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Characterisation by TPR, XRD and NO_x storage capacity measurements of the ageing by thermal treatment and SO₂ poisoning of a Pt/Ba/Al NO_x-trap model catalyst.

Sanaa ELBOUAZZAOUI, Xavier COURTOIS*, Patrice MARECOT, Daniel DUPREZ

Laboratoire de Catalyse en Chimie Organique, UMR 6503
CNRS-Université de Poitiers,
40 avenue du recteur Pineau, 86022 Poitiers cedex, France

Abstract

The deactivation of a Pt/Ba/Al₂O₃ NO_x-trap model catalyst submitted to SO₂ treatment and/or thermal ageing at 800°C was studied by H₂ temperature programmed reduction (TPR), X-ray diffraction (XRD) and NO_x storage capacity measurements.

The X-ray diffractogram of the fresh sample exhibits peaks characteristic of barium carbonate. Thermal ageing leads to the decomposition of barium carbonate and to the formation of BaAl₂O₄. The TPR profile of the sulphated sample shows the presence of i) surface aluminium sulphates, ii) surface barium sulphates, iii) bulk barium sulphates. The exposure to SO₂ after ageing leads to a small decrease of the surface barium-based sulphates, expected mainly as aluminate barium sulphates. This evolution can be attributed to a sintering of the storage material. TPR experiments also show that thermal treatment at 800°C after the exposure to SO₂ involves the decomposition of aluminium surface sulphates to give mainly bulk barium sulphates, also pointed out by XRD. Thus, the thermal treatment at 800°C leads to a stabilization of the sulphates.

These results are in accordance with the NO_x storage capacity measurements. On not sulphated catalysts, the treatment at 800°C induces to a decrease of the NO_x storage capacity, showing that barium aluminate presents a lower NO_x storage capacity than barium carbonate. Sulphation strongly decreases the NO_x storage capacity of catalysts, whatever the initial thermal treatment, showing that barium sulphates inhibit the NO₂ adsorption. Moreover, the platinum activity for the NO to NO₂ oxidation is lowered by thermal treatments.

Introduction

In 1997, many industrialized countries have adopted the Kyoto protocol aiming at the reduction of the greenhouse effect gas production. CO₂, which is largely produced by vehicles, was particularly concerned. Then, many car manufacturers have to reduce the fuel consumption of the vehicles to reach a production of CO₂ of 140g/km in 2008. In order to attain this objective, the manufacturers have developed gasoline engines working in lean mixture (with an excess of oxygen). They consume less fuel than the current engines functioning at the stoichiometry (reductant/oxidant ratio close to 1). However, the depollution of the exhaust gas from lean-burn engines is a difficult problem. Whereas in stoichiometric conditions, a three-way-catalyst simultaneously converts carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO_x), in lean mixture, it is not effective enough for the NO_x treatment.

* corresponding author : xavier.courtois@univ-poitiers.fr

Until now, commercial catalysts do not work satisfactorily in lean conditions and should be strongly improved.

A way to treat the exhaust gas from lean-burn engines is to use a three-way catalyst coupled with a NO_x-trap catalyst [1]. This system operates in two steps. In oxidizing atmosphere (period T), NO is oxidized over precious metals and NO_x are stored, mainly as nitrates, on an oxide storage material (usually barium oxide). During a short rich mixture period (~T/10 period), NO_x desorbs and are reduced on the precious metals. One of the disadvantages of this catalyst is its deactivation, which is mainly due to sulphur poisoning [1, 2, 3] and thermal ageing (sintering and/or phase transformation) [4].

In the present work, these two ways of deactivation were investigated over a Pt/Ba/Al₂O₃ model catalyst submitted to SO₂ treatment and/or thermal ageing (600°C or 800°C). The different samples were characterised by XRD, H₂ temperature programmed reduction (TPR) and NO_x storage capacity measurements.

Experimental

Catalysts preparation:

First, barium-alumina support was prepared by impregnation, with a barium nitrate solution, of an alumina powder (supplied by Rhodia, BET surface area: 115 m²/g), in order to obtain a 20 wt% BaO content. After drying the support was calcined at 600°C for 4 h under synthetic air (3.6 L.h⁻¹ flow rate and a 2°C.min⁻¹ heating rate). The BET surface area was then 80 m².g⁻¹. Secondly, platinum was impregnated with a dinitro-diamino platinum solution to obtain a 1 wt % Pt catalyst. After drying, the catalyst was calcined at 450°C under synthetic air, reduced at 500°C under H₂ and activated at 600°C for 6 h under a mixture of 10% O₂, 7% H₂O, 10% CO₂ and N₂ (noted fresh catalyst). Then, it was exposed to a 100ppm SO₂, 10% O₂, 7% H₂O and N₂ mixture at 400°C for 5 h and/or to a thermal ageing at 800°C (10% O₂, 7% H₂O, 10% CO₂ and N₂ mixture). Also, a 1 wt% Pt / Al₂O₃ (Pt/Al) catalyst was prepared in the same way.

Characterisation of the catalysts:

The different samples were characterised by temperature programmed reduction (TPR). The sample was in situ pretreated under oxygen at 400°C for 30 min and finally cooled to room temperature. After flushing under argon for 45 min, the reduction was then carried out between room temperature and 800°C under a 1 % H₂/Ar mixture, using a 5°C.min⁻¹ heating rate. Hydrogen consumption was followed by thermal conductivity.

The XRD measurements were carried out with a Siemens D500 diffractometer using the Cu K_α radiation ($\lambda=1.54 \text{ \AA}$).

Before NO_x storage capacity measurements, the samples were first pretreated at 400°C for 30 min under a 10% O₂, 5% H₂O in N₂ mixture (total flow rate : 10 L.h⁻¹). Then, the reactor was purged with N₂ at the same temperature. After this treatment, the sample was submitted to a 600ppm NO, 10% O₂, 5% H₂O in N₂ mixture (total flow rate : 10 L.h⁻¹), at 400°C. The NO_x (NO + NO₂) concentration in the mixture was followed by chemiluminescence. The NO_x storage capacity is estimated by integration of the recorded profile after subtraction of the "dead volume" reactor.

Results and discussion

The TPR profiles of the different samples are given figure 1. The fresh Pt/Al catalyst (Fig.1, trace a) exhibits only one peak at low temperature (near 60°C) which corresponds to the reduction of platinum. This relatively low reduction temperature is due to the low reoxidation temperature of the catalyst [5]. After exposure to SO₂, a second and broad peak, starting at

300°C, is observed with a maximum at 450°C (Fig.1, trace b). It can be attributed to the reduction of the surface aluminium sulphates [2].

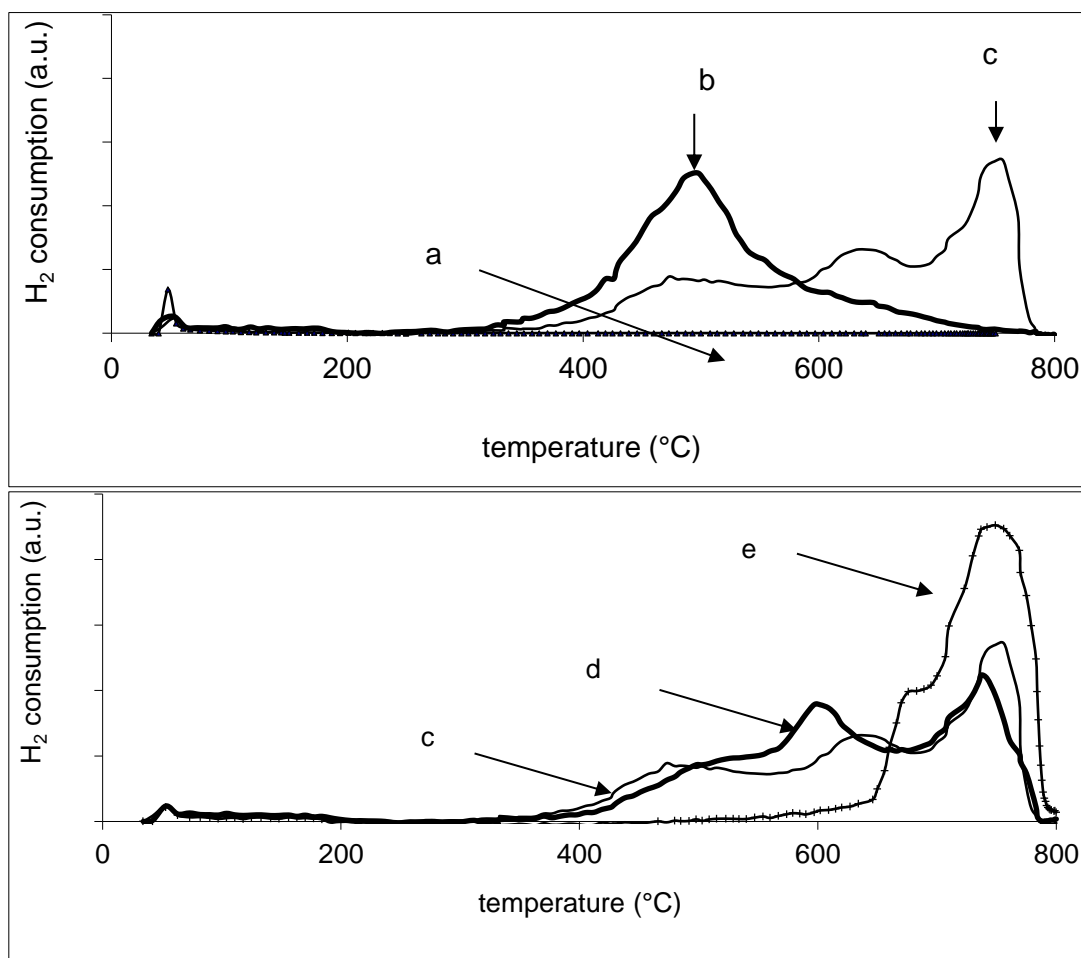


Fig. 1: TPR profiles: (a) fresh Pt/Al catalyst; (b) sulphated (400°C) Pt/Al catalyst; (c) sulphated (400°C) Pt/Ba/Al catalyst; (d) aged (800°C) Pt/Ba/Al catalyst and sulphated (400°C); (e) sulphated (400°C) Pt/Ba/Al catalyst and aged (800°C).

On the sulphated Pt/Ba/Al catalyst (Fig.1, trace c), the peaks ascribed to platinum and aluminium-sulphates reduction also appear but two new peaks are observed at higher temperatures (640°C and 750°C). Surface and bulk barium sulphates have been previously identified by FTIR on a sulphated Pt-Ba type catalyst [3]. The presence of crystallised BaSO_4 in our sample cannot be strictly confirmed by XRD because BaSO_4 and BaCO_3 give very narrow peaks. Nevertheless, the two TPR peaks at 640°C and 750°C can be attributed to reduction of surface and bulk barium sulphates, respectively. A comparison between sulphated Pt/Al and sulphated Pt/Ba/Al catalysts shows a decrease of the alumina sulphates contribution (consumption at 450°C). This indicates that for the Pt/Ba/Al catalyst, a large part of the alumina support is covered by the storage material. The integration of the aluminium sulphates reduction peaks of both samples gives a coverage ratio of 44%.

Thermal ageing at 800°C on fresh Pt/Ba/Al catalyst followed by exposure to SO_2 gives a similar TPR profile (Fig. 1, trace d). A small increase of the H_2 consumption corresponding to the aluminium sulphates reduction peak is observed (+7 %), whereas the H_2 consumption corresponding to the barium sulphates reduction peaks decreases in the same proportion. This can be attributed to a sintering of the storage material after the thermal treatment. Moreover,

the temperature of the peak attributed to surface barium sulphates decreases from 640°C to 600°C. Thus, these sulphates are less stable, because of the change in the storage material structure. In fact, the main effect of a 800°C treatment before sulphation is pointed out by the XRD experiments (Fig.2). The barium carbonate initially visible on the fresh sample (trace a) is no longer detected whereas bulk barium aluminate is clearly identified (trace b). The TPR peak at 600°C would be then attributed to sulphates adsorbed on barium aluminate.

Thermal treatment at 800°C after exposure to SO₂ involves the disappearance of the TPR peak ascribed to aluminium sulphates (Fig.1 trace e). Moreover, only the reduction peak of the bulk barium sulphates is remaining, with a higher intensity. In addition, the BaSO₄ phase appears in the XRD pattern of this sample (Fig.2), bearing out the attribution of the high temperature TPR peak. XRD also shows the formation of bulk barium aluminate on sulphated samples.

The integrations of (c), (d) and (e) profiles (Fig.1) between 200°C and 800°C give similar H₂ consumptions. Thus, a treatment at 800°C in oxidizing atmosphere does not eliminate the sulphates stored on the catalyst at 400°C. The thermal ageing leads to a restructuring and a stabilisation of the sulphates with formation of crystallised BaSO₄. Meanwhile, the thermal ageing also induces the BaAl₂O₄ formation.

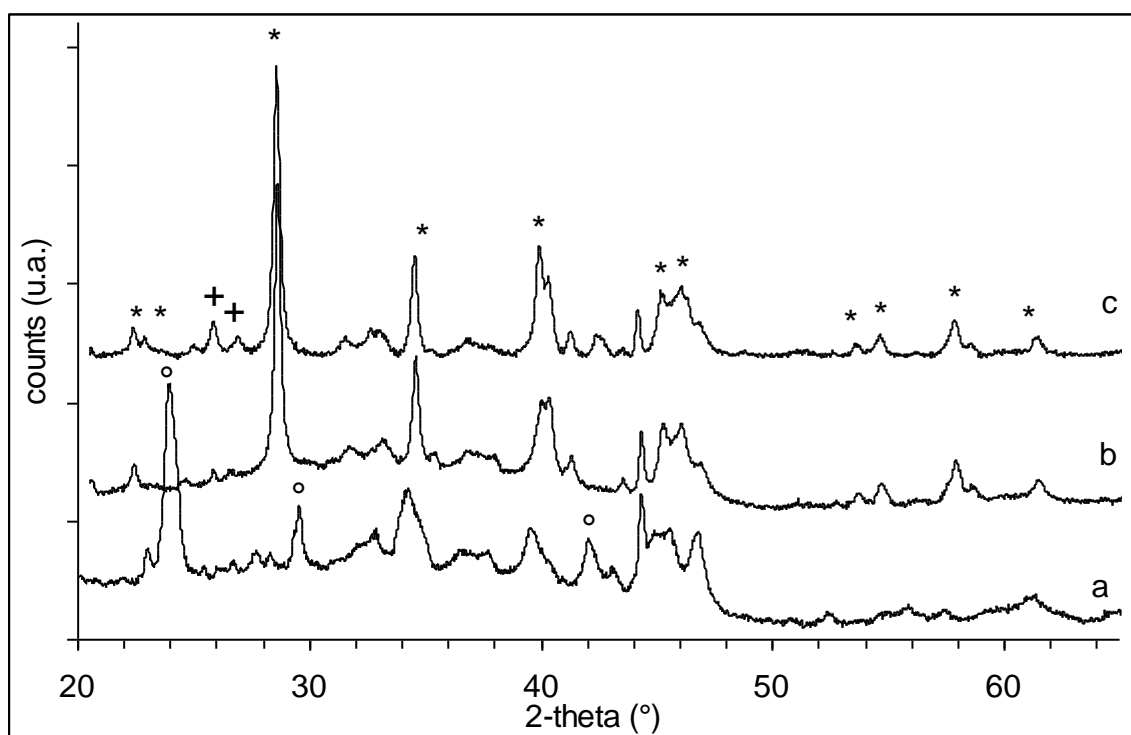


Fig.2: XRD patterns of (a) fresh Pt/Ba/Al catalyst; (b) aged (800°C) Pt/Ba/Al catalyst; (c) sulphated Pt/Ba/Al catalyst and aged (800°C).

(°) : BaCO₃ ; (*) : BaAl₂O₄ ; (+) : BaSO₄

NO_x storage capacities were measured at 400°C in dynamic conditions. Some examples of profiles are given in figure 3. The experiment time can be relatively long (more than one hour) in order to obtain the equilibrium adsorption on the catalyst.

The storage capacities of the different samples are calculated during the first 1000 s. The contribution of the apparatus (dead volumes), obtained from a test without any catalyst, has been subtracted. The calculated capacities are given in Table 1.

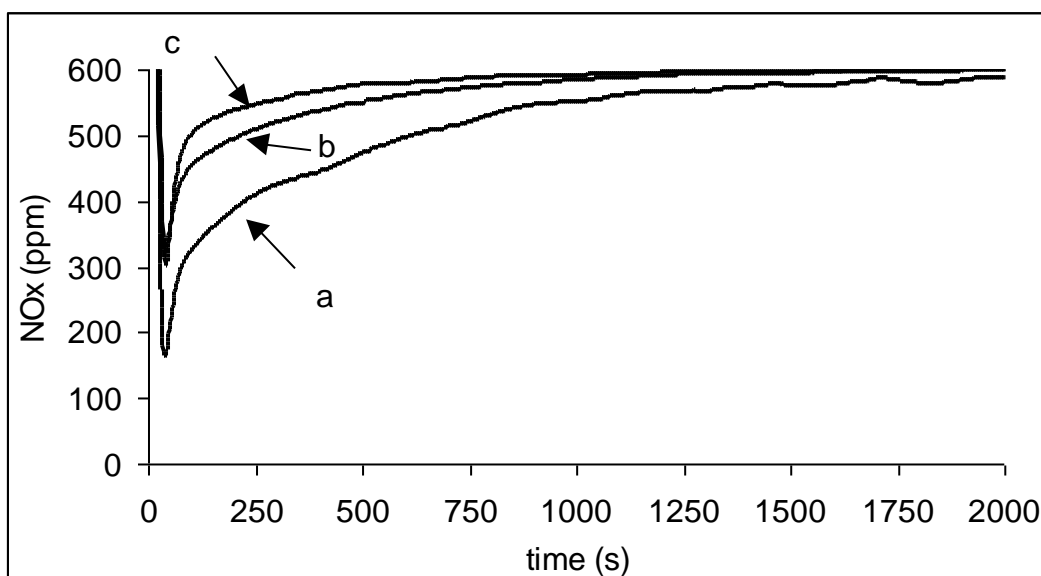


Fig.3: NO_x storage capacity measurements at 400°C on the Pt/Ba/Al catalyst treated in different conditions: (a) fresh Pt/Ba/Al catalyst; (b) aged (800°C) Pt/Ba/Al; (c) aged (800°C) Pt/Ba/Al catalyst and sulphated.

Table 1: NO_x storage capacities (contribution of the reactor is subtracted) and NO₂/NO_x ratios after saturation of the Pt/Ba/Al catalyst treated in different conditions.

Sample	fresh Pt/Al	fresh Pt/Ba/Al	aged (800°C) Pt/Ba/Al	sulphated Pt/Ba/Al	sulphated Pt/Ba/Al followed by ageing (800°C)	Aged (800°C) Pt/Ba/Al and sulphated
NO _x storage capacity (μmol _{NOx} /g)	11	194	103	40	35	45
NO ₂ /NO _x ratio at saturation	33	33	19	28	23	20

The test with the fresh Pt/Al catalyst gives a small storage capacity of 11 μmol_{NOx}/g. The fresh Pt/Ba/Al catalyst exhibits a storage capacity of 194 μmol_{NOx}/g. The thermal treatment at 800°C leads to a decrease of this capacity down to 103 μmol_{NOx}/g, corresponding to a loss of approximately 50%. This can be attributed to the small sintering of the storage material previously seen by TPR, but the main reason for this decrease is probably the formation of BaAl₂O₄.

For all samples, sulphation strongly decreases the NO_x storage capacity of the catalysts. The remaining capacities are between 35 μmol_{NOx}/g and 45 μmol_{NOx}/g, whatever the initial thermal treatment (loss of 77-82%, Table 1). As it has been shown in previous works [6, 7], these results confirm that sulphation inhibits the NO₂ adsorption.

Moreover, after saturation of the storage component, the NO₂/NO_x ratio gives information about the properties of the precious metal phase for the NO+1/2 O₂ ↔ NO₂ oxidation reaction. For all the studied samples the NO₂/NO_x ratio is lower than the thermodynamic value (conversion of 44% at 400°C). The fresh catalyst presents a ratio of 33%. A small decrease has been observed after SO₂ exposure (NO₂/NO_x of 28%). On the other hand, a treatment at 800°C leads to a stronger decrease of the NO₂/NO_x ratio to 19-23%, with no influence of the pre-exposure to SO₂. These worse oxidation properties can be ascribed to the platinum sintering.

CONCLUSIONS

This study showed that temperature programmed reduction, XRD and NO_x storage capacity measurements are good techniques to characterise the ageing of a Pt/Ba/Al NO_x-trap model catalyst.

The sulphation at 400°C of a fresh catalyst involves the formation of three types of sulphates observed by TPR : aluminium sulphates, surface and bulk barium sulphates. There remains only 20% of the initial NO_x storage capacity. The thermal ageing (800°C) of the fresh catalysts leads to a small decrease of the barium surface available for sulphates adsorption (TPR) but the NO_x storage capacity is reduced at 44%. These results can be explained by formation of BaAl₂O₄ (as seen by XRD). An oxidizing treatment at 800°C after exposure to SO₂ allows the decomposition of the surface aluminium sulphates but it gives mainly crystallised barium sulphates, more stable.

Finally, the oxidation activity of platinum is less affected by the sulphates poisoning than by the thermal treatments at high temperature.

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