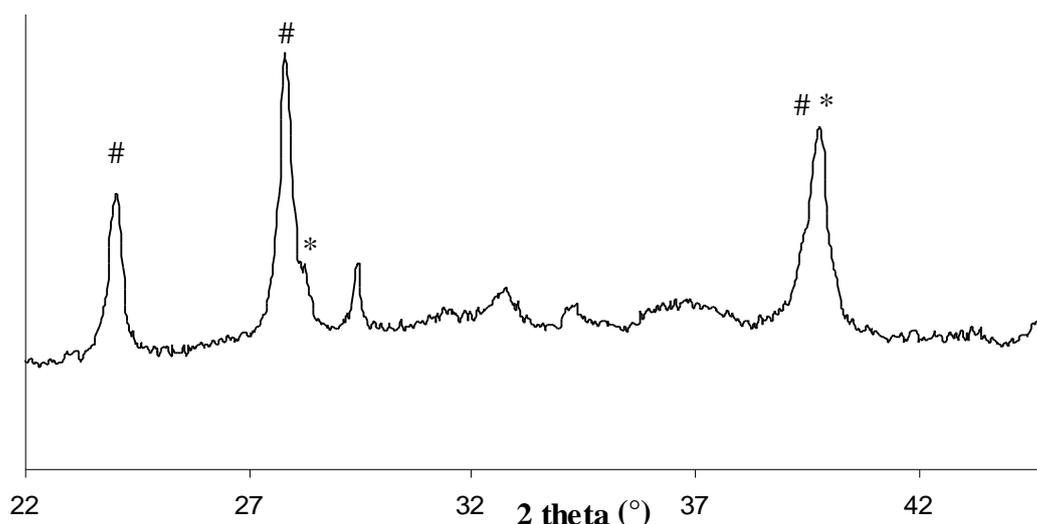


Figure 7: XRD spectrum of a sulfated catalyst (Pt/20Ba/Al+S) after reduction under 1 % H₂/Ar at 800°C. (#) : BaS, (*) : BaAl₂O₄

As H₂O and CO₂ are always present in the exhaust gas of a gasoline engine, the sulfated Pt/Ba/Al catalyst was regenerated with a rich gas mixture containing 2.5% H₂, 10% CO₂, 10% H₂O and N₂. The TPR profile of the catalyst after regeneration under this mixture at 800°C and subsequent reoxidation at 600°C (Figure 8 trace f) shows that this treatment leads to an almost complete elimination of sulfur deposited on the catalyst during sulfation. This result is in agreement with thermodynamic calculations [19] which have established that barium carbonates should replace barium sulfides in rich conditions at this temperature. Note that the formation of H₂S is enhanced in presence of water [7].

In order to examine the effect of temperature on sulfur release under the rich mixture containing CO₂, the Pt/20Ba/Al+S catalyst was regenerated at different temperatures ranging from 700°C down to 550°C. The TPR profiles of the corresponding samples reoxidized under oxygen at 600°C are reported in figure 8. The TPR profile of the sulfated catalyst is also given as a reference. It can be seen from figure 8 and table 4 that the amount of sulfur remaining on the catalyst after the regeneration increases as the temperature decreases. Of course, aluminum sulfates and “surface” barium sulfates are eliminated firstly and the quantity of released “bulk” sulfates increases with the temperature. Surprisingly, it can be noticed that the regeneration at 550°C (Figure 8 trace b) leads to an increase of the hydrogen consumption attributed to the reduction of bulk sulfates in comparison with the sulfated catalyst (Figure 8, trace a). This result can be explained by a migration of sulfur species during the CO₂ rich treatment. The augmentation of the hydrogen consumption with the increase of the reoxidation temperature

(Figure 9 traces (a) to (c)) tends to indicate that sulfur migrates as sulfides. In conclusion, very few sulfur is eliminated when the sulfated Pt/20Ba/Al catalyst is treated with the rich mixture containing CO₂ at 550°C.

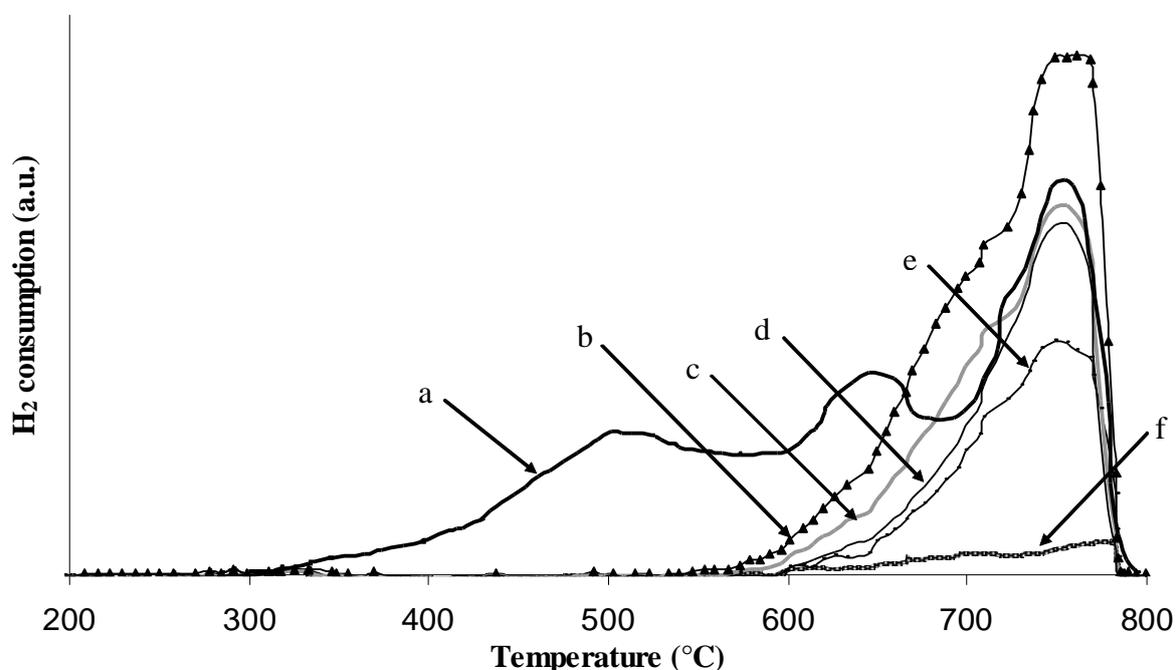


Figure 8: TPR profiles of (a) Pt/20Ba/Al+S and Pt/20Ba/Al+S regenerated under 2.5% H₂, 10% CO₂, 10% H₂O, N₂ at (b) 550°C; (c) 600°C; (d) 650°C; (e) 700°C and (f) 800°C.

Table 4: Hydrogen consumptions from TPR of a sulfated catalyst (Pt/20Ba/Al+S) regenerated under 2.5 % H₂, 10 % CO₂, 10 % H₂O and N₂ at different temperatures and reoxidized at 600°C 30 min under pure oxygen.

Catalyst	H ₂ consumption ($\mu\text{mol.g}^{-1}$ cata)	S (%)
Pt/20Ba/Al+S	2520	2.0
Pt/20Ba/Al+S regenerated at 550°C	2297	1.8
Pt/20Ba/Al +S regenerated at 600°C	1545	1.2
Pt/20Ba/Al +S regenerated at 650°C	1119	0.9
Pt/20Ba/Al +S regenerated at 700°C	995	0.8
Pt/20Ba/Al +S regenerated at 800°C	128	0.1

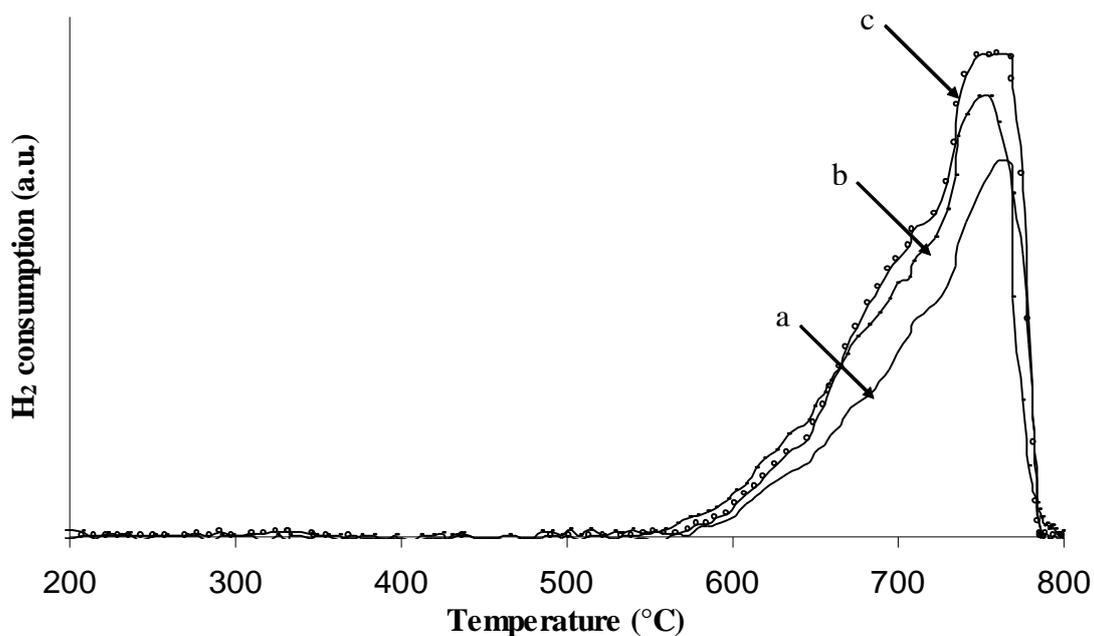


Figure 9: TPR profiles of sulfated catalyst (Pt/20Ba/Al+S) regenerated under 2.5% H₂, 10% CO₂, 10% H₂O and N₂ at 550°C : (a) without reoxidation ; (b) reoxidation at 400°C (c) ; reoxidation at 600°C.

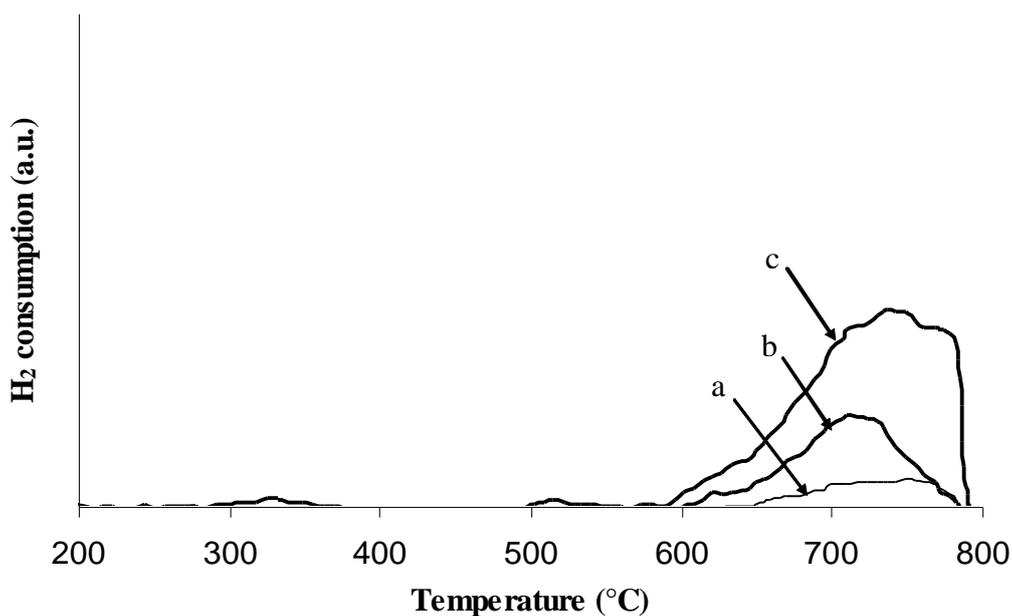


Figure 10: TPR profiles of the sulfated catalyst (Pt/20Ba/Al+S) heated:
 (a) under H₂-CO₂-H₂O-N₂ from ambient to 800°C, then 30 min at 800°C ;
 (b) under N₂ up to 800°C, then 30 min at 800°C under the former mixture;
 (c) under N₂ up to 800°C, then 15 min at 800°C under the former mixture.

In the preceding experiments, the sulfated catalyst has been treated under the reducing gas from ambient to the regeneration temperature (heating rate 10°C/min) and maintained at this temperature for 30 minutes before the characterization by TPR. Finally, we have examined the influence of time on the elimination of sulfur at 800°C under the H₂, CO₂, H₂O and N₂ mixture. The sulfated catalyst was heated under inert gas and the regenerating mixture was admitted only at 800°C for 30 or 15 minutes. The TPR profiles after reoxidation at 600°C are reported in Figure 10. It is clear from the figure that the regeneration strongly depends on time. This result can be explained by assuming that the reduction of sulfates under hydrogen in the presence of CO₂ and H₂O is a slow process and that less sulfates are reduced after a 15 minutes regeneration time. The widening of the TPR peak to higher temperatures after regeneration during 15 minutes (Figure 10 trace c) would corroborate this assumption. Another explanation can be that some BaS is formed during the reducing treatment and that it is progressively replaced by barium carbonates as the regeneration time increases. In order to check the second hypothesis, the Pt/20Ba/Al+S catalyst has been reduced under 1 % H₂/Ar until 800°C and cooled under argon. It was then treated under the rich mixture containing CO₂ at 800°C for 30 minutes after rising of the temperature under the gas mixture. After reoxidation at 600°C under oxygen, the catalyst sample was submitted to a TPR under hydrogen, the profile was exactly the same as that obtained after a direct regeneration of the sulfated catalyst under the mixture containing CO₂ (Figure 8 trace f). Such a result confirms that barium carbonates are able to replace barium sulfides under the conditions previously described. In conclusion, even if barium sulfides can be formed during the treatment in the presence of H₂-CO₂-H₂O up to 800°C, they are progressively eliminated with time at this temperature.

3.4 NO_x storage capacity measurements

NO_x storage capacities of the Pt/20Ba/Al were measured at 400°C in dynamic conditions and were calculated for the first 100s. The NO₂/NO_x ratios (%) after saturation are also reported. They give information about the properties of platinum particles for the oxidation of NO. Table 5 shows that sulfation induces a significant decrease of the NO_x storage capacity, from 51 μmol.g⁻¹ to 19 μmol.g⁻¹. It confirms that sulfur inhibits the NO_x storage capacity due to the formation of stable sulfates which are blocking the storage sites. On the other hand, the sulfation has no detrimental effect on the oxidizing activity of platinum since the NO₂ percentage is slightly higher on the sulfated catalyst. The thermal ageing of the catalyst at 800°C after sulfation leads to a storage capacity comparable to that of the sulfated sample (22 μmol.g⁻¹ versus 19 μmol.g⁻¹). This result points out that a thermal treatment at 800°C under oxidizing

conditions does not allow to regenerate the storage capacity of a sulfated Pt/20Ba/Al catalyst, in accordance with the TPR experiments presented in the first part of the paper. Moreover, the lower NO₂ percentage observed after the ageing of the sulfated catalyst at 800°C confirms the sintering of platinum particles.

Table 5: NO_x storage capacities (μmol.g⁻¹) and NO₂/NO_x ratio (%) of the fresh catalyst (Pt/20Ba/Al), sulfated catalysts aged at 400°C and 800°C, and the sulfated Pt/20Ba/Al catalyst regenerated under 1%H₂ up to 800°C (TPR protocol).

Catalyst	Pt/20Ba/Al	Pt/20Ba/Al+S	Pt.20/Ba/Al +S+T800	Pt/20Ba/Al+S +1%H ₂ 800°C (TPR)
NO _x (μmol.g ⁻¹)	51	19	22	29
NO ₂ /NO _x (%)	25	34	23	29

The treatment of the sulfated catalyst under 1%H₂/Ar up to 800°C for 30 minutes (TPR protocol) does not lead to the recovery of the initial storage capacity (29 μmol.g⁻¹ versus 51 μmol.g⁻¹), probably due to the formation of barium sulfides during this treatment. It means also that a part of sulfur interacts with barium sites which are active for NO_x storage, i.e. "surface" barium. However, even if sulfur is almost completely eliminated by regenerating the catalyst at the same temperature (800°C) with a gas mixture containing H₂, CO₂, H₂O (Figure 8 trace f), the storage capacity is not fully restored, 42 μmol.g⁻¹ versus 51 μmol.g⁻¹ (Figure 11 trace a). This fact can be explained by the deterioration of the storage material at high temperature with the formation of barium aluminates which are less active for the NO_x storage [16, 17]. For the catalyst regenerated at 700°C the same behavior is observed (Figure 11 trace a) even if a larger amount of sulfur is still present on the catalyst (Figure 8 trace e). On the other hand, the storage capacity is entirely recovered by regenerating the catalyst at 650°C under the same mixture. As almost all the bulk barium sulfates are still present after this treatment (Figure 8 trace d), this result confirms that the NO_x storage is a surface process occurring on small barium crystallites proximal to platinum sites [12, 14, 21]. At lower regeneration temperatures (600°C and 550°C), a part of these surface barium sites are still poisoned by sulfur which explains the decrease of the storage capacity as the temperature drops. Moreover, it can be noticed that the oxidizing activity of platinum is little affected by the regeneration temperature, which confirms that the evolutions observed for the NO_x storage capacities originate mainly from the storage material and not from the metal function (Figure 11 trace b).

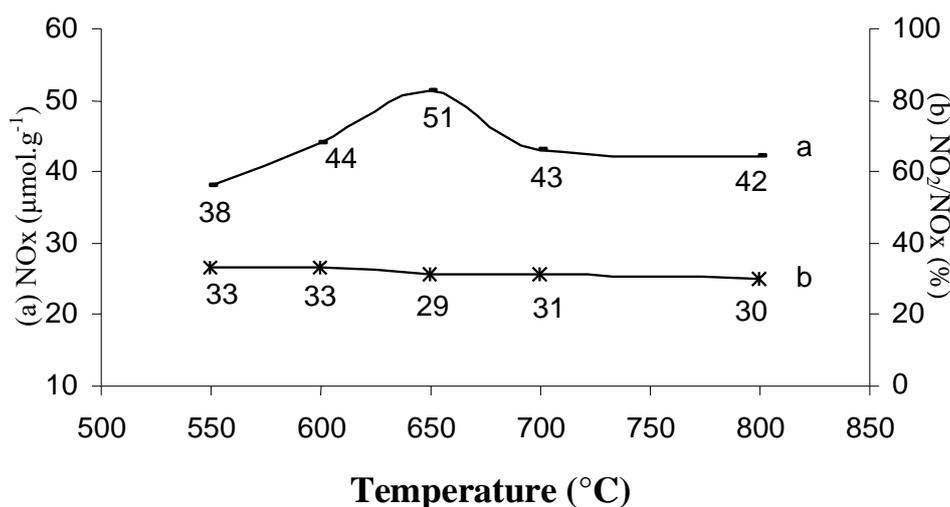


Figure 11: Evolution of: (a) NO_x storage capacity (μmol.g⁻¹) and (b) NO₂/NO_x (%) versus the regeneration temperature under the gas mixture containing H₂, CO₂, H₂O, for the Pt/20Ba/Al+S catalyst.

4 Conclusions

Three main types of sulfates, with different reducibility, were revealed by TPR under hydrogen of a sulfated Pt/Ba/Al model catalyst: aluminum sulfates (~ 500°C), “surface” barium sulfates (~650°C) and “bulk” barium sulfates (~750°C). The reduction of the two formers is promoted by platinum while the metallic phase has no effect on the reduction of the latter.

The thermal treatment of the sulfated Pt/Ba/Al catalyst in oxidizing conditions until 800°C does not eliminate sulfur. Indeed, sulfur coming from the decomposition of aluminum sulfates readsorbs on surface and bulk barium sites leading to less reducible sulfates.

The reduction under hydrogen at 800°C of the sulfated catalyst leads to an incomplete elimination of sulfur with the formation of crystallized barium sulfides identified by XRD. If the regeneration of the sulfated catalyst is undertaken at 800°C in rich hydrogen mixture containing CO₂ and water, all sulfur is eliminated but the initial NO_x storage capacity is not recovered, principally because of the deterioration of the storage material (barium aluminate formation). The regeneration in the former mixture at 650°C leads to the total recovery of the NO_x storage capacity even if the bulk barium sulfates are still present on the catalyst. The duration of the regeneration process at 800°C also plays a role in sulfur elimination, both in the reduction of barium sulfates to sulfides (H₂S and BaS) and in the elimination of barium sulfides by CO₂ and H₂O.

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