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E.C. Corbos, S. Elbouazzaoui, X. Courtois*, N. Bion, P. Marecot, D. Duprez

Laboratoire de Catalyse en Chimie Organique, UMR 6503 CNRS-Université de Poitiers, 40 avenue du recteur Pineau, 86022 Poitiers cedex, France
*Corresponding author: Tel: 33 (0) 549453994, Fax: 33 (0) 549453741, e-mail: xavier.courtois@univ-poitiers.fr.

Abstract
NOx storage capacity, sulphur resistance and regeneration of 1wt%Pt/$Ce_{0.7}Zr_{0.3}O_2$ (Pt/CeZr) and 1wt%Pt /10wt%BaO /$Ce_{0.7}Zr_{0.3}O_2$ (Pt/Ba/CeZr) catalysts were studied and compared to a 1wt%Pt/10wt%BaO/Al_2O_3 (Pt/Ba/Al) model catalyst submitted to the same treatments. Pt/Ba/CeZr presents the best NOx storage capacity at 400°C in accordance with basicity measurements by CO_2 TPD and Pt/CeZr shows the better performance at 200°C mainly due to a low sensitivity to CO_2 at this temperature. For all samples, sulphating induces a detrimental effect on NOx storage capacity but regeneration at 550°C under rich conditions generally leads to the total recovery of catalytic performance. However, the nearly complete sulphur elimination is only observed on Pt/CeZr. Moreover, an oxidizing treatment at 800°C leads to partial sulphates elimination on the Pt/CeZr catalyst whereas a stabilization of sulphates on Ba containing species is observed.

Keywords : NOx trap, SO_2, regeneration, ceria-zirconia.

Introduction
Lean burn engines are interesting regarding the CO_2 emissions. However, in excess of oxygen, the common three-way catalysts are unable to efficiently reduce the nitrogen oxides (NO_x) from the exhaust gas. With this type of engines, one possible way to meet the NOx emission standards is the use of a NOx-trap catalyst. It operates in cycling conditions, mainly under oxidising atmosphere (NO oxidation and NOx storage) with short excursions in rich conditions (NOx reduction). One of the disadvantages of this catalyst is the deactivation, mainly due to sulphur poisoning because sulphates are strongly adsorbed on NOx storage sites, and to thermal ageing.
Typical NOx trap catalysts contain a NOx storage material, classically a barium component, which is able to form sufficiently stable nitrates. Ceria-zirconia materials are usually added in three way catalysis for their oxygen storage capacity, but also they are able to store NOx [1-3]. In the present work, we have studied the NOx-trap properties of a CeZr material with or without barium addition. NOx storage capacity, sulphur resistance and regeneration of Pt/CeZr and Pt/Ba/CeZr catalysts were studied and compared to a Pt/Ba/Al model catalyst submitted to the same treatments.

Experimental

A reference 1wt%Pt/10wt%BaO/Al_2O_3 (Pt/Ba/Al) catalyst was prepared by impregnation of an alumina support with a barium nitrate solution. After calcination of the support at 700°C under air, platinum was impregnated with a $Pt(NH_3)_2(NO_2)_2$ solution. After calcination at 450°C and ageing at 700°C under O_2, H_2O, N_2 mixture, the S_{BET} area of the catalyst was 104 $m^2.g^{-1}$. A 1wt%Pt /10wt%BaO /$Ce_{0.7}Zr_{0.3}O_2$ (Pt/Ba/CeZr, S_{BET} : 47 $m^2.g^{-1}$) and a 1wt%Pt/$Ce_{0.7}Zr_{0.3}O_2$ (Pt/CeZr, S_{BET} : 61$m^2.g^{-1}$) catalysts were prepared by the same way. The sulphated catalysts were exposed to a 100ppm SO_2, 10%O_2, 10%H_2O and N_2 mixture at 300°C for 5h, in order to obtain a 2wt% S content if all the sulphur is adsorbed as sulphates on the catalysts.

The NOx storage capacities were measured in dynamic conditions at 200°C, 300°C and 400°C. Before measurements, the samples (60mg) were pretreated *in situ* for 30 min at 550°C (or 300°C for the sulphated samples), under a 10%O_2, 10%H_2O, 10%CO_2 and N_2 mixture (total flow rate: 10 $L.h^{-1}$). After cooling down to storage temperature, the samples were submitted to a 350ppm NO, 10%O_2, 10%H_2O, 10%CO_2 and N_2 mixture (total flow rate: 10 $L.h^{-1}$). Both NO and NO_2 outlet concentrations were followed by chemiluminescence. The NOx storage capacities are calculated by integration of the NOx recorded profiles for the first 100 seconds. The contribution of the apparatus dead volume is subtracted.

H_2-TPR was used to characterise the sulphur poisoning. Prior to the TPR, the catalyst (65 mg) was first pretreated *in situ* under oxygen at 300°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%H_2/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.

The basicity of catalysts was estimated by thermal programmed desorption (TPD) of CO_2. Adsorption of CO_2 was carried out on the activated material (500°C, 15min, 1%O_2/He flow) at room temperature for 1h. After flushing under 1%O_2/He mixture at room temperature to remove the physisorbed species, the CO_2 thermal desorption was followed by thermal conductivity from room temperature up to 800°C.

Results and discussion

The NOx storage capacities measured at 200°C, 300°C and 400°C for the fresh catalysts are given in Table 1. The Pt/Ba/Al catalyst exhibits its highest storage capacity at 400°C, with 18.3 $\mu mol.g^{-1}$. At lower temperature, it decreases down to 13.1 $\mu mol.g^{-1}$ and 13.7 $\mu mol.g^{-1}$ at 200°C and 300°C, respectively. Compared to the Pt/Ba/Al catalyst, the NOx storage capacity of the Pt/CeZr at 300°C is in the same range (14.6 $\mu mol.g^{-1}$ for Pt/CeZr). In opposition with the trend observed with Pt/Ba/Al, the NOx storage capacity of Pt/CeZr is similar at 300°C and 400°C (Table 1) and slightly increases at 200°C (17.1 $\mu mol.g^{-1}$). The Pt/Ba/CeZr catalyst has a Pt/Ba/Al like behaviour: the NOx storage capacity is nearly the same at 200°C and 300°C and increases at 400°C. At low temperature, the storage capacity is lower on Pt/Ba/CeZr and Pt/Ba/Al than on the barium free Pt/CeZr catalyst, at 9.4 $\mu mol.g^{-1}$, 13.1 $\mu mol.g^{-1}$ and 17.1 $\mu mol.g^{-1}$, respectively.

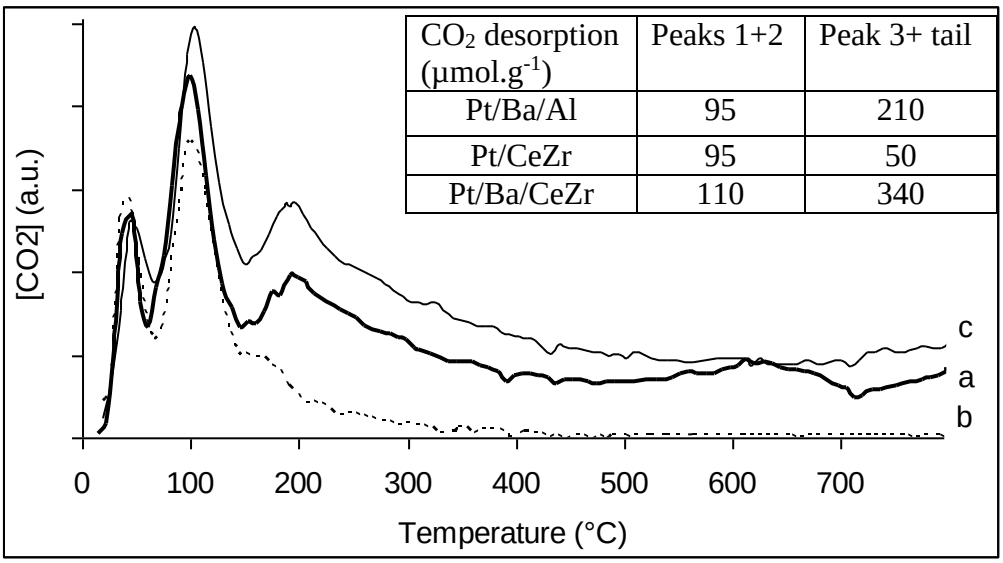
Table 1: NOx storage capacities (μmol.g^{-1}) calculated for the first 100 seconds (μmol.g^{-1}) and BET surface areas (m^2.g^{-1}, values between brackets). Influence of the catalyst treatment.

	Storage temperature (°C)	NOx storage capacity (μmol.g^{-1})			
Catalyst	.	fresh	sulphated	regenerated	sulphated + treated at 800°C
Pt/Ba/Al	200	13.1 (107)	4.6 (110)	10.2	3.4 (110)
	300	13.7	4.6	13.0	11.1
	400	18.3	6.2	13.8	9.8
Pt/CeZr	200	17.1 (61)	1.5 (54)	17.7	6.2 (39)
	300	14.6	5.3	15.8	8.2
	400	15.0	4.5	15.3	7.6
Pt/Ba/CeZr	200	9.4 (47)	5.5 (37)	7.8	5.5 (37)
	300	11.8	6.4	11.0	6.5
	400	23.3	9.7	21.3	8.5

To explain these different behaviours, basic properties of the catalysts were studied by CO_2 TPD. Flego and coll. [4] attributed different arbitrary basic strengths depending on the CO_2 desorption temperature for alkali modified alumina compounds. A low temperature peak, with a maximum near 100°C, was attributed to weak basic sites, a second peak in the 180-200°C range was correlated to medium basic sites and the CO_2 desorbed near 500°C was related to strong basic sites. The TPD profiles obtained with the catalysts studied in the present work are reported in Fig. 1. They all exhibit two peaks near 45°C and 100°C which are practically similar for the three samples after deconvolution. A small shoulder is then observed near 200°C with Pt/CeZr (curve b), whereas a more intensive peak at 200°C and a long CO_2 desorption tail until 800°C can be observed with Pt/Ba/Al (curve a). It is even more significant with Pt/Ba/CeZr (curve c).

These results indicate a weaker basicity for the Pt/CeZr catalyst. In addition, Pt/Ba/Al and Pt/Ba/CeZr catalysts present the same types of strong basic sites in the 200°C-800°C temperature range but Pt/Ba/CeZr exhibits the highest basic sites amount.

The basicity measurements are in accordance with the NOx storage capacities at 400°C, which are rising as the basicity increases: Pt/Ba/CeZr>Pt/Ba/Al> Pt/CeZr. The higher storage capacity at 400°C for Pt/Ba/Al and Pt/Ba/CeZr catalysts can be attributed to a larger amount of strong basic sites.



CO_2 desorption ($\mu mol.g^{-1}$)	Peaks 1+2	Peak 3+ tail
Pt/Ba/Al	95	210
Pt/CeZr	95	50
Pt/Ba/CeZr	110	340

Fig. 1: CO_2 TPD profiles of fresh catalysts: Pt/Ba/Al (a), Pt/CeZr (b), Pt/Ba/CeZr (c).

However, the stronger basic material does not exhibit the highest NOx storage capacity at 200°C. As the storage tests are carried out with CO_2 and H_2O in the feed stream whereas the CO_2 adsorption prior to TPD test is done without water, the effects of both CO_2 and H_2O on the storage capacities were investigated at 200°C. The different NOx storage capacities are reported in Table 2. The comparison of the NOx storage capacities at 200°C measured with or without CO_2 and water in the inlet gas shows that the addition of both CO_2 and H_2O leads to a more or less inhibiting effect depending on the catalyst composition. The more detrimental effect is observed for the Pt/Ba/CeZr catalyst, the low performance arising from the presence of CO_2. As for the Pt/Ba/Al and Pt/CeZr catalysts, they are a little sensitive to either CO_2 or H_2O, but when the two components are present at the same time in the gas stream, an inhibiting effect appears. The later is more significant on alumina sample where H_2O alone seems to present a slight negative impact. Our results regarding the effect of CO_2 and H_2O on the Pt/Ba/Al catalyst confirmed those reported by Epling and coll.[5].

Table 2: NOx storage capacities at 200°C of the fresh catalysts calculated for the first 100 seconds ($\mu mol.g^{-1}$). Influence of CO_2 and H_2O in the feed stream.

Catalyst	NOx storage capacity ($\mu mol.g^{-1}$) at 200°C			
	without CO_2 and H_2O	with only H_2O	with only CO_2	with CO_2 and H_2O
Pt/Ba/Al	26.2	19.9	24.1	13.1
Pt/CeZr	29.1	26.9	24.8	17.1
Pt/Ba/CeZr	26.0	25.1	8.7	9.4

In conclusion, the higher NOx storage capacity of the Pt/CeZr catalyst at 200°C results from its lower sensitivity to the presence of water and CO_2 in comparison with the Pt/Ba/Al and Pt/Ba/CeZr catalysts.

Then, the catalysts were sulphated to obtain a theoretical content of 2wt% S. The NOx storage capacities strongly decrease for all samples (Table 1). For instance, for the intermediate temperature of 300°C, it decreases from 13.7 to 4.6 µmol.g^{-1} for Pt/Ba/Al (-66%), from 14.6 to 5.3µmol.g^{-1} for Pt/CeZr (-64%) and from 11.8 to 6.4 µmol.g^{-1} for Pt/Ba/CeZr (-46%). It should be noted that Pt/CeZr is very sensitive to sulphating for NOx storage at 200°C, with a capacity of only 1.5µmol.g^{-1}.

The samples were characterised by BET surface area measurements (Table 1), TPR and XRD. The TPR profile of the fresh Pt/Ba/Al catalyst (Fig.2-1) exhibits only one small peak at low temperature which corresponds to the reduction of platinum and to the hydrogen adsorption on platinum (confirmed by tests with higher sample loadings). With Pt/CeZr, in addition to the platinum reduction, a significant hydrogen consumption is observed around 250°C, in agreement with literature [6,7]. It is attributed to cerium reduction promoted by noble metal and corresponds to several layers of the support. A small hydrogen consumption related to bulk reduction starts around 600°C and the reduction is not achieved at 800°C. After barium addition, the only change is about the main peak which is now broader and centred near 300°C. It means that the oxygen mobility of Pt/CeZr is affected by the presence of barium. The quantification of this peak shows a small decrease (-27% after barium addition, Table 3) which can be related to the decrease of the BET area from 61 to 47 $m^2.g^{-1}$ (-23%).

The TPR profile of the sulphated Pt/Ba/Al (Fig. 2-2) exhibits two main peaks related to sulphate reduction. It has been previously established [8] that the first one near 500°C can be ascribed to the reduction of surface aluminium sulphates, the second one at 600°C is related to surface barium sulphates, and the shoulder at 700°C corresponds to the reduction of bulk barium sulphates. Assuming a H_2/SO_4^{2-} ratio of 4 for the sulphate reduction ($X\text{-}SO_4 + 4H_2 \rightarrow X\text{-}S + 4H_2O$ or $X\text{-}SO_4 + 4H_2 \rightarrow X\text{-}O + H_2S + 3H_2O$), a total sulphur content of 1.6wt% was deduced from hydrogen consumption (Table 3). The TPR profile of the sulphated Pt/CeZr (trace b) exhibits a large H_2 consumption between 400 and 575°C, corresponding to a total sulphur content of 1.3% after subtraction of the support contribution. The reduction of the first layers of the support is observed near 250°C, giving a broader peak compared to the fresh Pt/CeZr catalyst. The oxygen mobility is partially inhibited at low temperature by sulphating treatment but the amount of reducible cerium is comparable on the fresh and sulphated samples (720 µmol.g^{-1} and 730 µmol.g^{-1}, respectively).

The addition of Ba to CeZr leads to a slight shift of the H_2 consumption due to the reduction of sulfates to higher temperature, in the 400-600°C temperature range (Fig. 2-2). However, the calculated amount of sulphur does not change, at 1.3wt%. The sulphating treatment does not induce significant change for the Ba/CeZr support reduction.

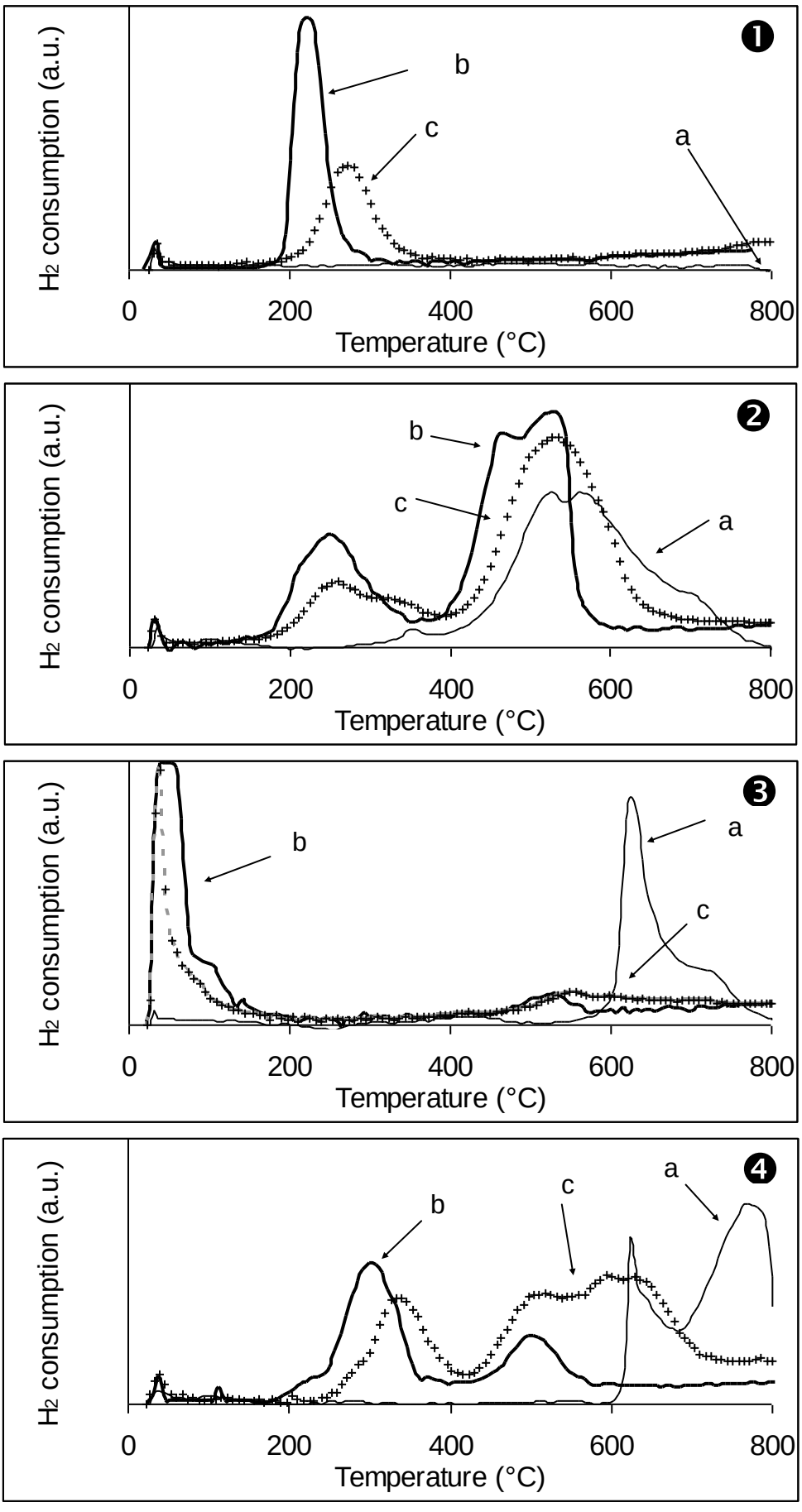


Fig. 2: TPR profiles of (❶) fresh, (❷) sulfated, (❸) regenerated and (❹) sulfated and re-oxidized at 800°C catalysts: Pt/Ba/Al (a), Pt/CeZr (b), Pt/Ba/CeZr (c).

Table 3: H_2 consumption ($\mu mol.g^{-1}$) from TPR experiments: low temperature peak (T<400°C) / sulphates reduction peak (400-800°C) / sulphur content (%).

Catalyst	fresh	sulphated	regenerated	Sulphated + treated at 800°C
Pt/Ba/Al	- / - / -	- / 1950 / 1.6	- / 1035 / 0.8	- / 1785 / 1.4
Pt/CeZr	720 / - / -	730 / 1580 / 1.3	750 / 130 / 0.1	645 / 245 / 0.2
Pt/Ba/CeZr	525 / - / -	500 / 1565 / 1.3	510 / 340 / 0.3	505 / 1445 / 1.2

In a previous study [8], the regeneration of a 1wt%Pt/20wt%BaO/Al_2O_3 model catalyst was studied. It was shown that a reducing treatment like a H_2-TPR does not allow to restore the initial NOx storage capacity and that only a fraction of the sulphur is eliminated because of the formation of BaS species. In accordance to other studies [9,10], the same result was obtained with Pt/CeZr, only 2/3 of the initial deposited sulphur are eliminated after a TPR under hydrogen (Table 3). It was also demonstrated in ref [8] that a regeneration treatment at high temperature under a H_2, CO_2, H_2O and N_2 mixture permits to fully recover the NOx storage capacity at 300°C of a Pt/Ba/Al catalyst. Thus, such a treatment at 550°C was applied to the three samples studied in this work. The characterization by TPR of the regenerated samples shows that only 38% of deposited sulphur is eliminated for Pt/Ba/Al while almost all sulphur is eliminated for Pt/CeZr and Pt/Ba/CeZr (Fig. 1-3). For both Pt/Ba/CeZr and Pt/CeZr catalysts, this reducing treatment also leads to a remarkable change of the cerium reducibility. The first layers are then reduced at much lower temperature, starting with platinum reduction near ambient. The shift of the peak towards lower temperature after a reducing treatment can be attributed, according to Fan and coll. [6], to a structural re-organization of ceria-zirconia and a re-dispersion of Pt particles. No change of the cerium reduction percentage is observed.

After the regeneration treatment, the initial NOx storage capacities are fully recovered for the three catalysts at 200°C and 300°C (Table 1). However, at 400°C only the catalysts supported on Ce-Zr material have recovered their initial NOx storage capacity. As shown, the storage capacity at 400°C depends on the basicity of the catalyst: the more the material is basic the higher is the storage capacity. The partial regeneration of NOx storage capacity at 400°C for the Pt/Ba/Al catalyst can be explained by the remaining sulphates which would decrease the basicity of the storage sites located in their vicinity or by the poisoning of the stronger basic sites by sulphates.

The influence of a thermal treatment under oxidizing atmosphere at 800°C on sulphated catalysts was also studied. Previously [8], it was observed that such a treatment on a sulphated 1%Pt/20%BaO/Al_2O_3 catalyst leads to a stabilization of barium sulphates (formation of bulk sulphates) and to the formation of barium aluminate in addition to a sintering of platinum particles. Figure 2-4 shows the same trend with the Pt/Ba/Al catalyst. Aluminium sulphates are eliminated but sulphates are remaining on the catalyst, mainly as bulk $BaSO_4$ which were also detected by XRD (Fig. 2 and 3). These very stable species are difficult to eliminate under reducing treatment. The Pt/Ba/CeZr catalyst also exhibits a sulphate stabilisation after the oxidising treatment at 800°C (Fig. 2), without no significant elimination of the deposited sulphur. However, the reduction temperature of the stabilized sulphates remains lower than that on Pt/Ba/Al, 600-650°C versus 750°C. Nevertheless, the X-ray diffractogramm of the sulphated Pt/Ba/CeZr catalyst indicates the presence of bulk barium

sulphate as in the case of Pt/Ba/Al catalyst. Then, the ceria-zirconia support should assist barium sulphate reduction.
Conversely, the TPR profile of the sulphated Pt/CeZr catalyst treated in the same conditions shows significant sulphate elimination from 1.3% to 0.2%, with SO_2 production detected by mass spectrometry. This result is in agreement with the literature [11], ceria sulphate decomposition is starting near 600°C.

The treatment at 800°C of sulphated catalysts leads to different behaviours for the NOx storage capacities. For the three tested temperatures, the Pt/CeZr catalyst recovers nearly half of its initial capacity, except at 200°C. In addition to the impact of residual sulphur, the loss of storage capacity in comparison with that of the fresh catalyst can also be attributed to the surface area decrease from 61 to 39 $m^2.g^{-1}$. For the Pt/Ba/CeZr catalyst, there is no change of both the NOx storage capacity and the surface area compared to the sulphated sample. The Pt/Ba/Al behaviour is more complex. The surface area remains constant whatever the treatment. However, compared to the sulphated catalyst, a supplementary capacity lost is observed at 200°C, a half recovery is obtained at 400°C and near 80% of the initial capacity is recovered at 300°C.

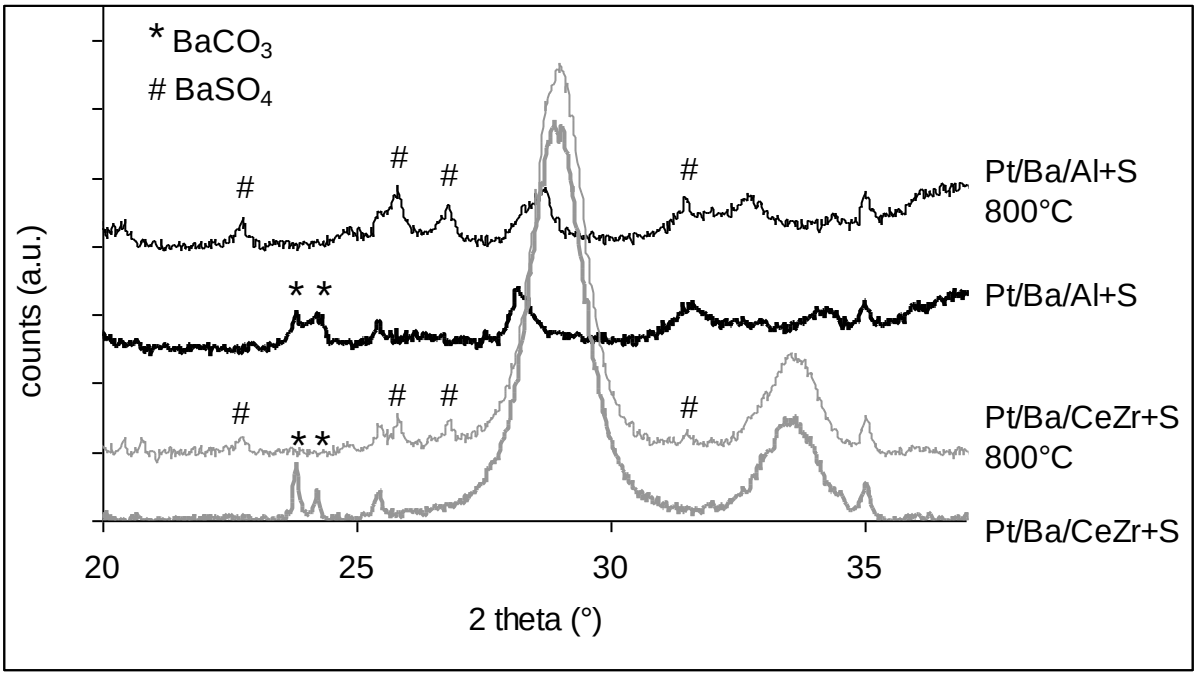


Fig. 3: XRD diffractogramm of sulphated catalysts (noted +S) and of sulphated catalysts treated at 800°C in oxidizing conditions (noted +S 800°C).

Conclusion

In this study, we investigated the NOx storage capacity, sulfur resistance and regeneration of three model catalysts: Pt/Ba/Al, Pt/Ba/CeZr and Pt/CeZr. At 400°C, the NOx storage capacity (for the first 100s) decreases following the sequence Pt/Ba/CeZr>Pt/Ba/Al>Pt/Ce/Zr, in accordance with basicity measurements by CO_2 TPD. However, the Pt/CeZr catalyst shows the better performance at 200°C mainly due to a low sensitivity to CO_2 at this temperature.
Sulphation induces a detrimental effect on NOx storage capacity whatever the catalyst. The regeneration at 550°C under rich conditions (H_2, CO_2, H_2O and N_2) generally leads to the

total recovery of catalytic performance whatever the catalyst sample. Nevertheless, this treatment allows the complete elimination of sulfur species only on the Pt/CeZr catalyst.
The thermal treatment under oxidizing conditions at 800°C allows to eliminate partly sulphates on the Pt/CeZr catalyst whereas on contrary it produces a stabilization of sulphates on Ba containing species.

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References
[1] P. Svedberg, E. Jobson, S. Erkfeldt, B. Andersson, M. Larsson, M. Skoglundh, Top. Catal., 30 (2004) 199
[2] S. Philip, A. Drochner, J. Kunert, H. Vogel, J. Theis, E.S. Lox, Top. Catal., 30, (2004) 235
[3] L.F. Liotta, A.Macaluso, G.E. Arena, M. Livi, G. Centi, G. Deganello, Catal. Today, 75 (2002) 439
[4] C. Flego, G. Cosentino, M. Tagliabue, Appl. Catal. A: General, 270 (2004) 113
[5] W. Epling, J.E. Parks, G. C. Campbell, A. Yezerets, N.W. Currier, L.E. Campbell, Catal. Today, 96 (2004) 21
[6] J. Fan, X. Wu, R. Ran, D. Weng Appl. Surf. Sci., 245 (2005) 162
[7] M.F. Luo, X.M. Zheng, Appl. Catal. A, 189 (1999) 15
[8] S. Elbouazzaoui, E.C. Corbos, X. Courtois, P. Marecot, D. Duprez, Appl. Catal. B, 61 (2005) 236
[9] P. Bazin, O.Saur, J.C. Lavalley, G. Blanchard, V. Visciglio, O. Touret, Appl. Catal. B, 13 (1997) 265
[10] T. Luo, J.M Vohs, R.J. Gorte, J. Catal 210 (2002) 397
[11] T. Luo, R.J. Gorte, Appl. Catal. B, 53 (2004) 77