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**NO_x storage properties of Pt/Ba/Al model catalysts prepared by different methods.
Beneficial effects of a N₂ pre-treatment before hydrothermal aging.**

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Abstract

The influence of a pre-treatment at 700°C, either under a O₂/N₂ mixture or only under N₂, and followed by a hydrothermal aging at 700°C under wet air, was studied for Pt/Ba/Al NSR model catalysts prepared by different methods: (i) successive impregnation of Ba and Pt, (ii) co-addition of Pt and Ba and (iii) barium precipitation followed by Pt impregnation. The catalysts were evaluated by NO_x storage capacity measurements and were characterized by N₂ adsorption, XRD, CO₂-TPD, H₂ chemisorption and H₂-TPR. The pre-treatment under N₂ largely improves the NO_x storage performance in the whole studied temperature range (200°C-400°C), with or without H₂O and CO₂ in the inlet gas. The better NO_x storage properties of the catalysts treated under N₂ before aging are due to (i) a higher NO oxidation activity (mainly linked to a higher platinum dispersion) (ii) a higher number of NO_x storage sites resulting from a higher barium dispersion, and consequently to (iii) a higher Pt-Ba proximity.

Keywords: NO_x storage, NO_x trap, Ba, barium, Pt, platinum, thermal aging, dispersion, proximity, N₂ treatment.

1. Introduction

Exhaust gases from automotive engines have an important impact on the air quality and consequently on the human health, especially in urban areas with high traffic density. In order to reduce this impact, more and more stringent regulations are imposed to automotive manufacturers. Diesel and direct injection gasoline engines have a potential for improving fuel consumption efficiency and so to reduce CO₂ emissions. However, as they operate under an excess of oxygen (lean conditions), it is difficult to reduce nitrogen oxides. A promising solution to overcome this issue was introduced in the mid-1990s by Toyota with the NO_x storage-reduction (NSR) concept [1]. NO_x traps contain essentially precious metals (Pt, Pd and Rh) for the redox functions and alkaline and/or alkaline earth metals (usually Ba) for the NO_x storage function. This system works under transient conditions. During the lean periods, NO is first oxidized into NO₂ which is then trapped as nitrite and/or nitrate on the basic storage material. Before unacceptable amounts of NO_x slip through the catalyst, the engine switches to rich conditions (excess of hydrocarbons) for a short period where the stored NO_x are released and reduced into N₂ over the precious metal (Rh).

Model Pt/Ba/Al₂O₃ NSR catalysts have been extensively studied during the last 15 years and several mechanisms were proposed for NO_x storage-reduction [2]. The first step of the NO_x storage, NO oxidation into NO₂, takes place mainly on platinum sites. The NO oxidation activity depends on both platinum dispersion and platinum oxidation degree. Putna et al. [3] showed that small platinum particles (about 2 nm) are less active for NO oxidation than larger ones (about 10 nm). This result is explained by the easier formation of platinum oxides on very small particles, platinum oxides being less active for NO oxidation than metallic form. As a result, the activity shows an optimum with the platinum dispersion. The platinum dispersion is strongly influenced by the treatment conditions of the catalysts. As Graham et al. [4] showed, platinum sintering is more marked when the catalyst is treated under O₂ and H₂O than without O₂ or under H₂. Recently, Kim et al. [5] showed that the platinum crystallite size in Pt/Ba/Al catalysts plays a critical role in determining the NO_x storage activity. They concluded that the prevention of the platinum sintering is a key factor for the design of durable NO_x trap catalysts. Concerning the NO_x storage, it is generally admitted that it takes place on multiple types of barium sites which have different activities. Surface barium sites located in platinum proximity are the most active [6-11]. Moreover, barium can be present in the catalyst as BaO, Ba(OH)₂ and BaCO₃, depending on the reaction conditions [12,13]. Lietti et al [13] have shown that the NO_x storage occurs more preferentially on BaO than on Ba(OH)₂ and then on BaCO₃. However, after exposure to CO₂, Ba-containing species were roughly present in the catalyst under two main carbonate forms characterized by their thermal stability: low temperature (LT-BaCO₃) and high temperature (HT-BaCO₃) species [11]. The LT-BaCO₃ species, which correspond to well dispersed species on the alumina support, exhibit a higher activity toward NO_x storage-reduction than bulk-like (HT-BaCO₃) sites. Thus, one of the main challenges is to improve the barium dispersion in order to obtain the highest NO_x storage capacity. Another parameter influences the NO_x storage performance: the Pt-Ba proximity. Kabin et al. have shown that the NO_x storage takes place in earlier stages mainly on the barium sites located in platinum proximity [14]. A spill-over mechanism involving oxygen and NO₂ migration from platinum to barium has been suggested [6,15]. The NO_x storage capacity also depends on the temperature, with a volcano like curve. At high temperature (usually T > 400°C), the NO_x storage is limited by the stability of adsorbed species, whereas at low temperature (usually T < 250°C), it is limited by the low NO oxidation rate.

We recently reported that barium and platinum dispersions, and thus Pt-Ba proximity of the catalyst and NO_x storage properties are influenced by both support oxide and Ba loading [16]. It is expected that these parameters can also be influenced by the preparation method of the catalysts and by the pre-treatment conditions. To our knowledge, only a few studies report the influence of the preparation method [4,5,17-19]. Cant et al. [17] have recently studied the influence of the barium precursor on the NO_x storage-reduction properties. They have shown that the use of nitrate or acetate as barium precursor does not significantly influence the NO_x storage activity. Dawody et al. [18] also studied the influence of the platinum precursor on the NO_x storage properties of Pt/Ba/Al catalysts. The authors have demonstrated that the nitrate precursor led to better properties compared to H₂Pt(Cl)₆, [Pt(NH₃)₄(OH)₂ and Pt(NH₃)₂(NO₂)₂. This result was attributed to a higher Pt dispersion. Li et al. have studied the influence of the preparation method of a Pt/Mg/Al catalyst [19]. They found that the impregnation method (Mg and then Pt on alumina) led to better NO_x storage properties than the co-precipitation method (Mg+Al and then Pt impregnation). Concerning the thermal treatments, Kim et al. [5] studied the catalyst aging under different atmospheres and observed, in agreement with the results of Graham et al. [4], that the sintering of platinum is less significant when the aging is undertaken under rich conditions. However, information about the barium behavior under different atmospheres is lacking.

Then, the characteristics of an efficient NO_x trap catalyst are well known and the aim of this work was to study the influence of the nature of the activation treatment (N₂ or N₂/O₂) before aging in order to improve Pt and Ba dispersions. The samples are Pt/Ba/Al model catalysts prepared by different methods. The influence of CO₂ and H₂O on the NO_x storage capacity (rapid NO_x uptake) of the different catalysts was systematically investigated to get an in-depth view of catalyst NO_x storage performance under realistic conditions.

2. Experimental

Catalyst preparation

The Pt/Ba/Al₂O₃ catalysts, with 1wt% Pt and 10wt% or 20wt% BaO, were prepared by three different methods. In the first method, the barium was impregnated on alumina (Axens, 230 m².g⁻¹) from a Ba(NO₃)₂ solution. After drying at 120°C, the material was calcined at 700°C for 4 h under air. Platinum was then impregnated from a Pt(NH₃)₂(NO₂)₂ aqueous solution. This method is named impregnation (noted I). In the second method, the Ba/Al₂O₃ material was prepared by the precipitation of barium salt (Ba(NO₃)₂) on alumina powder. First, the alumina was added in ultra-pure water and the temperature was raised to 60°C. After the pH was increased at 10 by adding an ammonia solution, the dry barium salt was added. After drying at 120°C and calcination at 700°C for 4h under air, platinum was then impregnated using the same way as described above. This protocol is named as the precipitation method and is noted (P). In the third method, platinum and barium were successively added without intermediate calcination. First, platinum was added into a solution containing the alumina powder at 60°C. After Pt addition, the barium salt was also added in the same solution. The catalyst was then dried at 120°C. This method is called co-addition and noted CA.

After drying, the different catalysts were pre-treated at 700°C for 4h under a mixture containing 10% O₂ balanced in N₂, or only N₂. Finally, the catalysts were aged at 700°C for 4h under a mixture containing 10% O₂, 5% H₂O and N₂, and cooled down under the same mixture until 100°C. The catalysts are noted Pt/xBa/Al where x is 10wt% or 20wt% BaO.

It is important to note that the catalysts may evolve during long storage at room temperature. Particularly, a growing of bulk BaCO₃ can be observed. As a consequence, all the tests presented in this study were performed using the same procedure, i.e. with the same delay between the catalyst preparation and the consecutive tests and characterizations. Only the delay for the XRD experiment was not rigorously controlled, and the data were used accordingly.

NO_x storage capacity measurements

Before the NO_x storage capacity measurements, the catalyst (60 mg) was pretreated at 550°C for 30 min under a 10% O₂ and N₂ mixture (total flow rate: 10 L.h⁻¹), and then cooled down to the storage temperature under the same mixture. The sample was then submitted to a 350 ppm NO, 10% O₂ and N₂ mixture (total flow rate: 10 L.h⁻¹) at 200°C, 300°C or 400°C. Effect of water and carbon dioxide was also studied. In this case, 10% H₂O and 10% CO₂ were added in both pretreatment and measurement mixtures. The gas flow was introduced using mass-flow controllers (Brooks), except for H₂O which was introduced using a thermostated saturator. Both NO and NO_x concentrations (NO+NO₂) were followed by chemiluminescence with a COSMA Topaze 2020 apparatus. H₂O was removed prior to NO_x analysis with a membrane dryer. The NO_x storage capacity was estimated by the integration of the recorded profile for the first 100s after subtraction of the contribution of the apparatus (dead volume) deduced from a test without catalyst. The platinum oxidation activity was estimated as the NO₂/NO_x ratio (%) at saturation (usually about 900s). Under the conditions used in the NO_x storage measurements (60 mg, 10 L.h⁻¹, 350 ppm NO), 67 μmol NO_x per gram of catalyst are injected in 100s.

Catalyst characterizations

- Nitrogen adsorption, XRD, and TEM

N₂ adsorption was carried out at -196°C with a Tristar 3000 Micromeritics apparatus. Prior to the measurements, the samples were pretreated at 350°C under vacuum for 12h in order to eliminate the adsorbed species. The specific surface areas were calculated using the BET method.

X-ray powder diffraction was performed at room temperature with a Siemens D5005 Bragg-Brentano (θ-θ) apparatus using a Cu Kα radiation (λ=0.154056 nm). The diffractograms were recorded with a step of 0.02° 2θ, with a dwell time of 2s. The powder was deposited on a silicium wafer. The crystalline phases were identified by comparison with the ICDD database files.

Transmission electron microscopy (TEM) images were obtained with a Philips CM 120 microscope operating at 120 kV, equipped with an energy-dispersive X-ray detector (EDX).

- Hydrogen chemisorption

The noble metal dispersion of Pt-containing catalysts was determined using the H₂ chemisorption method. The catalyst was first reduced under pure hydrogen at 500°C for 1h and then flushed at the same temperature under argon for 3h. The reactor was cooled under argon at room temperature, where hydrogen was dosed on the sample until saturation. After flushing under argon for 10 min, the sample was exposed to hydrogen again. The amount of chemisorbed hydrogen was taken as the difference between the two hydrogen exposures.

- CO₂ thermodesorption

Prior experiments, the catalyst was pre-treated at 550°C for 30 min under a 1% O₂/He flow and cooled down to 50°C. This temperature was chosen after IRTF and XRD experiments [16] in order to decompose only surface BaCO₃, without BaCO₃ bulk decomposition. The adsorption of CO₂ was carried out for 1h at this temperature. After flushing under a 1% O₂/He mixture at 50°C to remove the physisorbed species, the CO₂ temperature programmed desorption (TPD) was followed from 50°C up to 700°C by thermal conductivity.

- Temperature programmed reduction (TPR) of sulfated catalysts

In the sulfation process, the catalyst was exposed to a 100ppm SO₂, 10% CO₂, 10% O₂, 10% H₂O and N₂ mixture at 300°C for 5h. If all the sulfur is deposited on the catalyst, a maximum of 2wt% S is obtained. After flushing at 300°C under 10% CO₂, 10% O₂, 10% H₂O and N₂ mixture for 15min, the sample was cooled down to room temperature under the same mixture except for water which was removed from the flow at 100°C.

Prior to the TPR test, the sulfated 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 % 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.

Some experiments were also carried out on un-sulfated catalysts to study the platinum reduction. In this case, 500mg of hydrothermally aged catalyst were used and the *in situ* pre-treatment was carried out at 550°C under O₂.

3 Results and discussion

3.1 NO_x storage capacity measurements

NO_x storage capacity in the absence of H₂O and CO₂

Figure 1 reports the NO_x storage capacities measured for the first 100s (rapid NO_x uptake) in the absence of H₂O and CO₂ in the inlet mixture. Generally, the catalyst preparation method (I, P or CA) has only a weak effect on the NO_x storage capacity, whatever the storage temperature, the barium loading, and the pre-treatment before aging. Only the CA method leads to a slight improvement of the NO_x storage capacities when the catalysts were treated under O₂/N₂ before aging. However, this behavior is no longer observed when the catalysts are treated at 700°C under N₂. These results seem to contradict those recently obtained by Li et al. [19] who showed that the impregnation method led to a higher NO_x storage capacity than the precipitation one for a Pt/Mg/Al catalyst. It can be explained by the co-precipitation method of Al and Mg which led to a very low surface area: 42 m².g⁻¹ versus 142 m².g⁻¹ for the impregnation method. In our study, barium is precipitated on an alumina powder of 230 m².g⁻¹. Then, the preparation method has no significant impact on the surface area of our catalysts (Table 1).

In opposition to the preparation method, the NO_x storage performances are strongly influenced by the pre-treatment atmosphere before aging. Figure 1 shows that the N₂ pre-treated catalysts exhibit higher NO_x storage capacities whatever the barium loading, the barium deposition method and the temperature test. For the different Pt/10Ba/Al catalysts (Figure 1A), the N₂ pre-treatment led to an increase of the NO_x storage capacity by an average factor of 1.36. The improvement is even more

significant for the 20 % BaO catalysts (factor of 1.74), leading to a maximum value of $55\mu\text{mol.g}^{-1}$ at 400°C (Figure 1B).

It can be also noted in Figure 1 that the NO_x storage capacities of the 10% BaO loaded catalysts are generally not influenced by the temperature of the experiment. In opposition, the NO_x storage capacities of the 20% BaO loaded catalysts increase with the temperature test. This can be attributed to a stronger basic strength for the 20% BaO loaded catalysts [16]. As large Ba particles exhibit a higher basic strength than well dispersed barium particles [16], it induces that the barium dispersion should be higher for the 10% BaO loaded catalysts compared to the 20% BaO loaded catalysts. This idea is further developed in the “catalysts characterizations” part.

In order to know if the N₂ pre-treatment contributes to the increase of the total number of storage sites or just improve the rapid storage, the NO_x storage capacity was then calculated after 900s. Results are reported in Figure 2. The NO_x storage saturation is generally obtained at this time under the experimental conditions used in the present work. Figure 2 shows that the number of available NO_x storage sites depends on both the preparation method and the pre-treatment of the catalyst before aging. In comparison with the O₂/N₂ pre-treatment, the N₂ pre-treatment effectively leads to an increase of the total number of storage sites whatever the preparation method. Moreover, in this case, the NO_x storage curves exhibit a maximum at 300°C which can be attributed to a lower proportion of strong basic sites, and therefore to a higher barium dispersion [16]. This hypothesis will be discussed further in the text. For the 10% BaO catalysts, the higher performances are observed with the co-addition method, while the impregnation one leads to the worst storage properties whatever the pretreatment. The reverse behavior is observed for the 20 % BaO catalysts.

The NO_x storage capacity can also depend on the NO oxidation activity since it was established that the oxidation activity is the limiting step mainly at low temperature, whereas at higher temperature, the NO_x storage is limited rather by the nitrates stability [2]. Nevertheless, a higher oxidation activity would also lead to an increase of the nitrates stability due to the increase of the partial pressure of NO₂, thus shifting the decomposition temperature of nitrates [20].

As Figure 3 shows, the NO oxidation activity, estimated at saturation (900 s) by the NO₂/NO_x ratio (%), is also significantly improved by the N₂ pre-treatment. Compared to the O₂/N₂ pre-treatment, the NO₂/NO_x ratio increases by an average factor of 2 at 200°C and 300°C , and 1.4 at 400°C . Thus, the improvement of the NO oxidation activity should also contribute to the increase of the rapid NO_x storage in the 200°C - 400°C temperature range (Figure 1).

As previously suggested, the higher performance of the N₂ pre-treated catalysts can be also linked to a higher barium dispersion. Piacentini et al. [11] showed the existence of various types of barium species with different NO_x storage activities in the absence of H₂O and CO₂. The most active sites are the well dispersed barium particles. Their results are supported by those of Gangwal et al. [21] who proposed two different barium sites, semi-bulk and bulk species. The latter authors also showed that the NO_x trapping occurs first on semi-bulk species whereas the bulk sites are active only in the later stage of trapping. We also reported in a recent paper [16] that, in the presence of water and carbon dioxide, an increase in barium dispersion led to a higher NO_x storage capacity and to a decrease of the inhibiting effect of CO₂. So, in order to examine if the nitrogen pre-treatment has an influence on the barium dispersion, the influence of H₂O and CO₂ on the rapid NO_x storage (100s) was further investigated.

NO_x storage capacity measured in presence of H₂O and CO₂ in the inlet gas

The NO_x storage capacities measured for the first 100s in presence of CO₂ and H₂O are reported in Figure 4. The presence of water is known to affect the oxidation activity of the catalysts, leading to a decrease of NO oxidation activity of Pt. Concerning CO₂, it competes with NO_x for the adsorption on the storage sites. The more the basic strength of the storage sites is high, the more the carbon dioxide competes [2,16, 22].

The loss of the NO_x storage capacity (%) due to the presence of H₂O and CO₂ is near 50-60% for the O₂/N₂ pre-treated catalysts and lower than 40% for the N₂ pre-treated catalysts before aging. These results suggest that the nitrogen pre-treatment leads to a higher barium dispersion, since CO₂ has a lower inhibiting effect on the NO_x storage capacity. Finally, the differences of NO_x storage capacities between the two pre-treatments are even more significant in the presence of H₂O and CO₂. Thus, the N₂ pre-treated catalysts exhibit NO_x storage capacities more than two times higher than the O₂/N₂ pre-treated catalysts. In fact, the average increase factor is 2.0 and 2.4 for the 10 % BaO and 20% BaO contents, respectively. This beneficial effect is attributed to both a higher activity for the NO_x storage and a lesser inhibiting effect of H₂O and CO₂. Figure 4 also shows that the catalysts prepared by the impregnation method present the lower NO_x storage capacities and the higher inhibiting effect of CO₂ and H₂O, indicating that the impregnation method leads to a lower barium dispersion.

Otherwise, in the presence of CO₂ and H₂O, barium loading has nearly no significant influence on the NO_x storage capacity (Figure 4). These results are in agreement with those reported in a recent paper [16], and are attributed to an increase of the inhibiting effect of CO₂ and H₂O with the barium loading due to an increase of the basicity of the catalysts.

Besides, some additional tests were performed in order to show if the beneficial impact of the N₂ pre-treatment remains after sulfur poisoning and sulfur regeneration of the hydro-thermally aged catalysts. It was previously shown that for Pt/Ba/Al catalysts without N₂ pre-treatment, the initial NO_x storage capacity was recovered after regeneration [23]. Then, some similar tests were performed on the aged Pt/xBa/Al samples prepared by precipitation and pre-treated under N₂. The catalysts were sulfated at 300°C following the protocol detailed in section 2 for the H₂-TPR of sulfated catalysts. For the regeneration of the sulfated catalysts, the samples were submitted to a 2.5% H₂, 10% CO₂, 10% H₂O and N₂ mixture at 550°C for 30 min [23]. The NO_x storage measurements were carried out at 300°C with H₂O and CO₂ in the feed stream and the results are presented in Table 2. As expected, the sulfating treatment led to a strong decrease of the NO_x storage capacity, with a loss of more than 50%. However, the NO_x storage capacity is completely recovered after the regeneration step, indicating that N₂ pre-treatment effect still exists after sulfur poisoning and consecutive treatment in rich atmosphere.

In order to confirm the previous conclusions about the influence of the pre-treatment atmosphere on the physico-chemical properties of the catalysts, the samples were then characterized by nitrogen adsorption, XRD, H₂ chemisorption, TEM coupled to EDX analysis, CO₂ -TPD and H₂-TPR.

3.2 Catalysts characterizations

In this section, all the characterizations of catalysts were performed on the hydrothermally aged samples at 700°C, excepted for the material without platinum.

Nitrogen adsorption and XRD

The surface area and pore volume (V_p) of the different materials after barium deposition and calcination at 700°C are reported in Table 1. For comparison, the BET surface area of the alumina powder after calcination at the same temperature is also reported. Table 1 shows that the deposition method has no significant effect on the surface area and pore volume at this catalyst preparation stage. However, note that the higher is the barium loading, the lower are the surface area and pore volume. Also, after barium deposition and calcination at 700°C, the main crystalline phase detected by XRD was $BaAl_2O_4$ whatever the barium deposition method (results not shown). As the method of barium deposition has practically no effect on the structure and the surface area, only the catalysts with 10wt% and 20wt% BaO prepared by the impregnation (I) method were characterized after platinum deposition and subsequent thermal treatments (N_2 or O_2/N_2 pretreatment at 700°C followed by the hydrothermal aging at 700°C).

Table 3 reports the BET surface area, the pore volume (V_p) and the main XRD phases obtained with the aged Pt/xBa/Al catalysts prepared by the precipitation method. Table 3 shows that the catalyst pre-treatment under N_2 or O_2/N_2 has significant influence neither on the surface area nor on the nature of the crystalline phases detected by XRD ($BaAl_2O_4$ and $BaCO_3$). However, some phase transformation occurred during the platinum addition. Indeed, the XRD pattern of the obtained sample after drying at 120°C (without consecutive calcinations) does not exhibit the characteristic ray of $BaAl_2O_4$ anymore. Then, it was concluded that barium was leaching from the support [24, 25]. The barium carbonate formation can occur early in solution by reaction with the dissolved CO_2 coming from air. However, this species should disappear during the thermal treatment at 700°C, leading also to the formation of new $BaAl_2O_4$. More probably, the observed $BaCO_3$ is coming from reaction with CO_2 during air exposure.

The surface area measurements and XRD analysis do not allow one to explain the influence of the pre-treatment atmosphere on the NO_x storage behavior. These results seem to indicate that the catalyst pre-treatment influences mainly the surface structure of the catalyst and not its structural and textural properties. Thus, next we focus on the characterization of the surface sites.

Platinum accessibility

The H_2 chemisorption measurements were carried out as mentioned above in the experimental part. Only the aged Pt/20Ba/Al catalysts prepared by the precipitation method were studied. Platinum dispersion was of 4 % for the catalyst pre-treated under O_2/N_2 before aging, and 8 % for the nitrogen pre-treated catalyst. The higher platinum dispersion can be explained by the nature of the pre-treatment gas. Graham et al. [4] showed that platinum sintering strongly depends on the atmosphere of the thermal treatment. Thus, platinum sintering is lower when the catalyst was treated without oxygen in the gas feed. Nevertheless, note that in our study, the catalysts were aged at 700°C under a $O_2/H_2O/N_2$ mixture for 4 h after the pre-treatment. Thus, the nitrogen treatment contributes to maintain a higher dispersion of platinum even after the thermal aging.

Another parameter which can be influenced by the nature of the pre-treatment mixture is the oxidation state of platinum. A treatment under inert or reducing conditions would lead to a higher reduction state of platinum particles, while a treatment under O_2 should maintain the platinum

particles in a more oxidized state. To corroborate this assumption, the oxidation state of the platinum has been evaluated by H₂-TPR.

Temperature programmed reduction (TPR)

Before measurement, the aged catalysts were treated at 550°C under oxygen in the TPR apparatus. Only the aged Pt/20Ba/Al catalysts, previously treated under O₂/N₂ or N₂ before aging, were tested. The TPR profiles show a reduction peak at about 150°C (results not shown), which corresponds to the reduction of the platinum oxides. Nevertheless, the H₂ consumption depends on the catalyst pre-treatment. It increases from 30 μmol.g⁻¹ to 39 μmol.g⁻¹ for the N₂ and N₂/O₂ pre-treatments, respectively. These results indicate that the platinum is in a more reduced state for the nitrogen pre-treated catalyst. As metallic platinum is more active than platinum oxide for NO oxidation, this result can partially explain the higher NO oxidation activity of the N₂ pre-treated catalysts.

To summarize, the nitrogen pre-treatment contributes to maintain not only a higher dispersion of platinum but also a higher reduction degree of platinum. These two effects lead to the higher NO oxidation activity previously observed (Figure 3) and thus contribute to higher NO_x storage properties.

Transmission electron microscopy (TEM)

The Pt/20Ba/Al catalysts prepared by precipitation were characterized by TEM coupled to an EDX analysis. This study was performed on the aged samples pre-treated at 700°C either under N₂ or O₂/N₂. Representative micrographs of the catalysts are reported in Figure 5. The TEM analysis of numerous pictures indicates that the mean platinum particle size is about 20 nm for the O₂/N₂ pre-treated catalyst and 12 nm for the N₂ one, corresponding to platinum dispersions of approximately 5% and 9%, respectively (Figure 5 a,b). These results are in good agreement with those obtained by H₂ chemisorption. For both catalysts, the TEM analysis also shows the presence of two types of zones, clear (Figure 5c) and dark ones (Figure 5d). The EDX analysis of dark areas always showed the presence of Pt, Ba and Al for both catalysts. Concerning the clear areas, the EDX analysis showed that only Al was generally detected for the catalysts pre-treated under O₂/N₂, whereas Pt, Ba, and Al were generally detected for the catalysts pre-treated under N₂. These results indicate that the nitrogen pre-treatment before thermal aging at 700°C contributes not only to maintain a higher platinum dispersion, but also a higher barium dispersion. In order to confirm if the barium dispersion is really affected by the pre-treatment atmosphere, some CO₂ thermodesorption experiments were performed.

Carbon dioxide thermodesorption (CO₂-TPD)

The aged Pt/10Ba/Al and Pt/20Ba/Al catalysts prepared by the precipitation method were selected for this study. The catalysts were previously exposed to ambient air for the same time period in order to obtain a similar carbonation degree. Prior to the TPD experiments, the aged catalysts were treated at 550°C under 1% O₂/He and CO₂ was then adsorbed at 50°C. The TPD profiles are presented in Figure 6 and exhibit two main peaks near 100°C and 650°C.

We reported in a recent paper that the peak near 650°C corresponds to the decomposition of bulk BaCO₃ formed on the catalysts during the preparation and the air exposure. Concerning the CO₂ desorption in the 50°C – 550°C temperature range, it corresponds to the adsorption on the surface basic sites [16]. Figure 6 shows that the peak at high temperature (650°C) is more intense for the O₂/N₂ pre-treated catalysts compared with the N₂ one, whatever the barium loading. These results

suggest that, for the same barium loading, the amount of bulk barium carbonates is higher for the O₂/N₂ pre-treated catalysts, pointing out a lower dispersion of barium. On the other hand, the catalysts pre-treated under N₂ show a higher CO₂ desorption in the 50°C – 550°C temperature range, indicating a higher number of surface basic sites. This result is in accordance with the total NO_x storage capacity measured at 900s (Figure 2).

Thus, the results of H₂ chemisorption, TEM coupled with EDX analysis and CO₂-TPD show that the nitrogen pre-treatment before aging contributes to maintain higher platinum and barium dispersions. As a consequence, the Pt-Ba proximity would be also increased. A good Pt-Ba proximity is required to achieve high NO_x trapping performance due to the spill-over of NO₂ species from platinum to barium sites, especially for the rapid NO_x storage [14]. This Pt-Ba proximity parameter can be evaluated by H₂-TPR experiments of sulfated catalysts.

Temperature Programmed Reduction under hydrogen (H₂-TPR) of sulfated catalysts

As reported in the literature, sulfate stability is strongly influenced by barium dispersion and Pt-Ba proximity [23, 26]. Indeed, the sulfates formed on well dispersed barium particles in platinum proximity and the surface sulfates are less stable than bulk barium sulfates. In this way, the TPR profiles of sulfated catalysts can give information about the Pt-Ba proximity and Ba dispersion. This study was carried out over the aged Pt/20Ba/Al catalysts prepared by impregnation, precipitation and co-addition. To perform these experiments, the catalysts were first sulfated at 300°C in oxidizing atmosphere. The TPR profiles of sulfated Pt/20Ba/Al are reported in Figure 7. Concerning the N₂ pre-treated catalysts, three main reduction peaks are observed at about 500°C, 600°C and 750°C. According to a recent study [23], the peak at 500°C is ascribed mainly to the reduction of the well dispersed barium sulfates located in platinum proximity, with a small contribution of the aluminum sulfates reduction. The second peak is attributed to the reduction of more crystallized surface barium sulfates, more or less located in Pt neighboring. Finally, the third one is ascribed to the reduction of bulk barium sulfates.

Concerning the sulfated catalysts pre-treated under O₂/N₂, only two reduction peaks were observed, near 650°C and 750°C (Figure 7). Firstly, the O₂/N₂ pre-treatment leads to an increase of the H₂ consumption attributed to the bulk BaSO₄ reduction (peak near 750°C) compared to the N₂ pre-treatment. This is in accordance with a higher barium dispersion after the N₂ pre-treatment, as previously concluded from TEM and CO₂-TPD experiments. Moreover, the surface barium sulfates reduction is also affected by the pre-treatment. Only one peak is observed near 650°C after the oxidizing pre-treatment, whereas two peaks were obtained at lower temperature (500°C and 600°C) after the neutral pre-treatment. These results clearly show that the surface sulfates formed on the catalysts treated under nitrogen are less stable than those deposited on the catalysts treated under O₂/N₂. According to the literature [23, 26], it is explained by a higher Pt-Ba proximity and a higher Ba dispersion for the catalysts treated under N₂. This beneficial effect of the N₂ pre-treatment before aging is observed whatever the preparation method.

3.3 Discussion

This study shows the beneficial effect of a N₂ pre-treatment at 700°C (compared to a O₂/N₂ one) before a hydrothermal aging at the same temperature. Under realistic conditions, with H₂O and CO₂ in the feed stream, the rapid NO_x storage capacities (100s) are at least two times higher with the

N₂ pre-treated catalysts, whatever the storage temperature (200°C-400°C) and the catalyst preparation method.

Two main parameters can explain these results: an improvement of the barium dispersion and an improvement of the platinum dispersion.

About the first point, a large number of TEM pictures of the Pt/20Ba/Al samples were analyzed by EDX. Barium component was detected everywhere for the N₂ pre-treated samples, whereas barium-free alumina was detected for the O₂/N₂ pretreated catalysts. This result seems to indicate a higher barium dispersion for the N₂ pre-treated sample. Nevertheless, this technique is not sufficient to have a confident description of the samples and other characterizations confirm that the pre-treatment atmosphere (N₂ or O₂) before aging really influences the barium dispersion.

The CO₂ desorption results show that, for a same Ba loading, the proportion of bulk barium carbonates really decreased when the catalysts were treated under N₂ before aging. As the bulk barium carbonates are related to poorly dispersed Ba species, it can be concluded that the N₂ pre-treated catalysts exhibit a higher Ba dispersion than those pre-treated under O₂/N₂ before aging.

These results are corroborated with the TPR profiles of the sulfated samples. The bulk barium sulfates amount (reduction peak near 750°C, corresponding to large Ba species) is lower when the catalysts are pre-treated under N₂. Moreover, long time storage tests (900s) indicate an increase of the total number of the storage sites using the N₂ pre-treatment, even if some small nitrate diffusion into the large barium particles cannot be totally excluded. Finally, all these characterizations led to the same conclusion: the N₂ pre-treatment before aging improves the Ba dispersion, compared to the O₂/N₂ pre-treatment. As a consequence, the basic strength of the storage material pre-treated under N₂ is lower and it induces a lower inhibiting effect of CO₂ and H₂O during the storage tests.

Nevertheless, the TPD experiments of the N₂ pre-treated catalysts do not exhibit a two times higher “surface” CO₂ desorption (compared to the O₂/N₂ pre-treated catalysts), which would explain two times higher rapid NO_x storage capacities. However, platinum should not play a critical role for the CO₂-TPD experiments, in opposition with the NO_x storage tests, especially for the rapid storage. Then, the influence of the pre-treatment atmosphere on the platinum properties was examined.

The platinum dispersion of the aged Pt/20Ba/Al catalysts, deduced from H₂ chemisorptions and TEM measurements, increases from about 4-5% to 8-9% for the O₂/N₂ and N₂ pre-treatments, respectively. Even if the platinum particles are still large in both cases, it means that the number of particles increases of practically one order of magnitude when the catalyst is pre-treated under N₂ before aging. Furthermore, some TPR experiments under hydrogen indicate that the platinum particles are also in a more metallic state when the aged catalysts were pre-treated under N₂. The increase of both platinum dispersion and the metallic state explain the increase of the NO oxidation activity.

In conclusion, both platinum and barium are more dispersed on the aged catalysts pre-treated under N₂, leading to an improvement of the Pt-Ba proximity. These results are supported by the TPR characterizations of the sulfated samples. Whatever the preparation method used, the N₂ pre-treated catalysts exhibit a larger amount of surface barium sulfates related to a higher barium dispersion, and a weaker stability, resulting from a better Pt-Ba proximity. Note also that the N₂ pre-treatment effect on the NO_x storage properties of the aged catalysts remains after sulfating and sulfur regeneration in rich mixture.

4. Conclusion

In the present work, the influence of the pre-treatment atmosphere (O_2/N_2 or N_2) at $700^\circ C$ before aging at the same temperature under wet air was investigated on Pt/Ba/Al model catalysts. Two barium loadings were studied, 10wt% and 20wt%, respectively. The catalysts were prepared by platinum impregnation on Ba/Al materials previously calcined at $700^\circ C$ or by co-addition of Pt and Ba. For the Ba/Al materials, barium was deposited by impregnation or precipitation. The preparation method has a low impact on the rapid NO_x storage. On the contrary, the pre-treatment of the catalysts under N_2 before aging leads to higher NO_x storage properties than the catalysts pre-treated under O_2/N_2 . The difference is even more significant when the NO_x storage capacity is measured in the presence of H_2O and CO_2 ($\times 2.04$ and $\times 2.40$ for 10% and 20% BaO content, respectively). The nitrogen pre-treatment before the thermal aging induces:

- (i) a higher dispersion of platinum.
- (ii) a greater barium dispersion, thus leading to a higher number of active Ba sites for the NO_x storage. This effect is more significant for the 20wt% BaO catalyst than for the 10wt% BaO one because barium is already quite stabilized for the low barium content.
- (iii) a better Pt-Ba proximity, which leads not only to an increase of the rapid NO_x storage but also to the formation of less stable sulfates.

In conclusion, the pre-treatment of model Pt/Ba/Al catalysts under inert atmosphere at $700^\circ C$ improves both the oxidation and the storage functions, leading to more durable NO_x storage catalysts. It is remarkable that this effect is observed after a quite severe hydrothermal treatment at $700^\circ C$.

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Tables

Table 1: BET surface area, pores volume (V_p) and main phases detected by XRD for alumina and Ba/Al materials with 10 and 20wt% BaO after calcination at 700°C.

| Material | Al ₂ O ₃ | 10wt% BaO | | 20wt% BaO | |
|--|--------------------------------|----------------------------------|------|----------------------------------|------|
| | | I* | P* | I* | P* |
| BET (m ² .g ⁻¹) | 218 | 173 | 172 | 122 | 136 |
| V _p (cm ³ .g ⁻¹) | 0.46 | 0.44 | 0.42 | 0.35 | 0.35 |
| Main phases detected by XRD | | BaAl ₂ O ₄ | | BaAl ₂ O ₄ | |

* I: impregnation method; P: precipitation method.

Table 2: NO_x storage capacity (100s) at 300°C in presence of H₂O and CO₂ for the aged Pt/xBa/Al samples prepared by precipitation method and pre-treated at 700°C under N₂ before aging. Influence of sulfur poisoning and sulfur regeneration.

| | Pt/10Ba/Al | Pt/20Ba/Al |
|--|------------|------------|
| Aged catalyst (μmol.g ⁻¹) | 31.2 | 31.9 |
| Sulfated catalyst (μmol.g ⁻¹) | 13.2 | 14.9 |
| Regenerated catalyst (μmol.g ⁻¹) | 29.7 | 30.9 |
| Recovered (%) | 95 | 97 |

Table 3: BET surface area, pores volume (V_p) and main phases detected by XRD for the Pt/xBa/Al catalysts after hydrothermal treatment. Barium was deposited by the impregnation method.

| Aged catalysts | Pt/10Ba/Al | | Pt/20Ba/Al | |
|---|---|--------------------------------|---|--------------------------------|
| | 700°C | 700°C | 700°C | 700°C |
| Pre-treatment before aging | N ₂ | N ₂ +O ₂ | N ₂ | N ₂ +O ₂ |
| S _{BET} (m ² .g ⁻¹) | 175 | 162 | 136 | 130 |
| V _p (cm ² .g ⁻¹) | 0.46 | 0.42 | 0.36 | 0.38 |
| Main phases detected by XRD | BaAl ₂ O ₄ BaCO ₃ | | BaAl ₂ O ₄ BaCO ₃ | |

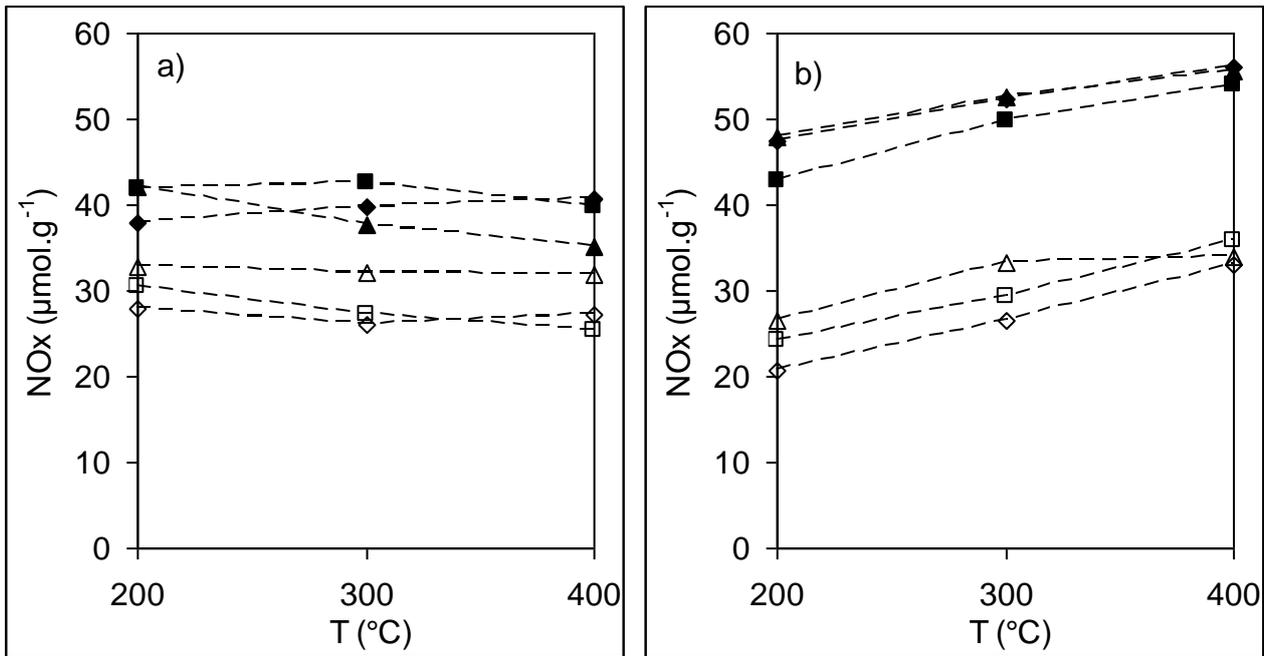


Figure 1: NOx storage capacity for the first 100s versus temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under O₂/N₂ (blank symbols) or N₂ (solid symbols); (◇,◆) Impregnation method, (□,■) precipitation method and (Δ,▲) co-addition method. Feed gas: 10% O₂, 350ppm NO and N₂.

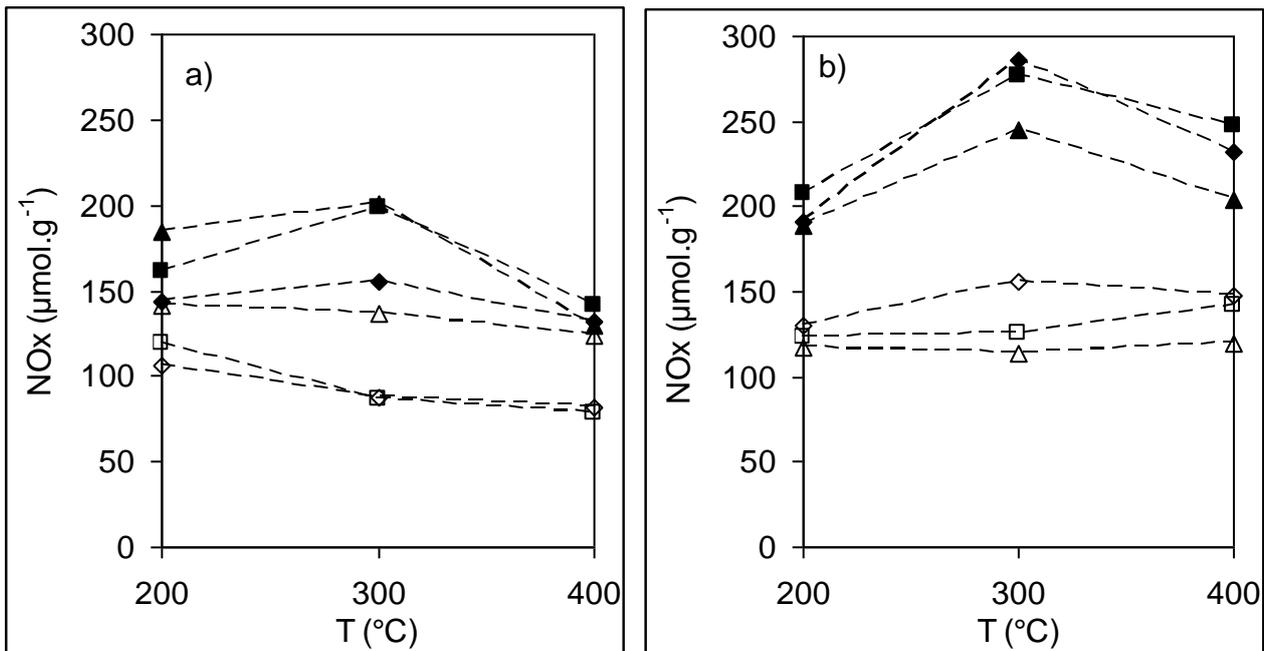


Figure 2: NOx storage capacity at 900s versus temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under O₂/N₂ (blank symbols) or N₂ (solid symbols); (◇,◆) Impregnation method, (□,■) precipitation method, and (Δ,▲) co-addition method. Feed gas: 10% O₂, 350ppm NO and N₂.

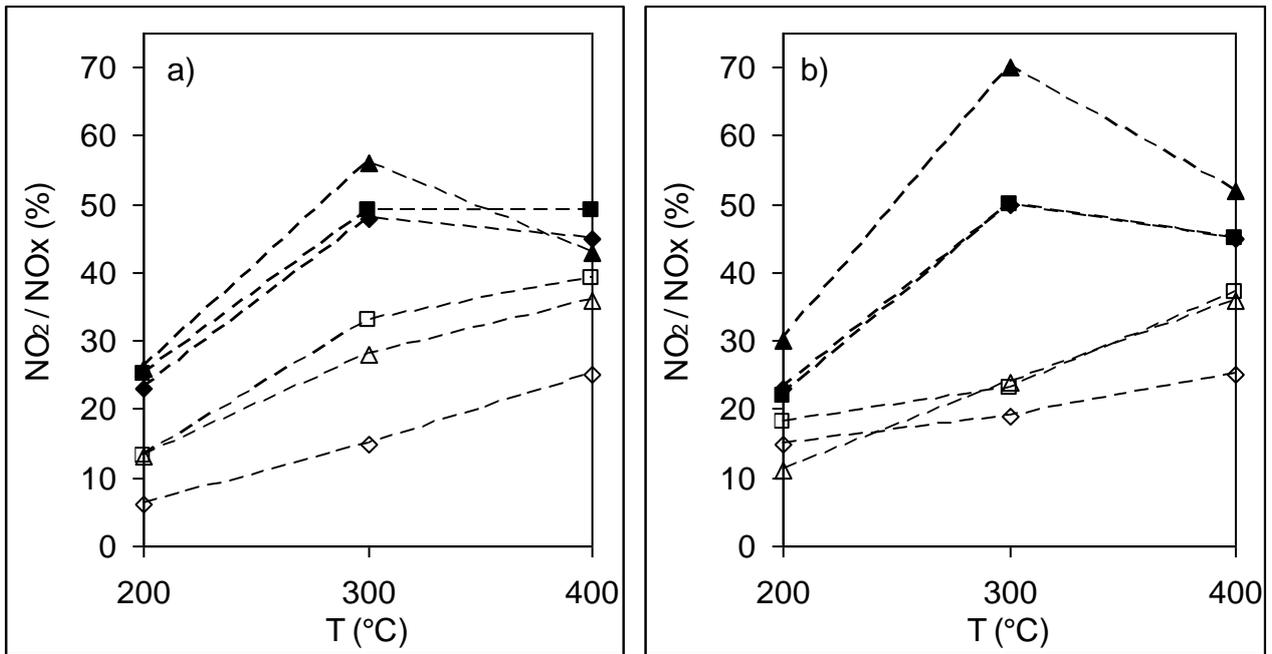


Figure 3: NO₂/NO_x ratio (%) determined at saturation (900s) versus temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under O₂/N₂ (blank symbols) or N₂ (solid symbols); (◇,◆) Impregnation method, (□,■) precipitation method, and (△,▲) co-addition method. Feed gas 10% O₂, 350ppm NO and N₂.

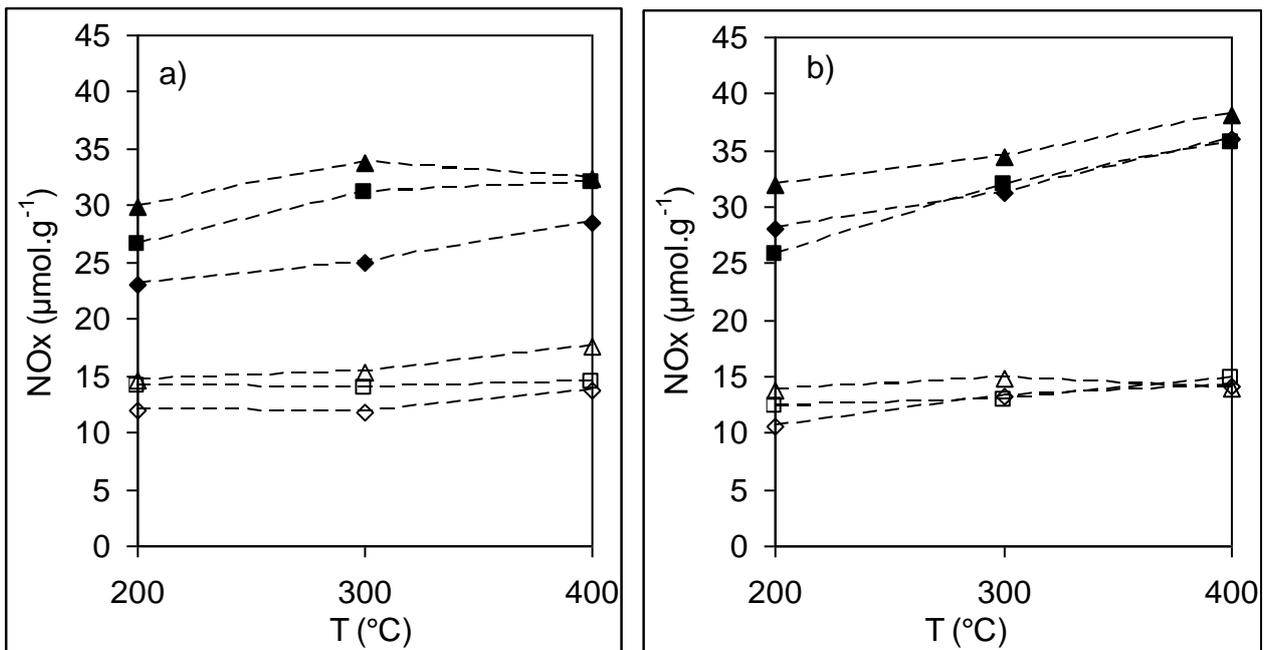


Figure 4 NO_x storage capacity for the first 100s versus temperature of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts pre-treated under O₂/N₂ (blank symbols) or N₂ (solid symbols); (◇,◆) Impregnation method, (□,■) precipitation method, and (△,▲) co-addition method. Feed gas: 10% O₂, 350ppm NO, 10% H₂O, 10% CO₂ and N₂.

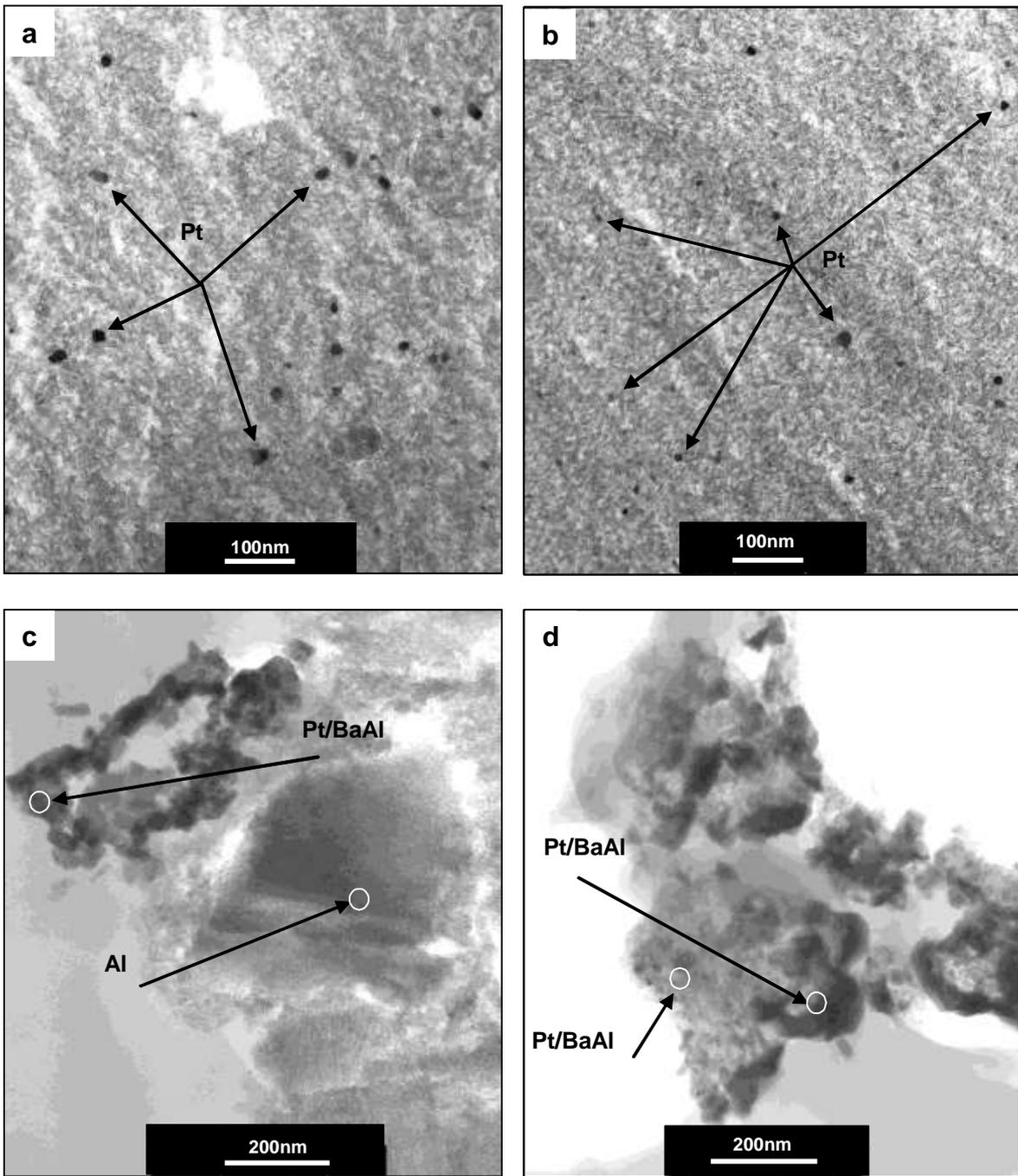


Figure 5: Micrographs of the aged Pt/20Ba/Al catalysts prepared by precipitation method and pre-treated either under (a and c) O_2/N_2 or (b and d) under N_2 .

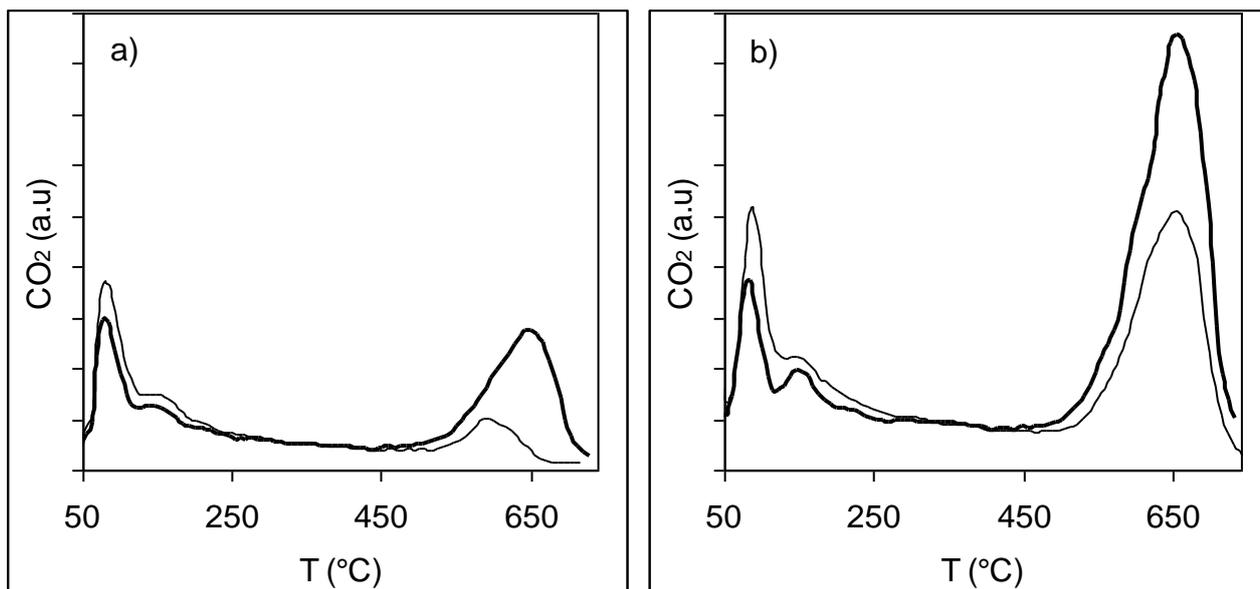


Figure 6: CO₂-TPD profiles of aged (a) Pt/10Ba/Al and (b) Pt/20Ba/Al catalysts prepared by precipitation method, and pre-treated either (—) under N₂ or (---) under O₂/N₂.

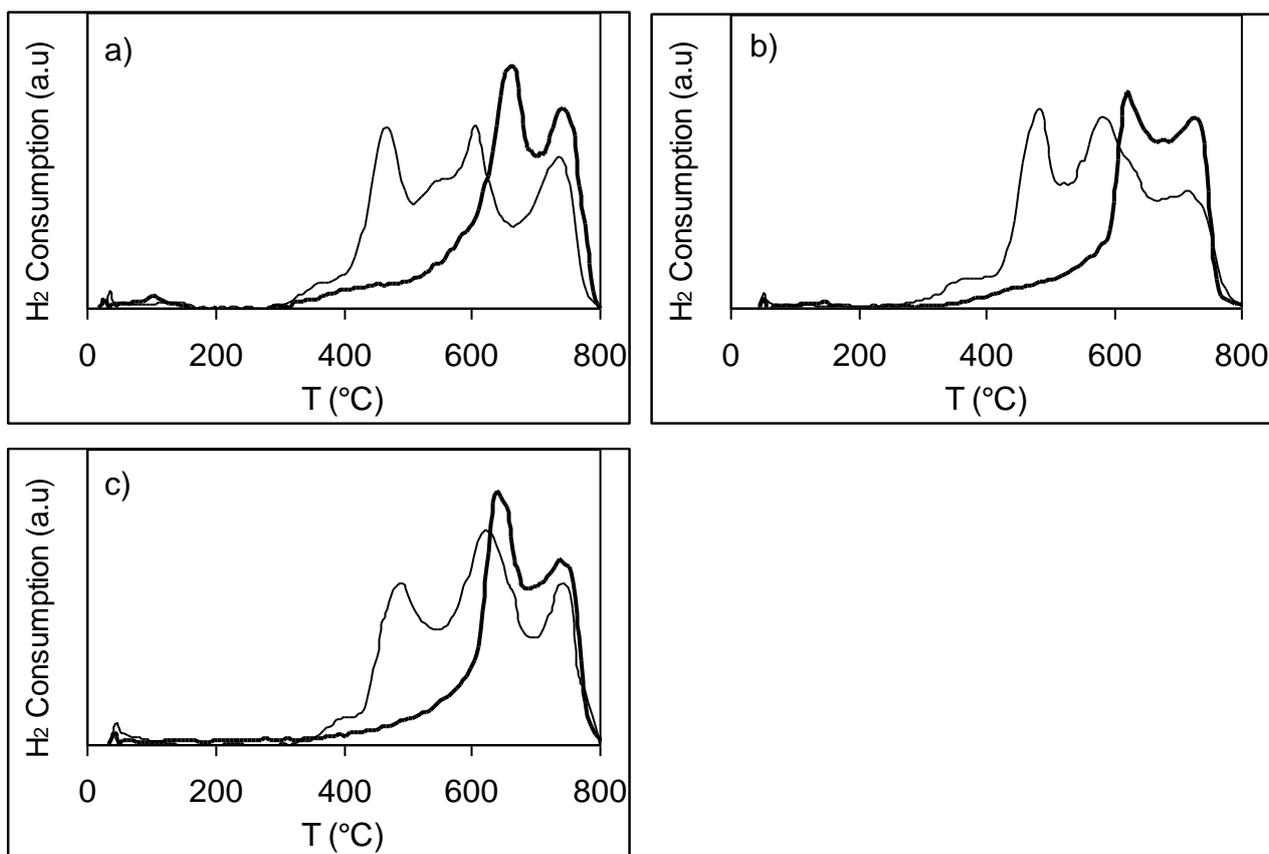


Figure 7: H₂-TPR profiles of aged Pt/20Ba/Al catalysts sulfated at 300°C, prepared by (a) impregnation method, (b) precipitation and (c) co-addition method. Before hydrothermal aging at 700°C, the catalysts were treated at 700°C under (—) N₂ or (---) O₂/N₂.