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NSR Catalytic materials

Fabien Can, Xavier Courtois* and Daniel Duprez

IC2MP, Université de Poitiers, CNRS UMR 7285, 4 Rue Michel Brunet, TSA 51106, 86073 Poitiers Cedex, France

*Corresponding contributor. E-mail: xavier.courtois@univ-poitiers.fr

Abstract

Imagined in the 90's, the NO_x-storage and reduction (NSR) process operates with alternative cycles of long lean phases (NO_x storage) and short rich phases (NO_x reduction). NSR catalysts should possess at least two components: a basic oxide for trapping the NO_x and a metallic component for the NO oxidation and the reduction of stored NO_x. The reference material is composed of barium oxide (10-20 wt-%) deposited on a Pt/Al₂O₃ (1-2 % Pt). Improvements of NSR catalysts were obtained by changing (i) the basic component (especially potassium but it can also damage the catalyst substrate; other alkaline or alkaline-earth oxides were also envisaged); (ii) the support (especially cerium-based supports, or titania, hydrotalcites, perovskites); (iii) the metal (Rh is often added to improve the NO_x reduction, and combinations of precious metals are considered). Noble metal-free catalysts were also developed, mainly based on cobalt, copper or manganese oxides. Perovskites including these transition metal oxides and potassium are also interesting for NSR applications. However, complete replacement of noble metal catalysts cannot be feasible yet. Usual NSR catalysts are sensitive to aging (sintering; strong of Ba-support interactions) and to sulphur poisoning but supports like TiO₂ or cerium-based oxides can protect the catalyst from stable sulphate adsorption.

3.1. Introduction

The NO_x-storage and reduction (NSR) or Lean-NO_x trap (LNT) technology was developed by Toyota in the mid-90s,^{1,2} and in parallel by Daimler-Benz in association with Johnson-Matthey³. The technology was initially implemented on lean-burn gasoline engines⁴, then on direct injection gasoline engines⁵ and finally extended to Diesel engines⁶ even though NSR technology is not considered as ideal solution for NO_x abatement in Diesel exhaust.⁷ Toyota's catalysts consisted in a noble metal (Pt and possibly other metals such as Rh) plus a basic oxide (Ba) deposited on alumina while similar catalysts were developed by Daimler-Benz except that the support comprised CeZrO_x oxides. Other formulations were improved by addition of transition metals (Fe, Ni, Co, Cu,...) to Pt/Ba/Al₂O₃ catalyst, essentially for applications in the presence of sulphur.⁸ The working scheme of the standard NSR process over Pt-Ba/Al₂O₃ catalysts is depicted in Figure 3.1. This is a two-step process with alternate periods of NO_x storage and reduction. In the storage step (typically 1 minute), exhaust gases issued from the engine are admitted on the NSR catalyst where NO is oxidized into NO₂ over Pt. Simultaneously, NO₂ is trapped over Ba oxide as nitrite or nitrate. Before the barium trap be saturated, the NSR catalyst is regenerated by reduction of surface nitrite/nitrate. An excess of fuel is admitted during a few seconds. Partial oxidation can lead to a mixture of H₂, CO and non-converted hydrocarbons with an increase of temperature on the catalyst. Nitrite and nitrate are desorbed and reduced to N₂ by the H₂-CO-HC mixture on Pt, or, preferably on Rh if Pt-Rh bimetallics are incorporated in the NSR catalyst.

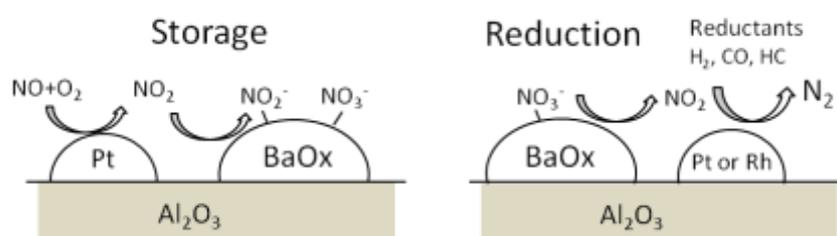


Figure 3.1. General scheme of the NSR process over the reference Pt (Rh)-Ba-Al₂O₃ catalyst.

The intimate mechanisms of NO_x storage have been the object of a huge number of papers and are out of the scope of this chapter. Recent reviews by Roy and Baiker⁹, Liu and Gao¹⁰ and Granger and Parvulescu¹¹ have detailed the literature on this question. We only summarize information useful for the design of new NSR catalysts are summarized in this chapter. It should be remarked that the formation of barium nitrate by reaction between NO₂ and BaO requires an additional oxygen atom (Eq. 3.1):



According to Olsson *et al.*¹², oxygen required for nitrate formation comes from NO₂ itself with intermediate formation of barium peroxide (Eqs. 3.2 - 3.4):



Broqvist *et al.*¹³ proposed a similar mechanism but with nitrite intermediate (Eq. 3.5-3.6)



Step 3.4 terminates the reaction scheme to barium nitrate. Olsson *et al.*¹² did not exclude a reaction in adsorbed phase between Pt-NO₂ and BaO-NO₃ instead of a reaction of NO₂ via the gas phase. In fact, Nova *et al.*¹⁴ confirmed that the interface Pt-BaO had a great impact for the NO_x storage performance. FT-IR coupled pulse experiments showed that nitrite would be preferentially formed at the Pt-Ba interface while nitrate would be formed by the gas phase reaction with NO₂. Finally, the oxygen implied in nitrate formation could also come from an O spillover between platinum and barium oxide. Again, the distance between the metal and the basic oxide is a crucial parameter in the storage process as well as the O mobility on the support. The requirement for NSR catalytic materials are first explored. Then, the most recent advances in term of storage materials will be examined, first with Pt (or other precious metals)-containing catalysts, then with formulations without any precious metal.

3.2. Requirements for NSR catalytic materials

NSR catalysts comprise two components having each specific function in the storage step: (i) component (1) for O₂ activation and NO oxidation and (ii) component (2) for NO_x storage. In the reduction step, two additional functions are required (iii) to transform the pulse of fuel into active reductants (H₂, CO) by partial oxidation and (iv) to catalyze the reduction of the NO_x desorbed from component (2). In the reference NSR catalyst, component (1) is a noble metal (Pt) which also assures

functions (iii) and (iv). In some cases, these functions can be allotted to a third component (Rh or any other additives), but in most cases NSR catalysts were recently developed on the two-component model. The main requirements for NSR materials are:

- a- Kinetics of NO_x storage on component (2) may be relatively slow since the storage period is long (typically 1 min.) but the storage capacity should be the highest possible.
- b- On the contrary, NO oxidation and NO_x reduction on component (1) should be very fast for two reasons: NO₂ should be always at equilibrium for an optimum NO_x storage, and NO_x reduction should be quasi-instantaneous during the short period of reduction (a few seconds).
- c- If the rate of NO oxidation and that of NO_x reduction on component (1) normally increase with the temperature T, the change of NO_x storage capacity with T is more complex. First, the NO conversion is thermodynamically limited at high temperature, which decreases the NO₂ content in gases when T increases. Second, inhibitors (CO₂) or poisons (SO_x) may have a greater impact at higher temperature up to their desorption from the catalyst. Carbon dioxide tends to form carbonates with the basic oxide, thus inhibiting nitrites/nitrates adsorption while SO₂ is a severe poison of all the catalyst components (metal and basic oxides) by formation of sulphates.
- d- As discussed in introduction, the proximity of component (1) and component (2) is generally required for an optimum NO_x conversion. This aspect should be taken into consideration in the protocol of preparation.
- e- Other aspects should be considered such as the formation of N₂O^{15,16} which should be minimized due to its very powerful greenhouse effect, or the formation of NH₃ which should benefit for the whole NO_x reduction. NH₃ selectivity is clearly related to the presence of H₂ in the rich gas¹⁷ but also depends on H₂O and CO₂ concentration due to the reverse-water gas shift reaction (CO₂+H₂ → CO + H₂O) which generates a certain amount of CO.¹⁸ Finally, it was proven that coupling NSR and SCR materials presents great advantage, the SCR catalysts allowing a supplementary conversion of NO_x thanks to ammonia formed in the NSR process.¹⁹⁻²¹ Progresses made on this new process were reviewed by Can *et al.* in 2012.²²

3.3. PGM-based catalytic materials

NSR materials were reviewed by Epling *et al.*²³ in 2004, Roy and Baiker⁹ in 2009 and Granger and Parvulescu¹¹ in 2011. Platinum is mainly used as component (1) in many formulations. We will review in detail the most recent studies using this metal in association with NO_x storage components (section

3.3.1 to 3.3.5). Finally, NSR catalysts based on other precious metals (Rh, Pd) or combinations of these metals with Pt will be reviewed in section 3.3.6..

3.3.1 Effect of preparations or activation procedures of Pt-Ba-Al₂O₃ catalysts.

Different precursors of Pt were investigated by Dawody *et al.*²⁴ who compared impregnation by (i) hexachloroplatinic acid [H₂Pt(Cl)₆], (ii) tetraammineplatinum hydroxide [Pt(NH₃)₄(OH)₂], (iii) diammineplatinum nitrite [Pt(NH₃)₂(NO₂)₂] and (iv) platinum nitrate [Pt(NO₃)₂]. Pt was impregnated on the same Ba(CO₃)/Al₂O₃ (11 or 18 % Ba) washcoated on a monolith. It was proven that Pt nitrate led to better performances in terms of NO_x storage. The main reason would be a better dispersion of Pt. However, as Pt was impregnated after Ba, no definitive conclusion can be drawn from this study. Number of papers reports results of NO_x storage on catalysts prepared in different orders of impregnation: Ba first and then Pt or the reverse. Lindholm *et al.*²⁵ investigated the effect of the order of impregnation with Pt(NO₃)₂ as Pt precursor and Ba(NO₃)₂ as Ba precursor. The catalyst prepared with Ba impregnated on Pt/Al₂O₃ is more active than Pt on Ba/Al₂O₃ (Figure 3.2). Moreover, NO_x storage capacity increases with temperature while it is the reverse for Al/Ba/Pt. Presence of CO₂ and H₂O can affect the NO_x storage capacity. Lindholm *et al.*²⁶ showed that NO_x storage was mostly influenced by H₂O at low temperature and by CO₂ at high temperature. Similar effects were observed by Corbos *et al.*²⁷ who showed that changing the support (Al₂O₃-SiO₂, CeZrO_x instead of Al₂O₃) can decrease the inhibiting effect of H₂O and CO₂. The support Al₂O₃ + 5.5 wt% SiO₂ allows to preserve good performances of Pt-BaO for the rapid NO_x storage capacity at 200-400°C.

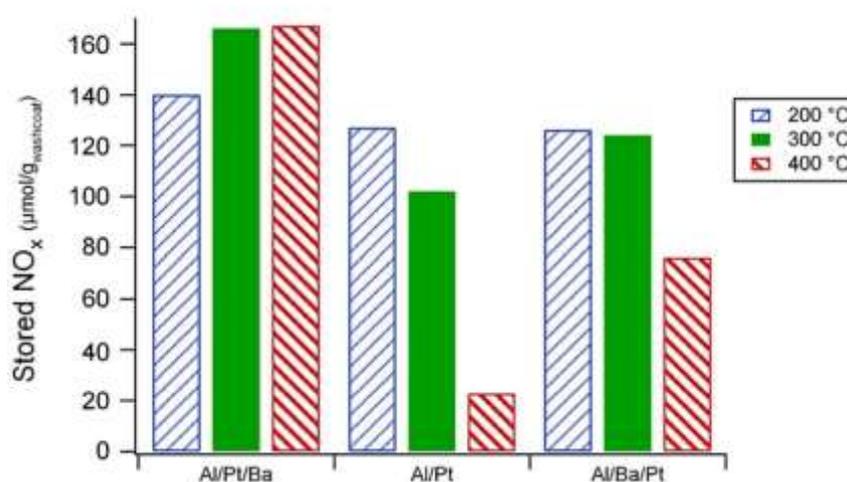


Figure 3.2. Comparison of NO_x storage properties of NSR catalysts based on 3 % Pt-Al₂O₃ (Al/Pt). The catalysts are monolith samples previously washcoated with alumina. Barium was impregnated after Pt (Al/Pt/Ba) or before Pt (Al/Ba/Pt). Ba content is 20 % and Pt dispersion is close to 20 % for all samples. NO_x storage is measured during 4 minutes in lean condition (300 ppm NO + 8 % O₂) after a rich period of 1 minute (300 ppm NO + 8000 ppm H₂). Reprinted from ref.25 with permission from Elsevier.

Pereda-Ayo investigated the procedure of Pt and Ba deposition on Al₂O₃-washcoated monoliths.²⁸ The precursor of platinum was Pt(NH₃)₄(NO₃)₂. High Pt dispersions and homogeneous Pt distributions within the monolith channels were obtained by wet impregnation at high pH (11-12). By contrast, Ba deposition by dry impregnation gave the best performances in terms of NO_x storage. The washcoat can also contain CeZrO_x materials. The presence of alumina (Al₂O₃-CeZrO_x support) is of great importance for a high NO_x storage.²⁹ In absence of alumina, Ba tends to form solid solutions with CeZrO_x, which is not beneficial to good storage properties.

Significant improvement of NO_x storage capacity was obtained with single-step flame-made Pt/MgAl₂O₄ catalysts.³⁰ However, these catalysts exhibit higher storage capacity than Pt-Ba-Al₂O₃ only with H₂ and H₂ + CO as reducing agent in rich phase. Pt/MgAl₂O₄ keeps its good properties even after a long series of rich/lean cycles while Pt-Ba-Al₂O₃ tends to form bulk Ba species.

Pre-treatments of NSR catalysts can have great effects on the storage capacity. To simulate driving in real conditions, it is recommended to calcine the catalysts in wet air at 600°C and preferably at 800°C. Calcination at 400-500°C gives high storage capacity not representative of the behavior of the catalyst in the exhaust pipe. But at very high temperatures (T > 800°C), strong modifications of the solids are generally observed. After treatment of 8-20% BaO/Al₂O₃ samples at 1000°C, stable surface BaO and BaAl₂O₄ phases are formed leading to very low NO storage capacity.³¹ When NO₂ is then adsorbed, nanosized barium nitrate are evidenced by XRD and NMR. A further treatment in H₂O transform this nitrate to bulk Ba(NO₃)₂ which decomposes easily at moderate temperature. Finally, water gives rise to a partial recovery of NO_x storage capacity. Corbos *et al.*³² have investigated the role of different atmospheres for the pre-treatment of Pt-Ba-Al₂O₃ NSR catalysts. Whether or not there are inhibitors (CO₂, H₂O) in the gas, better NO_x storage properties with catalysts treated under N₂ before aging were observed (Figure 3.3). This is due to higher Pt dispersion (favoring NO oxidation) and to better Ba dispersion (increasing the number of storage sites). This proves that the nature of the gas used for the pre-treatment during the first hours at high temperature is predominant for the final performance.

Non-conventional activation modes were proceeded in order to increase NO_x storage capacity. Hadjar *et al.*³³ used electrochemical activation of Pt-Ba/YSZ (Yttrium-stabilized zirconia) and showed that cathodic polarization promoted the NO_x storage capacity even under lean-burn conditions.

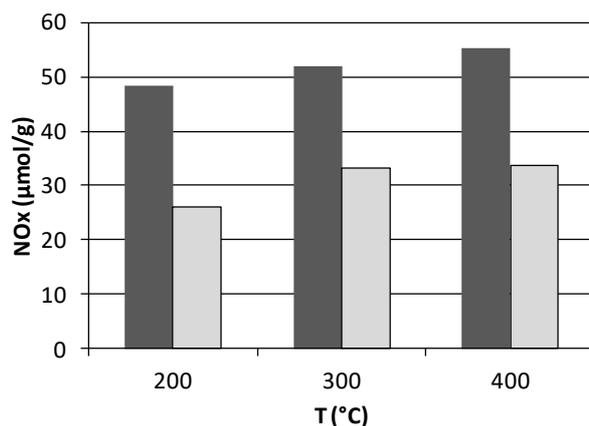


Figure 3.3. NO_x storage capacity of a 1%Pt-20%BaO/Al₂O₃ catalysts. Effect of the pretreatment of at 700°C in N₂ (black bars) or in O₂+N₂ (grey bars) before aging in N₂ + 10 % O₂ + 5 % H₂O at 700°C. NO_x storage was measured during the first 100 s in 350 ppm NO + 10 % O₂ + N₂. Maximum adsorption of NO is 67 μmol g⁻¹ corresponding to the totality of the 350 ppm of NO stored during 100 s. From ref.32.

3.3.2 Effect of support on the performance of Pt catalysts

Comparison of Al₂O₃ with other single oxides. Piacentini *et al.*^{34;35} have compared different Pt-Ba catalysts supported on Al₂O₃, SiO₂, ZrO₂ or CeO₂. Alumina and zirconia appear to have excellent performance for relatively high Ba loading while ceria would be the best support at low loading (Figure 3.4).

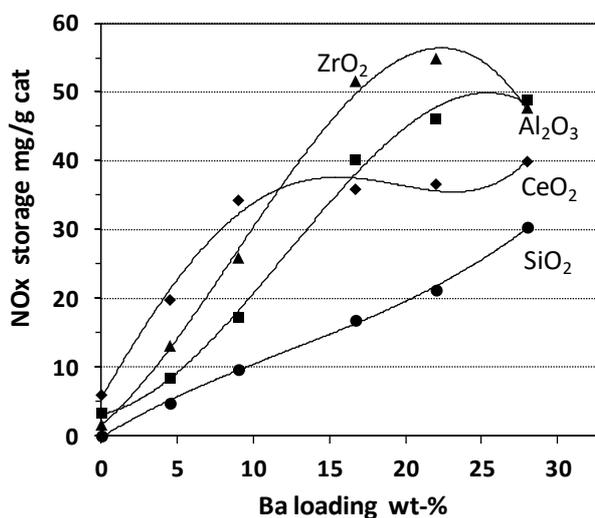


Figure 3.4. Effect of Ba loading on NO_x storage capacity of Pt-Ba NSR catalysts impregnated on different supports: SiO₂ (185 m² g⁻¹); CeO₂ (143 m² g⁻¹); Al₂O₃ (190 m² g⁻¹); ZrO₂ (34 m² g⁻¹). Reprinted from ref. 35 with permission from Elsevier.

Zirconia alone could have intrinsic NO_x storage properties. Eguchi and Kikuyama³⁶ have reported good performances of Pt-ZrO₂/Al₂O₃ at 200°C (800 ppm NO + 10 % O₂). The optimal NO_x abatement is obtained with the catalyst prepared by using ZrO(NO₃)₂·2H₂O and Al(NO₃)₃·9H₂O as precursors of the support and [Pt(NH₃)₆](OH)₄ as precursor of Pt. Chloride ions should be avoided or carefully eliminated. Good NO_x sorption behavior of zirconia was confirmed by Klotz *et al.*³⁷ on high-surface area YSZ prepared by a supercritical CO₂ process.

MgAlO_x supports. Layered double hydroxide (LDH) including Mg-Al elements (hydrotalcites) are potential supports for Pt-Ba catalysts. They can increase the solid basicity and improved NO_x storage capacity. Their properties were studied Jeong *et al.*³⁸ The Mg/Al ratio of 4:6 showed the highest NO_x storage performance after thermal treatment at 800°C. One of the beneficial effect of Mg-Al mixed oxides is to prevent the formation of BaAl₂O₄ after aging.³⁸ Hydrotalcites are precursor of MgAl₂O₄ spinel whose surface area is stable even after high temperature excursion. Kwak *et al.*³⁹ have prepared MgAl₂O₄-supported Pt-BaO lean NO_x trap catalysts by impregnation of Ba(NO₃)₂, then Pt(NH₃)₄(NO₃)₂ on a spinel of 150 m² g⁻¹. Impregnation of Ba first does not seem to have a negative impact on the NO_x storage capacity with better performances than Pt-Ba/Al₂O₃ in the 270-450°C temperature range. Ba-free formulations were proposed by Mei *et al.*⁴⁰ by supporting Pt-MgAlO_x over graphene oxide (GO). The performance of the catalyst containing only 7 wt% of GO could be attributed to the enhanced LDH particle dispersion and stabilization.

Titanates. Binary or ternary oxides based on titania were developed as supports of NO_x storage catalysts with the objective to increase sulphur resistance (see section 3.5.3). Imagawa *et al.*⁴¹ have described new formulations containing titanium-doped nanocomposites of Al₂O₃ and ZrO₂-TiO₂ (AZT) prepared by coprecipitation while Say *et al.*⁴² investigated similar ZT (ZrO₂-TiO₂) and AZT (Al₂O₃-ZrO₂-TiO₂) oxides prepared by a sol-gel method. It is essential to prevent the formation of ZrTiO₄ that can occur at T > 600°C with a severe decrease of surface area. Presence of alumina in AZT is a way to reach high stability of ZT materials. NO_x adsorbed on Pt/AZT are more easily reducible than on Pt/ZT. However, in both case, N₂O would be formed as a primary intermediate of the complete reduction to N₂ (and possibly NH₃).

3.3.3 Potassium-doped NSR catalysts

Konsolakis and Yentekakis⁴³ were among the first authors to show the potential of potassium for NO reduction by propene, which paved the way to the use of this alkaline for NO_x storage. Quantification

of the storage capacity of Pt-K/Al₂O₃ was performed by Toops *et al.*^{44,45} who used a DRIFT technique for measuring surface concentration under different atmospheres. Pt/Al₂O₃ adsorbs 0.087 μmol CO₂ m⁻² and 2.0 μmol NO₂ m⁻², and Pt/K/Al₂O₃ adsorbs 2.0 μmol CO₂ m⁻² and 6.4 μmol NO₂ m⁻². About 1 % of the surface is occupied by Pt particles, 34 % by pure Al₂O₃ and 65 % by K-Al₂O₃. Pure alumina can store a significant amount of NO_x but NO_x-Al₂O₃ is severely inhibited by CO₂ and H₂O, more than NO_x-K-Al₂O₃.⁴⁵ Prinetto *et al.*⁴⁶ have studied the surface properties of Pt-K/Al₂O₃ while Castoldi *et al.*⁴⁷ have compared Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃ in the NSR process. Although both catalysts have the same Pt dispersion (Pt particle size of 1.5 nm), higher oxidation activity are observed on Pt-K/Al₂O₃. It seems that Pt-K interaction keeps the noble metal in a more reduced state. Mechanisms of NO_x storage are similar on Pt-K and Pt-Ba even though Mⁿ⁺-O²⁻ ion pairs seems less basic in Pt-K/Al₂O₃ catalysts than in Pt-Ba/Al₂O₃.⁴⁶ FTIR characterization of the stored NO_x shows that nitrites and nitrates are formed in both cases, only the proportion of bidentates nitrates being different on Pt-K and Pt-Ba. Greater differences are observed during the reduction phase in H₂. Ammonia is first formed by reaction of H₂ on nitrates and then NH₃ reacts with nitrates stored downstream to yield N₂.⁴⁸ It seems that isocyanate intermediates could be formed by reaction of NH₃ on adsorbed nitrates in the presence of steam.⁴⁹ Higher reactivity of intermediate NH₃ and higher selectivity to N₂ are observed with the K-doped catalyst. These results are rather in contradiction with the study of Malpartida *et al.*⁵⁰ who showed that Pt-K can store less NO_x and that the reduction of the stored NO_x are less effective on Pt-K than on Pt-Ba, even with H₂ as reductant. Although the methods of preparation are similar in both studies, the amount of noble metal and the deposition of the alkaline component could play a predominant role on the final properties. Kim *et al.*⁵¹ investigated the effect of K loading on the performance of Pt-K/Al₂O₃ catalysts. A temperature T_{max} for the maximum of NO_x storage is recorded for every sample. However, T_{max} strongly increases with K loading: 300°C for 5 and 10 % K₂O versus 500°C for 20 and 30 % K₂O (Figure 3.5). In a further study, the group of Richland has reported somewhat different results⁵². A maximum NO_x storage was obtained with the 10 % K catalysts at 450°C. However, important differences should be noticed between the two studies. The alumina used by Luo *et al.*⁵² has a BET area of 150 m² g⁻¹ (instead of 200 m² g⁻¹ for Kim *et al.*⁵¹). Moreover, the catalysts of Luo *et al.* were calcined at 600°C. Finally, the NO_x storage capacity was measured by integrating the NO_x curve until outlet NO_x levels reached 60 ppm (instead of 30 ppm). The study of Luo *et al.* illustrates the very high mobility of potassium above 500°C, which can block Pt particles.⁵² As a rule, NO_x storage is limited by NO oxidation over Pt-K/Al₂O₃ catalysts.

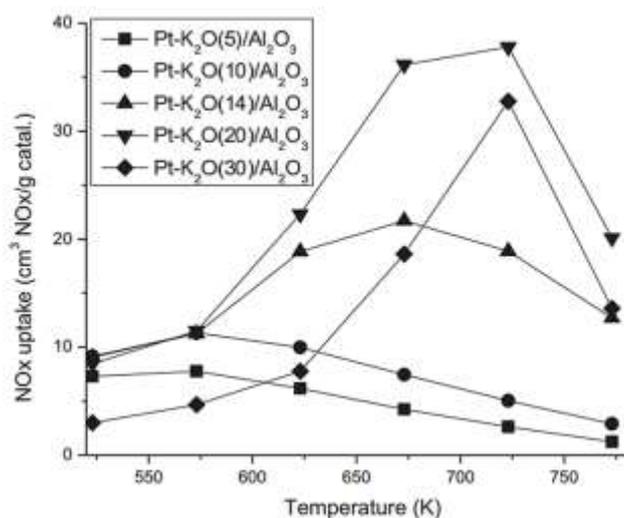


Figure 3.5. Change with the temperature of the NO_x storage capacity of 2%Pt/x%K₂O/Al₂O₃. Effect of the potassium content. K is introduced by impregnation of Al₂O₃ (200 m² g⁻¹) with aqueous solution of KNO₃, then Pt is impregnated with solutions of Pt(NH₃)₂(OH)₂. The catalysts are finally calcined at 500°C. NO_x storage is measured in lean condition (150 ppm NO + 5 % O₂ in He + 5 % CO₂ + 5 % H₂O) after 20 rich/lean cycles. NO_x is integrated until outlet NO_x levels reached 30 ppm. Reprinted from ref. 51 with permission from Elsevier.

Attempts at increasing NO_x trap efficiency or reductibility of the NO_x stored on K-doped catalysts were made by means of new methods of preparation, by adding new additives to the Pt-K/Al₂O₃ catalyst or by changing the support. Büchel *et al.*⁵³ reported improved activity of Pt-K/Al₂O₃ prepared by the flame-spray method. The rate of storage and reduction was increased, which leads to superior performance in dynamic conditions. The typical overshooting of the NO_x signal during the switch from fuel lean to fuel rich gases was significantly decreased. Hou *et al.*⁵⁴ showed that starting with potassium carbonate led to higher storage capacity provided by K₂CO₃ homogeneously dispersed on the support (ZrO₂). Above 15 % K₂CO₃, bulk carbonate is formed, which is unfavorable to NO_x storage.

Park *et al.*⁵⁵ showed that Mg-Al hydrotalcites are also excellent supports of Pt-K catalysts. The catalytic system of Park *et al.* is relatively complex since it comprises Pt and Pd in various proportions as noble metals. Pt-Pd gives higher performances than Pt at low temperature (200°C). The use of MgAl₂O₄ spinel instead of alumina was investigated by Takahashi *et al.*⁵⁶ and by Kim *et al.*⁵⁷ The researchers of Toyota⁵⁶ pointed out the good NO_x storage of Pt-K/MgAl₂O₄ at T > 400°C. The higher potassium basicity resulting from the interaction between the basic MgAl₂O₄ support and the potassium NO_x storage material would enhance the stability of the stored NO_x. Kim *et al.*⁵⁷ confirmed the good performance of the Pt-K/MgAl₂O₄ NSR catalyst at high temperature. Even though the maximum NO_x storage is observed in the 300-450°C temperature range, significant storage is still recorded at 500°C. Recently, good performances of Pt-K catalysts were obtained by deposition of Pt/K₂CO₃/MgAlO_x over reduced graphene oxide.⁵⁸ The GO support protects hydrotalcite from

agglomeration. High NO_x storage and NO_x conversion is obtained with a remarkable stability in steam environment.

Other supports for K-doped catalysts were also developed. Platinum performance was improved in Pt-LaCoO₃/K-Al₂O₃: the cobaltite contributes to NO oxidation and NO_x storage and thus allows drastic reduction of Pt content down to 0.3 %.⁵⁹ Pt-K/TiO₂-Al₂O₃ catalysts show significant NO_x storage properties which can be improved by addition of La₂O₃.⁶⁰ These materials also exhibit remarkable resistance to sulphur poisoning, in line with the general behavior of titania supported NSR catalysts⁴¹. Association of K and Ti in potassium titanates supports (K₂Ti₂O₅) seems to keep good NO_x storage capacity while stabilizing the potassium in the catalyst.⁶¹ Potassium titanates (“K₂Ti₆O₁₃-like”) can also be produced by calcination of Pt-K/TiO₂ at 550°C.⁶² An additional deposition of potassium on K-titanates of nanobelt-shape (KTN catalysts) can reinforce the NO_x storage capacity at high temperature.^{63,64} Nevertheless, these KTN supports require a lengthy preparation by reaction of TiO₂ with KOH, then heating in autoclave at 130°C for 4 days. Pt-K/TiO₂-ZrO₂ catalysts were investigated by Zou *et al.*⁶⁵ who showed that addition of Co or Ce improved their performances, especially their resistance to sulphur. Once more, the use of titania as supports is a key to improve the stability of the catalysts in driving condition. Finally, it should be mentioned that doping Pt-K catalyst with other elements can lead to highly active catalysts. Lesage *et al.*⁶⁶ have reported that Pt-K-Mn/CeO₂-Al₂O₃ catalysts combined excellent properties in NO oxidation and NO_x storage. Detailed characterizations showed that these improved properties were due to the formation of a hollandite-like potassium phase allowing fast diffusion of NO in the tunnel-structure of this particular phase.

There are optional configurations in which NSR catalysts are coupled or inserted in the DPF (Diesel particulate filter). This allows to implement more compact depollution systems in the car but requires to add a soot oxidation function to the NSR catalyst. In this respect, Pieta *et al.*⁶⁷ have investigated Sn-modified NO_x storage/reduction catalysts in which tin oxide in the presence of Pt is the soot oxidation component of the Pt-Ba-K catalyst. It was shown that Sn effectively improved soot combustion but had no detrimental effect on the NO_x storage/reduction properties of the catalyst.

The major problem to take into consideration when using potassium in NSR catalysts is the potential detrimental effect of this alkaline metal on both thermal stability of the catalyst and mechanical properties of cordierite substrate.^{68,69} The use of metallic monolith instead of cordierite can be a solution to this problem.⁷⁰

3.3.4 Cerium-doped NSR catalysts

In lean-burn gasoline engine, NSR catalyst has also the function to oxidize CO and hydrocarbons in the presence of steam to produce hydrogen, a powerful reductant of adsorbed nitrates-nitrites. Ceria-based oxides are generally introduced to boost this function.⁷¹ Shi *et al.*⁷² showed that ceria added to Pt-Ba/Al₂O₃ had beneficial effects, both in NO_x storage and reduction at low temperature (200-300°C). At 400°C, ceria has rather a detrimental effect (Figure 3.6). XPS characterization showed that BaO was mainly supported on CeO₂ rather than on alumina while H₂-TPR suggested that Pt particles (in the range of 1.7 to 2.4 nm) are located on ceria and on alumina.

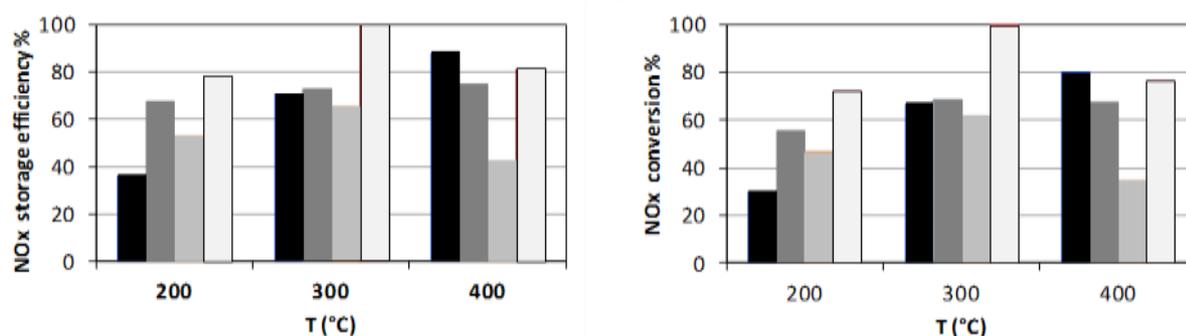


Figure 3.6. Temperature effect on NO_x storage efficiency and NO_x conversion in lean/rich cycling of Pt-Ba/Al₂O₃, Pt-Ba/CeO₂, Pt/CeO₂-Al₂O₃ and Pt-Ba/CeO₂-Al₂O₃ (from dark to light grey, respectively). Gas composition for NSE measurement: 300 ppm NO, 8 % O₂, 5 % CO₂, 5 % H₂O in He after reduction in H₂. Gas composition for NO_x conversion: same composition for the lean phase as for NSE; rich phase: NO+O₂ replaced by 0.64 % CO + 1.06 % H₂. From ref. 72.

Pereda-Ayo *et al.*⁷³ have prepared several 15%Ba-1.5%Pt-Ce/Al₂O₃ catalysts with increasing cerium loading, from 0 to 20.3 wt.%. Cerium nitrate was impregnated first on alumina. The support was then calcined at 500°C before successive wet impregnation of [Pt(NH₃)₄(NO₃)₂] and barium acetate Ba(CH₃COO)₂. NO_x storage capacity was determined in lean conditions after successive lean (680 ppm NO + 6 % O₂) / rich (680 ppm NO + 3 % H₂). Pt dispersion is close to 50-60 % before Ba introduction and 30 % after Ba impregnation. The main results, given in Table 3.1, show that the NO_x storage capacity (NSC %, ratio between the amount of stored NO_x and the amount of inlet NO_x) is improved by addition of low amount of ceria. Higher loading of ceria is detrimental to NO_x storage and N₂ selectivity.

Table 3.1: Effect of Ce loading on the NO_x storage capacity (NSC) and selectivity in regeneration by H₂ of Ba-Pt-Ce/Al₂O₃ catalysts. From. Ref. 70.

Sample	NSC %	S _{NH3} %	S _{N2O} %	S _{N2} %
Ba-Pt/Al ₂ O ₃	83.7	9.8	0.8	89.4
Ba-Pt-4.5%Ce/Al ₂ O ₃	89.6	7.7	0.9	91.4
Ba-Pt-15.4%Ce/Al ₂ O ₃	69.5	18.2	1.2	80.6

Say *et al.*⁷⁴ have investigated CeO₂/Al₂O₃ oxides and corresponding Pt-Ba catalysts for the NO_x storage and reduction with H₂. The role of the catalyst composition was studied step by step from pure alumina to the final Pt-Ba/CeO₂/Al₂O₃ catalyst. Ceria has several effects: (i) it allows a strong stabilization of Pt nanoparticles by the formation of Pt-O-Ce interstitial sites; (ii) although it has not a real impact on the NO_x storage process, it participates in the reduction step by H₂ activation. The reduction of surface nitrates/nitrites via NH species is clearly evidenced. N₂O would be an intermediate of N₂ production. Arena *et al.*⁷⁵ already observed the formation of N₂O on Pt-Ce/Al₂O₃ catalysts which could occur in transient regime at the lean/rich transition (Eq. 3.7)



Compared with alumina, pure ceria is not a good support of Pt-Ba⁷⁶: it seems that ceria maintains Pt in an oxidized state not favorable to the NSR process. A pre-reduction in H₂ at moderate temperature (<500°C) could overcome this drawback: Pt is then well reduced and well-dispersed. Increasing the pre-reduction temperature leads to a loss of performance due to the deep reduction of ceria which may encapsulate Pt nanoparticles. Ce_{0.9}Pr_{0.1}O₂ mixed oxides prepared by different routes (nitrate calcination, activated carbon template, precipitation with urea) were investigated by Rico-Pérez *et al.*⁷⁷ as support of Pt for the NSR process. XPS reveals that Pt is positively charged in every samples while the presence of praseodymium improves oxygen mobility. Catalysts prepared by the nitrate calcinations route have the best performances in NO_x storage (sample exposed to a flow of 300 ppm NO + 5 % O₂ + 5 % CO₂ + 3.5 % H₂O after reduction in 10 % H₂) and NO conversion in lean /rich cycling conditions. NO_x storage efficiency and NO_x conversions are 10 to 15 % higher on Pt/Ce_{0.9}Pr_{0.1}O₂ than on the ceria analogs.

Oxygen mobility and Ce³⁺/Ce⁴⁺ ion pairs play a determining role in storing and oxidizing adsorbed NO species (lean phase) and in promoting nitrite/nitrate reduction, especially by H₂ (rich phase). The oxygen vacancies on the NSR surface govern the NO_x storage capacity of ceria. For this reason, CeO₂-nanorod based NSR catalysts possess a superior NSC.⁷⁸ Replacing ceria by CeZrO_x mixed oxides is a classical way to increase oxygen mobility and reducibility of cerium⁷⁹⁻⁸¹ and these oxides are now currently used in automotive converters.⁸² CeZrO₂ oxides are solid solutions available in a large range of composition. However, some distortion to the ideal solution may exist with surface enrichment in one of the component, depending on the pre-treatment.⁸³ Le Phuc *et al.*⁸⁴ have compared the behavior of Pt-Ba/Al₂O₃ and Pt/Ce_xZr_{1-x}O₂ (x= 1; 0.70; 0.58; 0.20) catalysts in NSR process. All the catalysts

were stabilized at 700°C in wet air for 4h before NSC measurements. CeZrO_x-supported Pt catalysts have superior NSC performances than Pt-Ba/Al₂O₃ (Table 3.2). Moreover, a further treatment in H₂ at 700°C improves NSC of Zr-containing catalysts while a severe degradation of the performances of Pt/CeO₂ (x=1) is observed in such conditions.

Table 3.2: NO_x storage capacity of 1%Pt/Ce_xZr_{1-x}O₂ catalysts (μmol g⁻¹). The catalysts are denoted PtCeX where X is the Ce% in the support. Catalysts were stabilized in wet air at 700°C for 4h, then cooled down to the temperature of NSC measurement (NS gas: 350 ppm NO, 10% O₂, 10% H₂O, 10% CO₂ in N₂ during 100s). They are compared to a reference 1%Pt-10%BaO/Al₂O₃ catalysts. The PtCeZr catalyst were also pre-reduced in H₂ at 700°C and NSC was measured in the same conditions. Total NO_x storage in 100s amounts to 67 μmol g⁻¹. From ref. 81

Catalyst	Stabilized NSC catalysts			Reduced NSC catalysts		
	200°C	300°C	400°C	200°C	300°C	400°C
PtCe100	20.9	22.8	24.2	8.7	14.0	9.6
PtCe70	17.1	16.9	16.7	19.4	23.1	21.3
PtCe58	23.0	17.4	15.5	23.2	24.9	19.8
PtCe20	18.1	16.0	12.8	19.3	21.1	16.6
Pt-Ba/Al	13.1	13.8	18.3			

The regeneration of Pt/Ce_xZr_{1-x}O₂ catalysts strongly depends on the nature of the reductant with the following efficiency for NO_x conversion: H₂ > CO > C₃H₆.⁸⁵ Incidence on the selectivity is still much more marked. The presence of propene in rich gas leads to a relatively high selectivity to N₂O. This effect is reinforced if there remains some ppm of propene in the lean gas. Pt-Ba/Ce_{0.6}Zr_{0.4}O₂-Al₂O₃ catalyst doped with rare-earth oxides were described by Wang *et al.*⁸⁶ for their remarkable NO_x storage capacity coupled to a high stability. Authors underline that CZ-Al₂O₃ are widely used in TWC (three-way catalysis) for combined effects: (i) Al₂O₃ serves as a diffusion barrier between ceria-zirconia particles to prevent their sintering; (ii) CZ stabilizes Pt particles, maintaining high dispersion at high temperature. Catalysts of 230-260 m² g⁻¹ were then prepared and doped with La₂O₃, Nd₂O₃ or Y₂O₃.⁸⁶ The best performances are obtained with Pt-Ba/La-CZA with virtually total conversion of NO_x at 350°C while conversion is limited to 80 % on the undoped catalyst. And yet, NO_x storage capacity is close for all catalysts, which tends to prove that La doping improves the reduction of stored NO_x by H₂.

3.3.5 Platinum catalysts with other NO_x storage materials

Platinum associated with various basic materials. Comparison of Pt-X/Al₂O₃ catalysts with X=Mg, Ca or Ba was performed by Basile *et al.*⁸⁷ NO_x conversion efficiency was measured in lean (120 s)/rich (6 s) cycling conditions. Maximal NO_x conversion is observed at 200-250°C for every catalyst. Pt-Mg/Al₂O₃ is the most active catalyst at low temperature while Pt-Ba/Al₂O₃ has the best performance

at $T > 250^\circ\text{C}$. Association of Ba and Mg allows maintaining high conversion at high temperatures (Figure 3.7).

Barium was tentatively replaced by strontium or calcium in Pt/Al₂O₃ without clear improvement of the performances.⁸⁸ More recently, Tamm *et al.*⁸⁹ showed that Ba could also be replaced by silver as storage component in Pt/Ag/Al₂O₃ catalysts. Surprisingly, this material is remarkably more active for NO_x storage than the reference Pt-Ba/Al₂O₃ at low temperature ($T < 200^\circ\text{C}$). But, the barium-based NSR catalyst becomes more active at $T > 200^\circ\text{C}$. Coupling Ag and Ba or double-bed with Ag and Ba catalysts would be a way to keep a good activity over a large range of temperature.

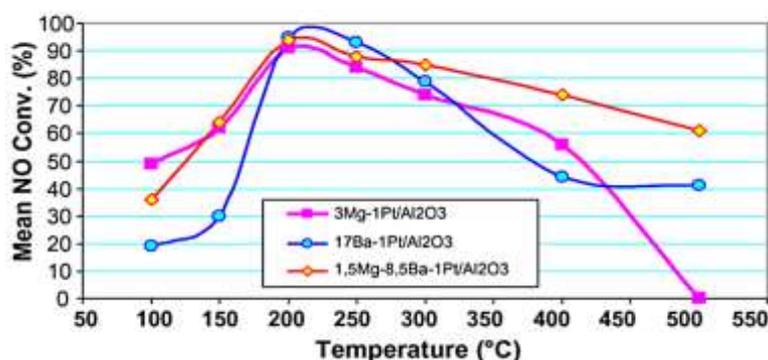


Figure 3.7. Comparison of Ba and Mg as basic component of NSR catalysts. Effect of the addition of the two dopants. Mean NO_x conversion is measured on 10 lean/rich pulses. Gas composition is 1000 ppm NO + 5 % O₂ + 9.8 % CO₂ in lean phase while O₂ is replaced by a H₂/CO/propylene mixture (1.1/3.2/0.6) in rich phase. Reprinted from ref. 87 with permission from Elsevier.

Platinum catalysts associated with transition metal oxides. Transition metal oxides were added to Pt-Ba catalysts to improve NO oxidation activity and/or nitrites/nitrates reduction. Pt-Ba-CoO_x/Al₂O₃ catalysts were investigated by Wang *et al.*⁹⁰ and Hu *et al.*⁹¹ Contrasted results were obtained. While Wang *et al.* concluded to a very positive effect of Co both on NO_x storage and adsorbed NO_x reduction, the conclusions of Hu *et al.* are less optimistic. It seems that a relatively high Co content is required for improving NO_x storage, but then, the selectivity to N₂ decreases with large formations of N₂O and NO release during the rich phase. These differences might come from subtle changes of the catalyst preparation: Co and Pt were successively impregnated on Ba/Al₂O₃ in the work of Wang *et al.* while Hu *et al.* prepared their samples by co-impregnation of Pt and Co on Ba/Al₂O₃. It should be noted that the best performances of Pt-Ba/Al₂O₃ are obtained by impregnating first Pt, which is not the case in these studies. Addition of Fe was also investigated with the objective to improve NO_x reduction by various reductants.⁹²⁻⁹⁴ Yamazaki *et al.*⁹² explored the use of Fe-doped catalysts with CO as reductant. They showed that Fe limited the CO-self poisoning of CO-NO_x reactions and thus increased the ability of CO to reduced adsorbed NO_x in the rich phase. Hendershot *et al.*⁹⁰ stressed the fact that Fe catalysts could produce N₂O (with CO + C₂H₄ as reducing agents) but the role of Fe is not clearly addressed.

Luo *et al.*⁹⁴ have characterized in detail their Pt-Fe/Ba/Al₂O₃ catalysts and showed that Pt is covered with FeO_x species in oxidative medium while Pt-Fe alloy should be formed in reducing medium (Figure 3.8)

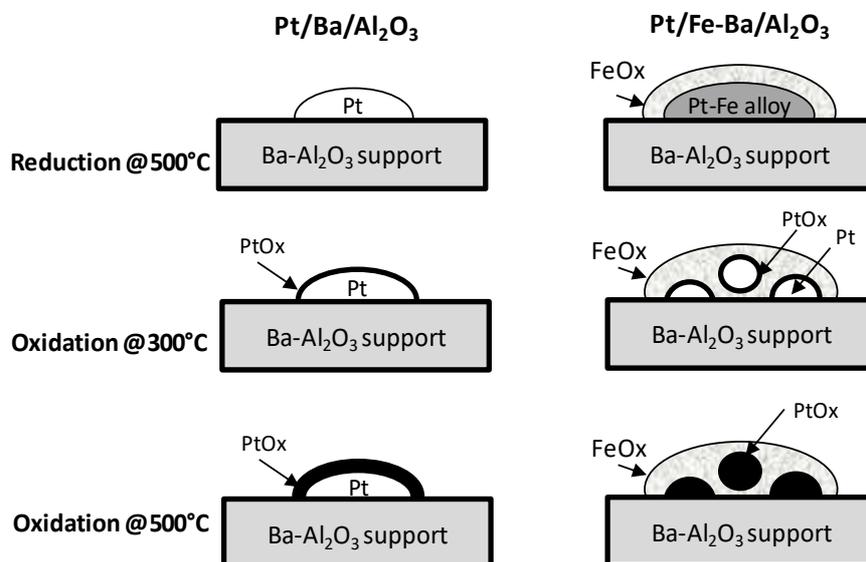


Figure 3.8. Model for the Pt state in Pt/Ba/Al₂O₃ and Pt/Fe-Ba/Al₂O₃ catalysts under different atmospheres. From ref. 94.

Copper was also studied as additive of Pt-Ba/Al₂O₃.⁹⁵ In fact, copper has rather a negative impact both on NO_x storage and NO_x reduction. However it confers to Pt-Ba catalyst a remarkable SO_x resistance: NSC is improved on Cu catalyst in the presence of sulphur and the NO_x conversion is only slightly diminished.

Manganese addition to Pt-Ba/Al₂O₃ was investigated by Deng *et al.*⁹⁶ and Xiao *et al.*⁹⁷ who compared Pt-Ba/Al₂O₃, Mn-Ba/Al₂O₃ and mechanical mixture of the two catalysts. Mn has a positive effect on NO_x storage and reduction, both in absence or in presence of SO₂. Two Mn oxides are evidenced on the surface of Ba/Al₂O₃: MnO₂ and Mn₂O₃ while Mn would be associated to Ba in the bulk phase as BaMnO₃. Manganese oxide is also a remarkable NH₃-SCR catalyst.⁹⁸ MnO_x/Al₂O₃ is very active but rather sensitive to the presence of SO_x. MnO_x-TiO₂ catalysts are more S-resistant while keeping a good SCR activity.⁹⁹ Another way to reinforce S-resistance is to combine Mn and Fe oxides.¹⁰⁰ In NSR processes, ammonia can be produced during the rich phase. It is interesting to take advantage of this NH₃ production to increase NO_x conversion by an ultimate step of NH₃-SCR in the NO_x-trap and reduction process. Le Phuc *et al.* have shown that adding Mn or Fe^{101,102} or Mn and Ce¹⁰³ led to significant improvement of NO_x conversion while NH₃ selectivity was reduced. A spectacular effect was observed when Mn and Ce were combined in Pt-Ba/Al₂O₃ catalysts (Figure 3.9).

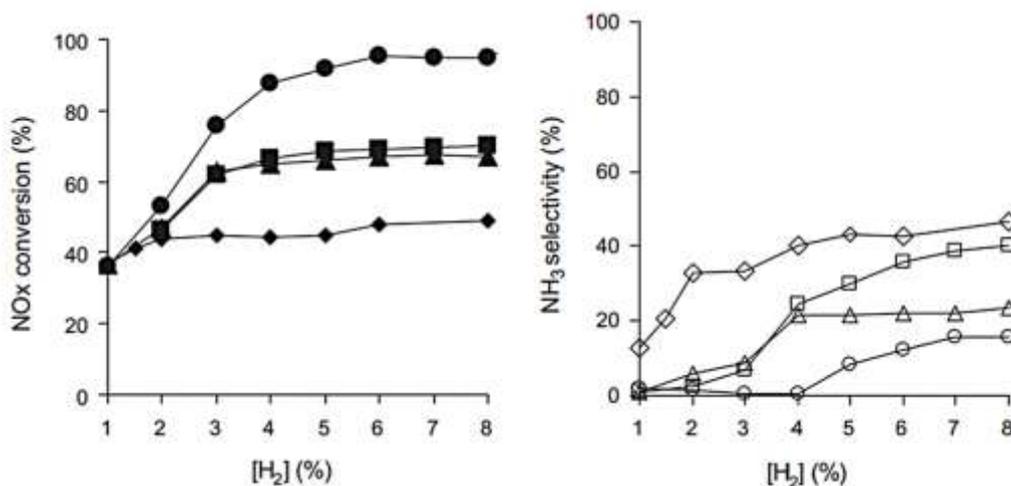


Figure 3.9. NO_x conversion rate (full symbols) and NH₃ selectivity (open symbols) measured at 400°C depending on hydrogen concentration in the rich pulses for Pt/20%Ba/Al (◆,◇), Pt/20%Ba-7%Mn/Al (■,□), Pt/20%Ba-18%Ce/Al (▲, △) and Pt/20Ba-7%Mn-9%Ce/Al (●,○). Gas composition in lean: 500 ppm NO + 10 % O₂ + 10 % CO₂ + 10 % H₂O. In rich phase, NO+O₂ is replaced by H₂. Reprinted from ref. 103 with permission from Elsevier.

On Pt/20Ba/Al₂O₃, NO_x conversion is limited to 40-50 %, while a severe NH₃ slip formed in the NSR process is observed up to 40-50 % selectivity. Addition of 7.2 % Mn and 0.5-1 % Ce to the catalyst allows to approach a 100 % conversion of NO and no NH₃ slip up to 4 % H₂ in the rich pulse.

H₂-plasma assisted NSR was carried out over a combined Pt-Ba/Al and LaMn_{0.9}Fe_{0.1}O₃ catalysts.¹⁰⁴ The plasma was applied during the rich phase with 2 % H₂ as reducing agent. Association of the Pt-Ba/Al₂O₃ catalyst with the LMF perovskite gives remarkable performances with plasma off (70 % NO_x conversion at 150°C in absence of H₂O and CO₂; 20 % with H₂O + CO₂). But when plasma is on in rich phases, almost total NO_x conversion is reached at low temperature (>85 % at 150°C with H₂O + CO₂).

3.3.6 NSR materials with other noble metals

Platinum-rhodium catalysts. Commercial NSR catalysts generally contain Pt and another noble metals, most often Rh to improve NO_x reduction and limit the formation of undesired products (N₂O formation, NO_x release, etc...). Comparison between Pt, Rh and Pt-Rh catalysts was carried out by Breen *et al.*¹⁰⁵ who confirmed the essential role of Rh in the reduction of the NO_x stored during the preceding lean phase. Platinum alone is hardly able to reduce all the stored NO_x, which requires to adapt the duration and frequency of lean/rich cycle. By contrast, rhodium alone cannot promote NO_x storage because Rh is a poor NO oxidation catalyst, which explains that Pt should necessarily be added to Rh in an efficient NSR catalyst. These results¹⁰⁶ were confirmed by Andonova *et al.*¹⁰⁶ who gave

interesting insights into the mechanism of NO_x reduction on Rh. Oxygen is easily released from Rh, which let the metal free for adsorbing NO_x. This could facilitate the rate of spill-over of NO_x from the storage site (BaO or Al₂O₃) to the noble metal for reaction with the reducing agent.

Platinum-ruthenium catalysts. Ru is an excellent three-way catalyst for NO abatement. It is by far the most active metal for the reduction of NO by H₂/CO mixtures.¹⁰⁷ Unfortunately, Ru tends to form volatile ruthenium oxides during lean excursions, which explains why it has been excluded from the formulation of automotive catalysts. Association with Pt could make Ru more stable. Chen *et al.*¹⁰⁸ have shown that the catalyst Pt–Ru/Ba/Al₂O₃–Ce_{0.33}Zr_{0.67}O₂ would have very good NSR performances. NO_x storage capacity is rather lower than on the Pt-only catalyst but the NO_x reduction activity is significantly higher, which leads to better performances in cycling regimes. The beneficial effect of Ru would be due to its ability to keep Pt in a reduced state.

Comparison between Pt, Rh and Pd. Several studies have compared the efficiency of noble metals with various basic components: BaO¹⁰⁹, CaO¹¹⁰ or MgAl₂O₄.¹¹¹ Some of these studies also compared the reactivity of various reducing agents: H₂, CO, C₃H₆ and C₃H₈ on PM–BaO/Al₂O₃¹⁰⁶; CO/C₃H₆ on PM/CaO/Al₂O₃¹¹⁰ and H₂, CO or C₃H₆ on PM/MgAl₂O₄.¹¹¹ The overall activity depends on both the precious metal and the nature of reductant. For instance, Roy *et al.*¹¹¹ showed that Pt was more efficient with H₂ as reducer while Rh catalysts have better performances with CO and C₃H₆ as reducing agents. Abdulhamid *et al.*¹⁰⁹ confirmed the good behavior of Pt catalysts with H₂ in rich phase. They also underline the fact that Pd is rather effective when hydrocarbons are used in rich phase.

Moreover, water can intervene in the transformation of CO and hydrocarbons in rich phase.¹¹² Pt is the best catalyst for the water-gas shift reaction while Rh is the best metal for the steam reforming reaction. Palladium has intermediate activity in both reactions. Hydrogen may thus be produced from CO and hydrocarbons even if it is not injected in the rich pulse.

Palladium catalysts. Palladium is less expensive than Pt and Rh (703 \$/Oz for Pd, 1011 \$/Oz for Rh and 1273 \$/Oz for Pt, Johnson-Matthey mean price over the last 5 years). Even though the differences between the prices of the noble metals tend to decrease, it is always interesting to develop Pd catalysts for automotive applications. Performances of Pd–Ba/Al₂O₃ and Pt–Ba/Al₂O₃ were compared by Salasc *et al.*¹¹³ and Su *et al.*¹¹⁴ with propene as reducing agent. In spite of significant differences in the mode of preparation (PGM precursors: [Pt(NH₃)₄][OH]₂ and [Pd(NH₃)₄][NO₃]₂ for a final content of 2.7 wt-% for Pt and Pd in the study of Salasc *et al.*; H₂PtCl₆ and Pd(NO₃)₂ for a final content of 1 wt-% in the

study of Su *et al.*), both studies led to similar conclusions. It is worth noting that Pd is not so active than Pt in oxidation of NO. However, it is more active than Pt for NO_x conversion at moderate temperature (T<300°C) while the reverse is observed at high temperature (400°C). Pd tends to form more nitrites than Pt and NO₂ is more strongly adsorbed on Pd than on Pt. A drawback of Pd catalysts is the tendency to re-form NO during the lean/rich switch.¹¹³

Interesting improvements of Pd catalysts were recently reported by Zhang *et al.*^{115,116} and by Chen *et al.*¹¹⁷ Better NO oxidation activity of Pd was obtained by addition of Mn to Pd-Ba/Al₂O₃¹¹⁵, which favors NO_x storage. In this work, H₂ is used as reductant and an improvement of the NO_x conversion is observed over the entire range of temperature (150-400°C). Addition of Co can also improve NO oxidation activity. Combining Pd-Co-Ba/Al₂O₃ and activation by non-thermal plasma allows Zhang *et al.*¹¹⁶ to obtain 100 % NO conversion at 150°C, while such performances are obtained only at 350-400°C when the plasma is off. Excellent NSR activity was reported by Chen *et al.* over Pd-K/MgAlO_x mixed with Pd/MgAlO_x by using CO as the reductant.¹¹⁷ It seems that CO oxidation by NO_x in rich phase plays an important role in the overall NO_x conversion.

More complex formulations of Pd-based catalysts was reported by Jabłońska *et al.*¹¹⁸ The catalyst, a hydrotalcite-like materials containing Mg, Zn, Al and Fe, is active with C₃H₆ as reducer agent. It possesses both redox and basic sites required for the NSR process. Pd is simply added to improve the NO oxidation activity. Palladium may also be incorporated in perovskite structures. The catalyst (La_{0.7}Ba_{0.3})(Fe_{0.776}Nb_{0.194}Pd_{0.03})O₃ was developed by Ueda *et al.*¹¹⁹ In fact, the perovskite LaFe_{0.97}Pd_{0.03}O₃ had significant NO_x reduction properties. Partial substituting of La for Ba in the A site allowed to reinforce storage properties. The catalyst leads to a 47 % conversion of NO_x at 250°C with CO as reducing agent (lean: 512 ppm NO+ O₂, 54 s / rich: 512 ppm NO + 4 % CO, 6 s).

Trimetal catalysts. Commercial NSR catalysts may contain the three noble metals (Pt, Pd, Rh). The great advantage of these formulations is to combine the positive effect of Rh in the NO_x reduction step and the positive effect of Pd on the platinum thermal stability. Standard compositions of 2.0 g Pt+ 0.9 g Pd + 0.2 g Rh per liter were described in a recent patent by Mitsubishi.¹²⁰

3.4 Noble metal-free catalytic materials

Transition metal oxides (most often, Co, Mn or Cu) were generally added to NSR catalysts for replacing noble metals. The complete formulation generally requires to impregnate the support with a basic oxide to improve NO_x storage behaviours. We will examine the perovskite-based catalysts are examined first, and then those where transition metal oxides are not inserted in a definite structure.

3.4.1 Perovskites-based NSR catalysts

Cobaltites. Several cobaltites were reported as active Pt-free catalysts for the NSR process. They are based on LaCoO₃^{121,122} or La_{1-x}Sr_xCoO₃.¹²³⁻¹²⁴ Potassium compounds are added to LaCoO₃ as basic materials while the presence of Sr in La_{1-x}Sr_xCoO₃ seems to be sufficient for a good NO_x storage. A remarkable improvement of La_{0.5}Sr_{0.5}CoO₃ for NSR catalysis was obtained by treating the solid by acetic acid.¹²⁴ This treatment induces a Co exsolution and a partial dissolution of Sr. The surface is then composed of Co³⁺/Co²⁺ species and SrO_x aggregates (Figure 3.10). All the NSR functions are located on the same materials: NO oxidation can occur on cobalt while NO₂ is stored on SrO_x.

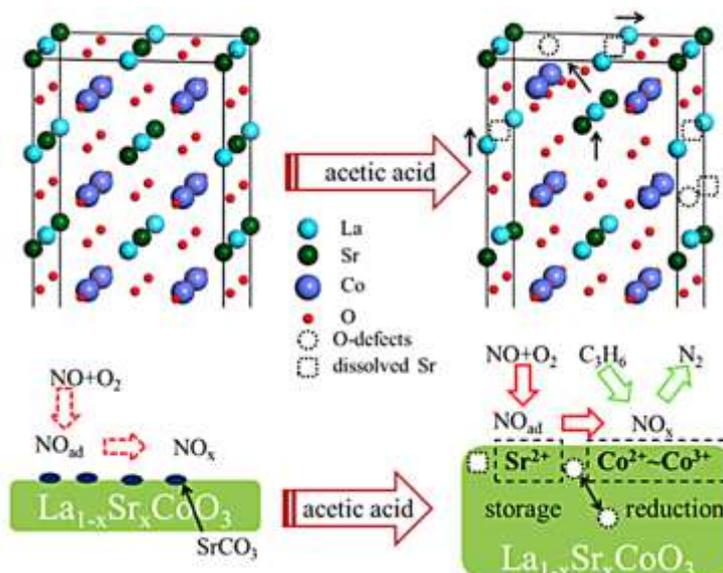


Figure 3.10. Improvement of La_{1-x}Sr_xCoO₃ perovskite by acetic acid for the NSR reaction. Co³⁺/Co²⁺ ion pairs and SrO_x aggregates are created at the surface, thus forming sites for NO storage and reduction. Reprinted from ref. 124 with permission from ACS Publications.

Manganites. LaMnO₃ perovskites were studied in the NSR process^{125,126} as possible Pt-free catalysts. However, LaMnO₃ seems active only in the NO oxidation reaction. Basic material (such as BaO) should be added to promote the NSR reactions (storage and reduction) and it was proven that a noble-metal catalyst placed after the perovskite bed significantly improved NO conversion.¹²⁵ In the work of

Constantinou *et al.*¹²⁶, the perovskite is doped with Pd and Rh required to activate the hydrocarbon used as reductant and to promote the reduction of stored NO_x. La_{1-x}Sr_xMnO₃ perovskites are much more active than the undoped LaMnO₃ perovskite because they virtually contains a basic component (SrO_x) and the Mn⁴⁺ content is modified by the presence of Sr. In an attempt to implement Pt-free catalysts to treat diesel exhaust, Kim *et al.*¹²⁷ showed that La_{1-x}Sr_xCoO₃ catalysts could replace Pt-based DOC catalysts, while La_{0.9}Sr_{0.1}MnO₃ catalyst achieved NO_x reduction performance comparable to that of a commercial platinum-based counterpart. Nevertheless, the perovskite should be doped with Pd and Pt to reach performances close to that of Pt-Ba/Al₂O₃ catalysts. A study of the NSR performances of Sr-doped LaMnO₃ catalysts without any addition of PGM was carried out by Peng *et al.*¹²⁸ The perovskite was treated in solution of nitric acid to create active site at the oxide surface. This is similar to activation of La_{1-x}Sr_xCoO₃ perovskite by acetic acid (see Figure 3.10). Peng *et al.* confirmed the good behavior of the catalyst in NO oxidation and NO_x storage. The best performances are obtained with the sample having the highest Mn⁴⁺ surface concentration.

Copper-based perovskites. Copper was substituted in SrTiO₃ titanates to form SrTi_{0.89}Cu_{0.11}O₃ catalysts combining NO_x storage properties and NO_x reduction activity.¹²⁹ The non-substituted perovskite (SrTiO₃) possesses interesting storage properties. Addition of copper allows the catalyst to reduce stored NO_x with a greater efficiency. The copper titanate was prepared by a sol-gel method (hydrolysis of titanium isopropoxide, redissolution in citric acid/H₂O₂ and incorporation of nitrate of Sr and Cu)¹³⁰. It is worth noting that this material, initially developed for soot combustion, appears to have interesting NSR properties, which authorizes the development of NSR-soot combustion coupled systems.

Mixed perovskites. More complex perovskite catalysts including Mn and Co were also developed for the NSR process. Peng *et al.*¹³¹ showed that a Sr₂Mn_{0.8}Co_{0.2}O₄ perovskite-like mixed oxide supported on Ba/Al₂O₃ exhibited remarkable performances for NO_x storage and reduction. This system is more active than similar catalysts with Mn and Cu (Sr₂Mn_{0.8}Cu_{0.2}O₄) or with Mn only (Sr₂MnO₄). The performance can be improve by doping the catalyst with K (SrKMn_{0.8}Co_{0.2}O₄ /BaO/Al₂O₃). Coupling catalysis with non thermal plasma (8-12 kV) allows to reach 80-90 % NO_x conversion at 300°C. It is not necessary to have a reducing agent in rich cycles: alternate cycles of 500 ppm NO + 5 % O₂ (lean) with pure Ar (rich) give almost the same conversion than with H₂, CO, C₃H₆ in rich cycles.

3.4.2 Non-perovskitic NSR catalysts based on transition metal oxides

Cobalt oxides. Addition of transition metal oxides (M=Ce, Fe, Cu, Co) to a $K_2CO_3/K_2Ti_8O_{17}$ catalyst was investigated by Zhang *et al.*¹³² Among all the catalysts, $CoO_x-K_2CO_3/K_2Ti_8O_{17}$ exhibits the best performance (Co > Cu > Fe > Ce). It is confirmed that K_2CO_3 is the site for NO_x storage while Co oxide is the active species for NO_x reduction. Interestingly, the catalysts reduced NO_x with a very high selectivity to N_2 with virtually no N_2O in the outlet gas. Excellent performances of Co-based catalysts were reported by Palomares *et al.*¹³³ who prepared a Co-hydrotalcite catalyst of $152\text{ m}^2\text{ g}^{-1}$. Hydrotalcite Co/Mg/Al with the composition 14/70/16 presents the highest performance after doping with 3.4 % Na.

Non-thermal plasma is also a way to activate transition metal oxide catalysts for NSR applications. Zhang *et al.*¹³⁴ have prepared a series of MO_x-Ba/Al_2O_3 catalysts (M = Mn, Fe, Co, Ni, Cu). All these materials possess a good storage capacity at 300-400°C. Only Mn and Co have a capacity at 200°C almost equal to that of 300°C, which makes them good candidates for NSR catalysis. However, they are not excellent in lean/rich cycling regime because their reduction activity remains relatively modest. When the reaction is assisted by non-thermal plasma, a 100 % NO_x conversion is obtained on Mn and Co catalysts at 200°C whereas the reference Pt-Ba/ Al_2O_3 reach only 70 % conversion.

Copper catalysts. Copper catalysts are potentially interesting because they combined a good activity for NO_x reduction and a remarkable resistance to SO_x poisoning.¹³⁵ NO_x storage is ensured by a basic component added to the Cu catalyst. A Cu/Ba/bauxite catalyst was developed by Wang *et al.*¹³⁶ who compared this new material to the reference Pt-Ba/Al catalyst. The Cu/Ba/bauxite catalyst has a much better NO oxidation activity, a similar NO_x trap capacity and a higher NO_x conversion, particularly in the 200-300°C temperature range. Cu oxides exhibit very interesting properties when they are supported on cerium-based oxides. Bueno-López *et al.* have studied the NSR performances of copper (5 wt-%) supported on Ba-CeO₂¹³⁷ and on Ce_{0.8}M_{0.2}O_δ (M = Zr, La, Ce, Pr or Nd) mixed oxides.¹³⁸ The reactivity was followed by rapid-scan DRIFT with injection of pulses of H₂ or CO every 30, 60 or 120 s in the lean gas (850 ppm NO + 5 % O₂ in N₂).¹³⁹ On these catalysts, the NO_x are stored as nitrites and nitro-groups at low temperatures and as nitrates at high temperatures. CuO_x/BaO has the highest NO_x storage capacity but its oxidation activity (NO_x -to-nitrates) is much lower than that of CuO/CeO₂. In every case, H₂ is a more powerful reductant of the stored NO_x than CO. Ceria supports doped with Zr, La, Pr and Nd were compared with pure ceria. The basicity of the M cation ($La^{3+} > Pr^{3+}$

$> \text{Nd}^{3+} > \text{Zr}^{4+}$) dominates the reactivity, both in NO_x storage and in stored NO_x reduction. The best NO_x removal in NSR experiments performed at 400°C with $\text{CO} + \text{H}_2$ pulses was achieved with the catalyst with the most basic dopant ($\text{CuO}/\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_\delta$).¹³⁸

Manganese catalysts. MnO_x -base catalysts were more rarely studied. Zhang *et al.*¹³⁹ extended their investigation of $\text{K}_2\text{CO}_3/\text{K}_2\text{Ti}_8\text{O}_{17}$ supports (see ref. 132) to the case of 10 % MnO_x catalysts. The content of potassium carbonate was varied between 0 and 30 %. The 25 % K_2CO_3 sample shows the highest NO_x storage capacity while maintaining a high redox activity of manganese oxide. A mean NO_x conversion of 98.5 % with a very high selectivity to N_2 (virtually no N_2O) is reached upon 10 lean/rich cycles (lean: 400 ppm $\text{NO} + 5\% \text{O}_2$; rich 1000 ppm C_3H_6). At higher carbonate content in the catalyst, potassium tends to cover MnO_x and decreases its activity.

3.5 Durability and deactivation of catalytic materials

Eternal catalysts do not exist: their performances slowly decline with time-on-stream. Most frequent causes of activity decrease are: (i) sintering by long-term use of the catalyst (including excursions at high temperature), (ii) sulphur poisoning, (iii) poisoning by other elements (phosphorus, ...). Item (i) more specifically refers to the durability of the material while items (ii) and (iii) concern the deactivation by poisons coming from fuel or lubricant combustion.

3.5.1 Durability. Effect of thermal deactivation.

Relatively few studies were devoted to thermal deactivation effects. It is possible to find in the papers cited in previous sections some comments on the stability of the catalysts after either treatment at $T > 600^\circ\text{C}$ or after several lean/rich cycles. Keeping in mind that the catalyst should be operative during almost 200 000 km, these indications cannot give a real view of the tendency of the catalyst to be stable over a so long distance. Jang *et al.*¹⁴⁰ have investigated the mode of barium deterioration in NO_x storage catalysts. The catalyst (5%Pt-15%BaO on $\gamma\text{-Al}_2\text{O}_3$, $151 \text{ m}^2 \text{ g}^{-1}$) was initially treated at 550°C in air (fresh catalyst), then treated in air for 24 h at 850, 950 and 1050°C . The loss of surface area is not the main factor affecting the performances of the catalyst. After impregnation of Pt and Ba, the BET area falls to $103 \text{ m}^2 \text{ g}^{-1}$ in the fresh catalyst, and to $80 \text{ m}^2 \text{ g}^{-1}$ in the sample aged at 1050°C . XRD characterization reveals that a severe Pt sintering is observed in the aged catalysts: the particle size of Pt, of 1.84 nm in the fresh catalyst, grows to 12.4 nm at 850°C and to 17.4 nm at 1050°C . On the contrary, BaO_x particles are stable, around 4-5 nm. The loss of NO_x storage capacity was ascribed to

the progressively stronger interaction of Ba with alumina leading to the formation of barium aluminate BaAl_2O_4 . It is worth noting that the effect of barium aluminate formation on the NO_x trap capacity is still a matter of debate. For instance, Zhou *et al.*¹⁴¹ found that $\text{BaO-Al}_2\text{O}_3$ and BaAl_2O_4 are equally effective as NO_x -storage materials. In the work of Jang *et al.*¹⁴⁰, the main factor affecting NO_x storage might thus be the severe Pt sintering.

Adams and Graham¹⁴² have investigated the effect of a lean aging (air, 950°C, 3 h) versus a rich aging (1 % H_2 , 950°C, 3 h) over a Pt-Ba/ Al_2O_3 NO_x -trap catalyst. Some complementary results were obtained on a cerium-containing catalyst (Pt-Ba-Ce/ Al_2O_3). Catalytic tests were performed on "degreened" samples, *i.e.* treated at 600°C for 1 h in lean/rich cycles before testing from 150° to 600°C. Effects of aging are compared in Figure 3.11.

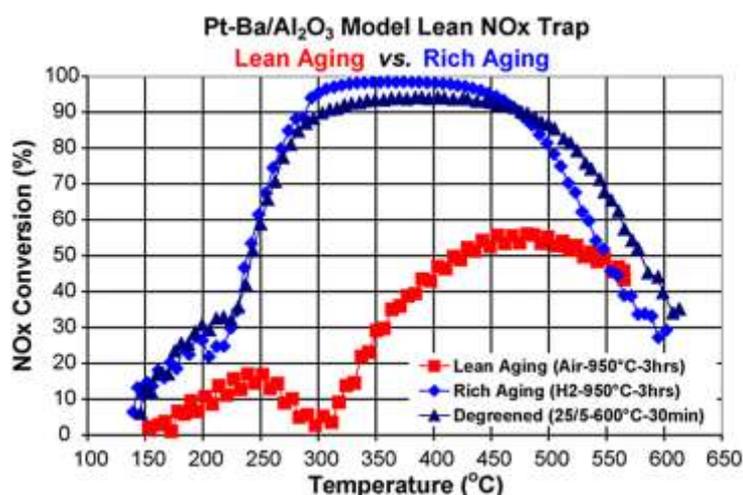


Figure 3.11. Effects of lean and rich aging on the performance of the Pt-Ba/ Al_2O_3 catalyst. NO_x conversion is measured in lean (25 s) / rich (5 s) cycles. Gas composition lean: 500 ppm NO + 100 ppm C_3H_6 + 500 ppm CO + 167 ppm H_2 + 10 % O_2 in N_2 + 5 % CO_2 + 5 % H_2O ; rich: 500 ppm NO + 1650 ppm C_3H_6 + 4 % CO + 1.3 % H_2 + 1 % O_2 in the same N_2 + CO_2 + H_2O gas. "Degreened" catalysts are fresh samples pre-treated at 600°C in lean/rich cycles. Reprinted from ref.142 with permission from Elsevier.

Rich aging (in H_2) has virtually no effect on the NO_x conversion whereas lean aging severely affects the catalyst performances. Aging also changes the selectivity to NH_3 and N_2O . The catalyst aged in H_2 has a 45 %-maximum of NH_3 formation at 300°C while the sample aged in air has a 35 %-maximum of NH_3 formation at 450°C. Similar temperature shifts are observed for the formation of N_2O : maximum of 18 % at 225°C for the H_2 -aged catalyst and 10 % at 300°C for the air-aged sample. The Ce-containing catalyst gives higher NO_x conversion at low temperature. However, it is more difficult to totally regenerate this catalyst than the Ce-free sample.

3.5.2 Sulphur poisoning

Sulphur dioxide present in exhaust gases tends to form stable sulphates which lead to a severe decrease of the NO_x trap capacity. Regeneration of the trap is performed by sulphate elimination in rich conditions at high temperature. Due to incomplete S elimination and to thermal damage, the catalyst gradually loses its initial properties. Sulphur poisoning has been the subject of a great number of investigations, summarized in Table 3.3 (Pt-Ba-Al₂O₃ catalysts), and Table 3.4 (others, including Ce-based catalysts).

Table 3.3: Overview of the studies on sulphur deactivation of Pt-Ba-Al₂O₃ catalysts. Compositions are given in wt-%. For instance, 1Pt-8Ba means 1%Pt+8%BaO

Catalysts	Techniques	Main conclusions	Ref.
1Pt-8Ba	DRIFT, Thermodynamics	Bulk sulphate (1144 cm ⁻¹) increases with time. Bulk carbonates (1450 cm ⁻¹) decrease. No effect of O ₂ . Partial regeneration by H ₂ at 700°C	Breen et al. ¹³⁹
2Pt-1Rh-20Ba	Reactivity studies	NSC decreases linearly with the dose of SO ₂ down to 20% of the initial capacity	Engström et al. ¹⁴⁰
2Pt-20Ba	Reactivity studies, DRIFT, modeling	More severe deactivation when SO ₂ is injected in the rich phase. Poisoning of NSC sites closed to Pt.	Fridell et al. ¹⁴¹
0.72Pt-0.14Rh-17Ba	Reactivity studies	Crucial effect of the presence of water for the regeneration of sulphates. Dry conditions: no reduction before 1000°C.	Mahzoul et al. ¹⁴²
0.19Pt-3.5Ba	Reactivity studies, FTIR	When the extent of sulphatation is low (30% of BaO), the catalyst can be totally regenerated under reducing conditions (H ₂ /CO/C ₃ H ₆ /H ₂ O).	Courson et al. ¹⁴³
Pt-Ba commercial	Reactivity studies. FTIR, EXAFS	Sulphates are hardly reducible by C ₃ H ₆ below 550°C. Sulphides are formed as intermediates blocking the Pt particles.	Sedlmair et al. ¹⁴⁴
1Pt-5Ba	Reactivity studies, In situ Raman	Nitrites/nitrates can be characterized on Ba or bare alumina. Sulphate progressively replaced nitrates on Ba and alumina. They could block oxidation of nitrites to nitrates.	Uy et al. ¹⁴⁵
2Pt-1Rh-15Ba	Reactivity studies, Thermodynamics	Comparison of SO ₂ , H ₂ S and COS. All the sulphur compounds lead to very close catalyst deactivation, more severe under rich exposure. H ₂ S and COS cause also loss of noble metals.	Amberntsson et al. ¹⁴⁶
Pt-Rh-15Ba, NM: various contents	Reactivity studies, XPS,	Pt is the essential metal for a good behavior in the NSR process. Rh increases the NO _x reduction in rich medium. A good combination of Pt and Rh also increases the S-resistance and regeneration of the catalyst	Amberntsson et al. ¹⁴⁷
Pt-Rh-15Ba, NM: various contents	Reactivity studies, XPS, FTIR	Confirmation of the stronger deactivation in rich exposure. Rh allows a better resistance and a better regeneration of the catalyst. Pt sites are blocked by sulphates.	Amberntsson et al. ¹⁴⁸
2Pt-10Ba	Reactivity studies, XPS	Important role of CO ₂ during rich regeneration. H ₂ alone is not sufficient. Rich exhaust gas involving H ₂ and CO ₂ is more powerful for a complete regeneration. CO ₃ ²⁻ can displace S ²⁻ from Ba under rich conditions.	Poulston, Rajaram ¹⁴⁹
1Pt-20Ba	Reactivity studies, XRD, H ₂ -TPR	Presence of aluminium sulphates, surface and bulk barium sulphates after SO ₂ . An oxidizing treatment at 800°C allows the decomposition of the surface aluminium sulphates but it gives mainly crystallised barium sulphates, more stable.	Elbouazzaoui et al. ¹⁵⁰
1Pt-10 or 20 Ba	Reactivity studies, XRD, H ₂ -TPR	TPR-peaks of sulphated catalyst (aluminum sulphates at ≈ 550°C, “surface” barium sulphates at ≈ 650°C and “bulk” barium sulphates at ≈ 750°C) allows to follow the regeneration. Presence of CO ₂ and H ₂ O in the rich mixture allows eliminating sulfides and sulphates at 650°C even if there remains some bulk Ba sulphate.	Elbouazzaoui et al. ¹⁵¹
3Pt-15Ba 0.2Rh	Reactivity studies, Raman, DTG	Two types of Ba sulphates of different crystal size. Type I (< 3nm) reduces at 650°C while type II reduces at 750°C. Role of H spillover in regeneration. Aluminum sulfate forms only in the presence of Pt. Rhodium seems to promote S ads. on Ba.	Wei et al. ¹⁵²

Table 3.4: Overview of the studies on sulphur deactivation of catalysts involving Ce and other elements. Compositions are given in wt-%.

Catalysts	Techniques	Main conclusions	Ref.
Ce-based catalyst			
1Pd-CeZrOx	FTIR, TPD	The quantity of sulphates formed at 400°C increased linearly with the Ce content. The sulphates on ZrO ₂ were stable to higher temperatures than those formed on CeO ₂ .	Luo, Gorte ¹⁵³
Commercial PtPdRh-BaCe catalyst	Reactivity studies, OSC, NSC measurements	Low S dosing (1.7 g L ⁻¹) does not affect performances. Higher S dosing (3.4 g L ⁻¹) decreases all performances. NSR is globally affected more than NO oxidation activity. Global selectivity for N ₂ O remained low at all sulphur loadings, but NH ₃ selectivity increased significantly with sulphur loading.	Choi et al. ¹⁵⁴
2Pt-10Ba-CeO ₂	Reactivity studies, XPS, TEM-EDX,	The ceria-supported catalyst can store higher amounts of NO _x than the Pt-Ba-Al catalyst. It is also more resistant to sulphur poisoning and ceria prevents Pt sintering.	Kwak et al. ¹⁵⁵
1Pt-CeZrOx	Reactivity studies, TPR, XRD	SO ₂ -treated catalysts: decrease of NO _x -storage more pronounced over Zr rich samples. Sulphates are less stable than on Pt-Ba-Al and can be eliminated by H ₂ at 550°C. NH ₃ selectivity is decreased on CeZr catalysts.	Le Phuc et al. ¹⁵⁶
Copper catalysts			
1Pt-4Cu-MgAl	NO _x storage measurement	Pt-Cu catalysts on hydrotalcite shows good activity at 250°C and better sulphur resistance than Pt-Ba/Al ₂ O ₃	Centi et al. ¹²⁵
5Cu-ZrO ₂ sulf.+ K-Al	NO _x storage measurement	Cu supported on sulfated zirconia, mixed with alkaline-doped alumina, shows very high sulphur resistance for NO _x storage. Better basic materials: K/Al ₂ O ₃ . Copper cannot oxidizes SO ₂ to SO ₃ .	Clacens et al. ¹⁵⁷
7.5Cu/KTiOx	Reactivity studies, XRD, XPS, TPR	Cu deposited on K ₂ Ti ₂ O ₅ shows good NSR performance and reinforced resistance to S-poisoning. Sulphur accumulation is 3 times less than on Pt catalysts. It can be regenerated at 550°C in H ₂ .	Wang et al. ¹⁵⁸

3.5.3 Improvement of sulphur resistance.

Addition of a transition metal to platinum. As seen in Table 3.4, certain transition metal oxide catalysts shows higher S-resistance than monometallic Pt catalysts. Yamazaki *et al.*¹⁶³ took advantage of this properties to investigate several Pt-M/Ba/Al₂O₃ (M = Fe, Ni, Co, Cu). Addition of Cu to Pt-Ba/Al₂O₃ has no beneficial impact on NO_x conversion in the presence of SO₂. Better performances were obtained with the Pt-Ba-Fe/Al₂O₃. Iron prevents a sulphate deposit on the catalyst and inhibits the growth in size of BaSO₄. Regeneration is achieved at lower temperature than Pt-Ba. Lê *et al.*¹⁰¹ have confirmed the beneficial effect of Fe on the NO_x-storage capacity in presence of SO₂. The temperature of complete sulphate reduction is shifted of 50°C to lower temperatures on Pt-Ba-Fe catalysts. The formation of Ba-Fe mixed oxides is not excluded.

Modifications of the storage component. Barium is the standard component of the NO_x-trap catalyst. Toops *et al.*¹⁶⁴ succeeded in improving NSR catalysts by adding a second basic material to Ba. Association of Ba with Ca gives promising performances by decreasing the temperatures of sulphate elimination. Ba-Ti composites were also investigated by Tanaka *et al.*¹⁶⁵ as a way to enhance sulfur desorption efficiency. The composite was prepared by a sol-gel method using Ti isopropoxide and Ba acetate solutions in citric acid and H₂O₂. It was deposited on the support (Al₂O₃, ZrO₂ or TiO₂)

impregnated with Pt and Rh. Compared to Ba-only catalysts, the materials prepared with the Ba-Ti composite allows much easier desorption of sulphur and higher NO_x conversion in lean/rich regime.

Modifications of the support. Higher sulphur resistance were achieved by using alumina modified by titania.^{166,167} Huang *et al.*¹⁶⁷ used an alumina support impregnated with Ti butoxide while Matsumoto *et al.*^{Erreur ! Signet non défini.} used mechanical mixture of alumina and titania. Other strategies were also developed, all involving TiO₂ supports. For instance, Hirata *et al.*¹⁶⁸ have reported that addition of Pt/TiO₂ to the Pt-Ba/Al₂O₃ allowed sulphur desorption at much higher temperature while Takahashi *et al.*¹⁶⁹ obtained significant improvement with TiO₂-ZrO₂ supports (30 % TiO₂-70 % ZrO₂). It seems that a high acidity of the support is required for a better S resistance. This was confirmed with AZT (Al₂O₃/ZrO₂/TiO₂) mixed oxides used as support of Pt/BaO¹⁷⁰. The superior resistance to sulphur is correlated with an increase of the Lewis acidity. Pt-Ba/AZT is more active than Pt-Ba/Al₂O₃ after S-poisoning and easily regenerable at 700°C (1 % H₂, 5 % CO₂ and 5 % H₂O for 1 h).

3.6 Conclusions and perspectives

NSR catalysts should contain two components in adequate interaction: a basic component for NO_x storage and a metallic component for NO oxidation and adsorbed NO_x reduction. The Pt-Ba/Al₂O₃ reference NSR catalyst has been the subject of a huge number of investigations. Most of them were devoted to the mechanism of NO_x storage-reduction. However, the preparation of this catalyst has been improved to reach a very high efficiency. Nature of Pt and Ba precursors, order of impregnation, pre-treatment,... are essential for a good performance of this catalyst.

A great number of studies were devoted to the improvement of NSR catalysts by changing the basic component. Potassium catalysts show very interesting performances at high temperature. However potassium may affects the mechanical stability of the cordierite substrate. Addition of ceria to alumina or CeZrO_x supports can lead to remarkable improvements of the Pt-Ba catalyst in terms of activity, selectivity etc... Other transition metal oxides (Fe, Mn, Co, Cu,...) added to Pt-Ba also lead to very interesting performances. Though Pt is generally required in NSR catalysts, addition of Rh and/or Pd was investigated in detail. Some Pt-free compositions (with Pd-only) were also tested. Many researchers were interested in replacing platinum group metals (PGM) by transition metal oxides. LaCoO₃, LaMnO₃ or LaFeO₃ perovskites or mixed perovskites of these elements were investigated to get PGM-free catalysts with good performances. Non-perovskitic materials based on supported Co,

Mn and Fe oxides were also developed. However, the complete replacement of noble metals is not feasible yet.

Nature of the active components and optimization of the catalyst preparation as well as its pre-treatment are determining factors of the stability of the catalyst. Pt-NSR catalysts deactivate more rapidly in lean aging than in rich aging but accumulation of transient lean/rich cycles, even at moderate temperatures, may affect the performances. Sulphur is a strong poison of the NO_x storage because sulphates are more stable than nitrates and carbonates. Cerium-based supports, titania, zirconia, ... can potentially prevent a too high S deposition. As sulphates are less strongly bound on these supports, the regeneration by H₂ is also easier. Other reductants added to H₂ (CO, hydrocarbons) and especially the presence of CO₂ and H₂O are important factors for an effective regeneration, keeping in mind that all the sulphur should not be necessarily eliminated for a complete recovery of the performances.

At present, the NSR process tends to be replaced by urea-selective reduction in many DeNO_x applications. However, it is necessary to pursue efforts to decrease the noble metal content and to get more and more stable catalysts, for instance by decreasing the regeneration temperature. Finally, it is also important to develop new catalysts having improved performances at low temperature, especially at 150-200°C.

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TABLE CAPTIONS

Table 3.1

Effect of Ce loading on the NO_x storage capacity (NSC) and selectivity in regeneration by H₂ of Ba-Pt-Ce/Al₂O₃ catalysts. From. Ref. 73.

Table 3.2

NO_x storage capacity of 1%Pt/Ce_xZr_{1-x}O₂ catalysts (μmol g⁻¹). The catalysts are denoted PtCeX where X is the Ce% in the support. Catalysts were stabilized in wet air at 700°C for 4 h, then cooled down to the temperature of NSC measurement (NS gas: 350 ppm NO, 10 % O₂, 10 % H₂O, 10 % CO₂ in N₂ during 100 s). They are compared to a reference 1%Pt-10%BaO/Al₂O₃ catalysts. The PtCeZr catalyst were also prerduced in H₂ at 700°C and NSC was measured in the same conditions. Total NO_x storage in 100 s amounts to 67 μmol g⁻¹. From ref. 84.

Table 3.3

Overview of the studies on sulphur deactivation of **Pt-Ba-Al₂O₃** catalysts. Compositions are given in wt-%. For instance, 1Pt-8Ba means 1%Pt-8%BaO.

Table 3.4

Overview of the studies on sulphur deactivation of catalysts involving Ce and other elements. Compositions are given in wt-%.

FIGURES CAPTIONS

Figure 3.1. General scheme of the NSR process over the reference Pt (Rh)-Ba-Al₂O₃ catalyst.

Figure 3.2. Comparison of NO_x storage properties of NSR catalysts based on 3%Pt-Al₂O₃ (Al/Pt). The catalysts are monolith samples previously washcoated with alumina. Barium was impregnated after Pt (Al/Pt/Ba) or before Pt (Al/Ba/Pt). Ba content is 20 % and Pt dispersion is close to 20 % for all samples. NO_x storage is measured during 4 minutes in lean condition (300 ppm NO + 8 % O₂) after a rich period of 1 minute (300 ppm NO + 8000 ppm H₂). Reprinted from ref.25 with permission from Elsevier.

Figure 3.3. NO_x storage capacity of a 1%Pt-20%BaO/Al₂O₃ catalyst. Effect of the pretreatment at 700°C in N₂ (black bars) or in O₂+N₂ (grey bars) before aging in N₂ + 10 % O₂ + 5 % H₂O at 700°C. NO_x storage is measured during the first 100s in 350 ppm NO + 10 % O₂ + N₂. Maximum adsorption of NO is 67 μmol g⁻¹ corresponding to the totality of the 350 ppm of NO stored during 100 s. From ref. **Erreur ! Signet non défini.**

Figure 3.4. Effect of Ba loading on NO_x storage capacity of Pt-Ba NSR catalysts impregnated on different supports: SiO₂ (185 m² g⁻¹); CeO₂ (143 m² g⁻¹); Al₂O₃ (190 m² g⁻¹); ZrO₂ (34 m² g⁻¹). Reprinted from ref. 35 with permission from Elsevier.

Figure 3.5. Change with the temperature of the NO_x storage capacity of 2%Pt/x%K₂O/Al₂O₃. Effect of the potassium content. K is introduced by impregnation of Al₂O₃ (200 m² g⁻¹) with aqueous solution of KNO₃, then Pt is impregnated with solutions of Pt(NH₃)₂(OH)₂. The catalysts are finally calcined at 500°C. NO_x storage is measured in lean condition (150 ppm NO + 5 % O₂ in He + 5 % CO₂ + %H₂O) after 20 rich/lean cycles. NO_x is integrated until outlet NO_x levels reached 30 ppm. Reprinted from ref. 51 with permission from Elsevier.

Figure 3.6. Temperature effect on NO_x storage efficiency and NO_x conversion in lean/rich cycling of Pt-Ba/Al₂O₃, Pt-Ba/CeO₂, Pt/CeO₂-Al₂O₃ and Pt-Ba/CeO₂-Al₂O₃ (from dark to light grey, respectively). Gas composition for NSE measurement: 300 pm NO, 8 % O₂, 5 % CO₂, 5 % H₂O in He after reduction in H₂. Gas composition for NO_x conversion: same composition for the lean phase as for NSE; rich phase: NO+O₂ replaced by 0.64 % CO + 1.06 % H₂. From ref. 72.

Figure 3.7. Comparison of Ba and Mg as basic component of NSR catalysts. Effect of the addition of the two dopants. Mean NO_x conversion is measured on 10 lean/rich pulses. Gas composition is 1000 ppm NO + 5 % O₂ + 9.8 % CO₂ in lean phase while O₂ is replaced by a H₂/CO/propylene mixture (1.1/3.2/0.6) in rich phase. Reprinted from ref. 87 with permission from Elsevier.

Figure 3.8. Model for the Pt state in Pt/Ba/Al₂O₃ and Pt/Fe-Ba/Al₂O₃ catalysts under different atmospheres. From ref. 94.

Figure 3.9. NO_x conversion rate (full symbols) and NH₃ selectivity (open symbols) measured at 400°C depending on hydrogen concentration in the rich pulses for Pt/20%Ba/Al (◆,◇), Pt/20%Ba-7%Mn/Al (■,□), Pt/20Ba-18%Ce/Al (▲, △) and Pt/20Ba-7%Mn-9%Ce/Al (●,○). Gas composition in lean: 500 ppm NO + 10 % O₂ + 10 % CO₂ + 10 % H₂O. In rich phase, NO+O₂ is replaced by H₂. Reprinted from Ref. 103 with permission from Elsevier.

Figure 3.10. Improvement of La_{1-x}Sr_xCoO₃ perovskite by acetic acid for the NSR reaction. Co³⁺/Co²⁺ ion pairs and SrO_x aggregates are created at the surface, thus forming sites for NO storage and reduction. Reprinted from ref. 124 with permission from ACS Publications.

Figure 3.11. Effects of lean and rich aging on the performance of the Pt-Ba/Al₂O₃ catalyst. NO_x conversion is measured in lean(25s)/rich(5s) cycles. Gas composition lean: 500 ppm NO + 100 ppm C₃H₆ + 500 ppm CO + 167 ppm H₂ + 10 % O₂ in N₂ + 5 % CO₂ + 5 % H₂O; rich: 500 ppm NO + 1650 ppm C₃H₆ + 4 % CO + 1.3 % H₂ + 1 % O₂ in the same N₂ + CO₂ + H₂O gas. "Degreened" catalysts are fresh samples pre-treated at 600°C in lean/rich cycles. Reprinted from ref.142 with permission from Elsevier.

Tables

Table 3.1

Effect of Ce loading on the NO_x storage capacity (NSC) and selectivity in regeneration by H₂ of Ba-Pt-Ce/Al₂O₃ catalysts. From. Ref. 73.

Sample	NSC %	S _{NH₃} %	S _{N₂O} %	S _{N₂} %
Ba-Pt/Al ₂ O ₃	83.7	9.8	0.8	89.4
Ba-Pt-4.5%Ce/Al ₂ O ₃	89.6	7.7	0.9	91.4
Ba-Pt-15.4%Ce/Al ₂ O ₃	69.5	18.2	1.2	80.6

Table 3.2

NO_x storage capacity of 1%Pt/Ce_xZr_{1-x}O₂ catalysts (μmol g⁻¹). The catalysts are denoted PtCeX where X is the Ce% in the support. Catalysts were stabilized in wet air at 700°C for 4 h, then cooled down to the temperature of NSC measurement (NS gas: 350 ppm NO, 10 % O₂, 10 % H₂O, 10 % CO₂ in N₂ during 100 s). They are compared to a reference 1%Pt-10%BaO/Al₂O₃ catalysts. The PtCeZr catalyst were also prereduced in H₂ at 700°C and NSC was measured in the same conditions. Total NO_x storage in 100 s amounts to 67 μmol g⁻¹. From ref. 84.

Catalyst	Stabilized NSC catalysts			Reduced NSC catalysts		
	200°C	300°C	400°C	200°C	300°C	400°C
PtCe100	20.9	22.8	24.2	8.7	14.0	9.6
PtCe70	17.1	16.9	16.7	19.4	23.1	21.3
PtCe58	23.0	17.4	15.5	23.2	24.9	19.8
PtCe20	18.1	16.0	12.8	19.3	21.1	16.6
Pt-Ba/Al	13.1	13.8	18.3			

Table 3.3

Overview of the studies on sulphur deactivation of **Pt-Ba-Al₂O₃** catalyts. Compositions are given in wt-%. For instance, 1Pt-8Ba means 1%Pt-8%BaO

Catalysts	Techniques	Main conclusions	Ref.
1Pt-8Ba	DRIFT, Thermodynamics	Bulk sulphate (1144 cm ⁻¹) increases with time. Bulk carbonates (1450 cm ⁻¹) decrease. No effect of O ₂ . Partial regeneration by H ₂ at 700°C	Breen <i>et al.</i> ¹⁴³
2Pt-1Rh-20Ba	Reactivity studies	NSC decreases linearly with the dose of SO ₂ down to 20 % of the initial capacity	Engström <i>et al.</i> ¹⁴⁴
2Pt-20Ba	Reactivity studies, DRIFT, modeling	More severe deactivation when SO ₂ is injected in the rich phase. Poisoning of NSC sites closed to Pt.	Fridell <i>et al.</i> ¹⁴⁵
0.72Pt-0.14Rh-17Ba	Reactivity studies	Crucial effect of the presence of water for the regeneration of sulphates. Dry conditions: no reduction before 1000°C.	Mahzoul <i>et al.</i> ¹⁴⁶
0.19Pt-3.5Ba	Reactivity studies, FTIR	When the extent of sulphatation is low (30 of BaO), the catalyst can be totally regenerated under reducing conditions (H ₂ /CO/C ₃ H ₆ /H ₂ O).	Courson <i>et al.</i> ¹⁴⁷
Pt-Ba commercial	Reactivity studies, FTIR, EXAFS	Sulphates are hardly reducible by C ₃ H ₆ below 550°C. Sulphides are formed as intermediates blocking the Pt particles.	Sedlmair <i>et al.</i> ¹⁴⁸
1Pt-5Ba	Reactivity studies, In situ Raman	Nitrites/nitrates can be characterized on Ba or bare alumina. Sulphate progressively replaced nitrates on Ba and alumina. They could block oxidation of nitrites to nitrates.	Uy <i>et al.</i> ¹⁴⁹
2Pt-1Rh-15Ba	Reactivity studies, Thermodynamics	Comparison of SO ₂ , H ₂ S and COS. All the sulphur compounds lead to very close catalyst deactivation, more severe under rich exposure. H ₂ S and COS cause also loss of noble metals.	Amberntsson <i>et al.</i> ¹⁵⁰
Pt-Rh-15Ba, NM: various contents	Reactivity studies, XPS,	Pt is the essential metal for a good behavior in the NSR process. Rh increases the NO _x reduction in rich medium. A good combination of Pt and Rh also increases the S-resistance and regeneration of the catalyst	Amberntsson <i>et al.</i> ¹⁵¹
Pt-Rh-15Ba, NM: various contents	Reactivity studies, XPS, FTIR	Confirmation of the stronger deactivation in rich exposure. Rh allows a better resistance and a better regeneration of the catalyst. Pt sites are blocked by sulphates.	Amberntsson <i>et al.</i> ¹⁵²
2Pt-10Ba	Reactivity studies, XPS	Important role of CO ₂ during rich regeneration. H ₂ alone is not sufficient. Rich exhaust gas involving H ₂ and CO ₂ is more powerful for a complete regeneration. CO ₃ ²⁻ can displace S ²⁻ from Ba under rich conditions.	Poulston, Rajaram ¹⁵³
1Pt-20Ba	Reactivity studies, XRD, H ₂ -TPR	Presence of aluminium sulphates, surface and bulk barium sulphates after SO ₂ . An oxidizing treatment at 800°C allows the decomposition of the surface aluminium sulphates but it gives mainly crystallised barium sulphates, more stable.	Elbouazzaoui <i>et al.</i> ¹⁵⁴
1Pt-10 or 20 Ba	Reactivity studies, XRD, H ₂ -TPR	TPR-peaks of sulphated catalyst (aluminum sulphates at ≈ 550°C, “surface” barium sulphates at ≈ 650°C and “bulk” barium	Elbouazzaoui <i>et al.</i> ¹⁵⁵

			<p>sulphates at $\approx 750^\circ\text{C}$) allows to follow the regeneration. Presence of CO_2 and H_2O in the rich mixture allows eliminating sulfides and sulphates at 650°C even if there remains some bulk Ba sulphate.</p>	
3Pt-15Ba 0.2Rh	Reactivity Raman, DTG	studies,	<p>Two types of Ba sulphates of different crystal size. Type I ($< 3\text{nm}$) reduces at 650°C while type II reduces at 750°C. Role of H spillover in regeneration. Aluminum sulfate forms only in the presence of Pt. Rhodium seems to promote S ads. on Ba.</p>	Wei <i>et al.</i> ¹⁵⁶

Table 3.4

Overview of the studies on sulphur deactivation of catalysts involving Ce and other elements. Compositions are given in wt-%.

Catalysts	Techniques	Main conclusions	Ref.
Ce-based catalyst			
1Pd-CeZrOx	FTIR, TPD	The quantity of sulphates formed at 400°C increased linearly with the Ce content. The sulphates on ZrO ₂ were stable to higher temperatures than those formed on CeO ₂ .	Luo, Gorte ¹⁵⁷
Commercial PtPdRh-BaCe catalyst	Reactivity studies, OSC, NSC measurements	Low S dosing (1.7 g L ⁻¹) does not affect performances. Higher S dosing (3.4 g L ⁻¹) decreases all performances. NSR is globally affected more than NO oxidation activity. Global selectivity for N ₂ O remained low at all sulphur loadings, but NH ₃ selectivity increased significantly with sulphur loading.	Choi <i>et al.</i> ¹⁵⁸
2Pt-10Ba-CeO ₂	Reactivity studies, XPS, TEM-EDX,	The ceria-supported catalyst can store higher amounts of NO _x than the Pt-Ba-Al catalyst. It is also more resistant to sulphur poisoning and ceria prevents Pt sintering.	Kwak <i>et al.</i> ¹⁵⁹
1Pt-CeZrOx	Reactivity studies, TPR, XRD	SO ₂ -treated catalysts: decrease of NO _x -storage more pronounced over Zr rich samples. Sulphates are less stable than on Pt-Ba-Al and can be eliminated by H ₂ at 550°C. NH ₃ selectivity is decreased on CeZr catalysts.	Le Phuc <i>et al.</i> ¹⁶⁰
Copper catalysts			
1Pt-4Cu-MgAl	NO _x storage measurement	Pt-Cu catalysts on hydrotalcite shows good activity at 250°C and better sulphur resistance than Pt-Ba/Al ₂ O ₃	Centi <i>et al.</i> ¹³⁵
5Cu-ZrO ₂ sulf.+ K-Al	NO _x storage measurement	Cu supported on sulfated zirconia, mixed with alkaline-doped alumina, shows very high sulphur resistance for NO _x storage. Better basic materials: K/Al ₂ O ₃ . Copper cannot oxidizes SO ₂ to SO ₃ .	Clacens <i>et al.</i> ¹⁶¹
7.5Cu/KTiOx	Reactivity studies, XRD, XPS, TPR	Cu deposited on K ₂ Ti ₂ O ₅ shows good NSR performance and reinforced resistance to S-poisoning. Sulphur accumulation is 3 times less than on Pt catalysts. It can be regenerated at 550°C in H ₂ .	Wang <i>et al.</i> ¹⁶²