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Perovskite-Based Formulations as Rival Platinum Catalysts for NO_x Removal in Diesel Exhaust Aftertreatment

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Abstract

NO_x removal is still a technological challenge in diesel engines. NO_x storage and reduction (NSR), selective catalytic reduction (SCR), and combined NSR-SCR systems are the efficient approaches for diesel exhaust aftertreatment control. However, NSR and combined NSR-SCR technologies require high noble metal loadings, with low thermal stability and high cost. Recently, perovskites have gained special attention as an efficient alternative to substituting noble metals in heterogeneous catalysis. Up to date, few studies analyzed the application of perovskites in automobile catalytic converters. This chapter overviews recent research on development of novel perovskite-based catalysts as a component of single-NSR and hybrid NSR-SCR systems for NO_x removal from diesel engine exhaust gases. Results in our laboratory are compared with similar work reported in the literature by other authors. Under realistic conditions, 0.5% Pd–30% La_{0.5}Ba_{0.5}CoO₃/Al₂O₃ catalyst achieves NO_x-to-N₂ conversion higher than 92% when is coupled with an SCR catalyst placed downstream. The results show promise for a considerably higher thermal stability and lower cost diesel exhaust treatment system.

Keywords: perovskite, Pt-free catalyst, NO_x removal, lean-burn engine, NSR, NSR-SCR

1. Introduction

Diesel and lean-burn engines operate with high air-to-fuel (A/F) ratios in the range of 20–65 depending on the design of the engine and the type of fuel being combusted. This environment leads to a better fuel economy, with lower CO₂, CO, and HC emissions than stoichiometric gasoline engines (A/F~14.6). As a result, diesel and lean-burn engines gained popularity during the last decades, especially in Europe. However, operation under such net oxidizing environment makes three-way catalysts (TWC) not efficient enough to meet Euro VI standards regarding NO_x emissions in those engines (**Table 1**). Furthermore, the production of particulate matter, also known as soot, is still unavoidable [1, 2]. As a result, diesel and lean-burn engines require the implementation of

Type of vehicle	Euro level [*]	NO _x emission limit	Year of implementation	Aftertreatment system composition
Heavy-duty engines	1-3/I-III			DOC
	3/III	5 ^a	2000	DOC + DPF
	4/IV	3.5 ^a	2005	DOC + DPF
	5/V	2 ^a	2008	DOC + DPF + DeNO _x
	6/VI	0.4/0.46 ^a	2014	DOC + DPF + DeNO _x + ASC
Passengers vehicles	1-3/I-III			DOC
	3/III	0.5 ^b	2001	DOC + DPF
	4/IV	0.25 ^b	2006	DOC + DPF
	5/V	0.18 ^b	2011	DOC + DPF + DeNO _x
	6/VI	0.08 ^b	2015	DOC + DPF + DeNO _x + ASC

^aType approval test for HDVs is conducted on an engine dynamometer, and limits defined as mass emitted per unit of mechanical work done ($g\ kW\ h^{-1}$).

^bType approval test for LDVs is conducted on an engine dynamometer, and limits defined as mass emitted per unit of distance driven ($g\ km^{-1}$).

^{*}European Union heavy-duty engine emission standards are denoted by Roman numerals, while light-duty vehicle standards are denoted by Arabic numbers.

Table 1.
Evolution of Euro regulations for heavy-duty engines and passenger vehicles.

aftertreatment systems to control pollutant emissions, especially those related to NO_x and soot emission.

Current diesel engine exhaust treatment system can contain: (i) diesel oxidation catalyst (DOC); (ii) diesel particulate filter (DPF); (iii) NO_x reduction catalyst; and (iv) ammonia slip catalyst (ASC) [3]. NO_x storage and reduction (NSR) and selective catalytic reduction (SCR) technologies are the most promising approaches to control NO_x emission [4]. NSR system, also known as lean NO_x trap (LNT), operates cyclically under lean-rich periods with 1.5% Pt–15% BaO/Al₂O₃ as model catalyst. On the other hand, NH₃-SCR systems are based on the selectively catalyzed reduction of NO_x-to-N₂ with externally added NH₃ (produced by hydrolysis of urea) in an oxygen-rich environment. Cu or Fe/zeolite catalysts are the model NH₃-SCR formulations [5]. Current status of these technologies has some drawbacks that are limiting their extended implementation.

During the last years, a reasonable interest in linking NSR and NH₃-SCR systems is growing [6–9], because NSR systems generate NH₃ as byproduct during the short-rich period, whereas this compound is the usual selective reducing agent in the SCR technology. As a result, NO_x removal efficiency of the hybrid system increases notably with a simultaneous decrease in the NH₃ slip. Hence, the combined NSR-SCR system is considered as a potential solution to overcome main limitations of the stand-alone NSR and stand-alone SCR technologies. The hybrid NSR-SCR technology consists of two catalysts (NSR and SCR) arranged in series or in a single brick, which runs cyclically similarly to single-NSR systems. Up to now, the behavior of hybrid LNT-SCR systems has been mainly verified with the model 1.5% Pt–15% BaO/Al₂O₃ NSR catalyst. As already mentioned, the presence of platinum makes this formulation costly and limits hydrothermal stability.

Libby [10] and Voorhoeve et al. [11] proposed firstly in early 1970s a perovskite-based catalyst for automotive applications. From then, several studies were carried out related to the utilization of perovskite-based catalysts in diesel exhaust control. The perovskite formulation corresponds to oxides with ABO₃ and/or A₂BO₄ structure, where A is the larger cation located in the center edge of the structure and B is a smaller cation

located in the center of the octahedron [12]. Specifically, A can be a lanthanide, alkaline, or alkaline-earth cation, and B cation can be any metallic element from 3, 4, or 5d configuration. One of the main advantages of the perovskite structure is the possibility to adopt a wide range of different compositions, changing either the A or the B cation or partially substituting each of them by other cations with same or different valences without destroying the perovskite structure. This leads to the formation of oxygen vacancies or changes in the oxidation state of A and B cations, allowing modulation of catalytic properties of the sample to better adapt to automotive applications [13].

All above in mind, the objective of this chapter is to provide a general outlook on utilization of perovskite-based formulations as stand-alone NSR catalysts as well as combined with a zeolite SCR catalyst to conform an efficient hybrid NSR-SCR system. First, a general overview of the application of perovskite-based formulations to control nitrogen oxide emissions from diesel engines is addressed. Then, the applicability of the perovskite-based formulation to single-NSR and combined NSR-SCR technologies will be emphasized. Special attention is paid to the promise and viability of this type of materials as alternative to Pt-based NSR model catalysts.

2. General overview on application of perovskite-based catalysts for NO_x emission control

Perovskite oxides exhibit a range of stoichiometry and crystal structures. In fact, they could accommodate around 90% of the metallic natural elements of the periodic table. The A and B cations can be partially replaced inside the structure, allowing tailoring their catalytic properties to better adapt to their application. Furthermore, physicochemical properties can be controlled by the modification of preparation method. As a result, these materials have been widely implemented in heterogeneous catalysis. Moreover, their high-hydrothermal stability enables their application in catalytic processes carried out at high temperatures [12, 13].

Many works suggest the application of perovskite oxides as alternative formulations to those based on platinum-group metals (PGMs) in automotive exhaust catalytic converters [10, 11, 14, 15]. This type of material has shown excellent activity in oxidation reaction working as diesel oxidation catalyst (DOC) [15–23]. Perovskite oxides demonstrated to be efficient for the simultaneous removal of NO_x and soot combustion in diesel engines allowing their implementation in diesel particulate-NO_x reduction filter (DPNR) [24–31]. Furthermore, NO_x decomposition in the form of nitrous oxide or nitric oxide has been proposed as a one their potential applications [32–38]. Finally, these formulations have been widely implemented for NO_x reduction in both stoichiometric gasoline engines (three-way catalyst, TWC) [24, 39–45] and diesel or lean-burn gasoline engines. Indeed, their implementation in the control of NO_x emission from diesel engines has gained special attention during the last decades, both in the selective catalytic reduction (SCR) and in the NO_x storage and reduction (NSR) systems.

2.1 Selective catalytic reduction (SCR)

SCR technology consists in the selective reduction of NO_x by different reducing agents (NH₃, H₂, or HC) in a net oxidizing environment. The NH₃-SCR alternative became as the most promising avenue for NO_x control in diesel engines. This technology was initially implemented in stationary emission sources. However, their characteristics permit to adopt it for automobile applications. SCR technology runs under steady-state operation conditions with continuous admission of NH₃ to stoichiometrically reduce NO_x in an oxygen-rich environment. A urea tank is usually required for NH₃ supply (by hydrolysis of urea) to achieve the SCR reactions. Due to the

requirement of large space to house the urea tank, the implementation of this alternative is limited to heavy-duty vehicles. Another disadvantage is the need of a NH_3 -slip catalyst to avoid NH_3 emission. Furthermore, the ammonia decomposition occurs above 180°C , which limits the NO_x removal efficiency at low temperatures.

It is widely accepted [46–48] that the following three main reactions occur during NO_x reduction through NH_3 -SCR: (i) standard SCR ($4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{H}_2 + 6\text{H}_2\text{O}$); (ii) fast SCR ($2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$), and (iii) slow NO_2 SCR ($4\text{NH}_3 + 3\text{NO}_2 \rightarrow 3.5\text{N}_2 + 6\text{H}_2\text{O}$). The extent of these reactions depends on the NO/NO_2 ratio, which in turn is related to the oxidation capacity of the catalyst. NO_x removal efficiency is favored with NO/NO_2 ratio around 1 as promoting the fast SCR reaction [49] and occurring reaction at lower temperature. Nevertheless, side reactions such as NH_3 oxidation, NO oxidation, or N_2O formation from ammonium nitrate decomposition can also occur.

NH_3 -SCR formulations have evolved from vanadia-based catalysts, first adopted in stationary sources, to the current Cu or Fe supported over new nano-pore zeolites with chabazite-type structure, such as SSZ-13 or SAPO-34. These formulations have already been implemented for NO_x emission control in heavy-duty vehicles and some recently in some passenger's cars in Europe, mainly due to high NO_x removal efficiency in a wide temperature window discovered with this small pore zeolite structure.

Figure 1 shows the NH_3 -SCR behavior of a 4% Cu/SAPO-34 prepared in our laboratory by the solid state ion exchange method [50]. Experiments were carried out with a feed stream composed of 660 ppm NO, 660 ppm NH_3 , 6% O_2 , and Ar to balance. NO conversion increased with temperature as the NH_3 -SCR reactions are promoted, reaching almost full conversion in an extended range from 200 to 350°C and decreasing afterward as the oxidation of ammonia with O_2 is favored at higher temperatures [51]. NH_3 conversion also increases with temperature, but 100% conversion was maintained above certain temperature where the NH_3 - O_2 reaction prevails. Regarding selectivity toward N_2 is around 95–100% below 350°C , whereas above this temperature, it starts to decrease due to the NH_3 partial oxidation, which partially limits NO_x NH_3 -SCR reactions. The excellent De NO_x activity of this formulation is attributed to the preferential presence of copper as isolated Cu^{2+} ions in the double six member rings (d6r)²; however, the presence of CuO aggregates also plays an important role in the NO-to- NO_2 conversion oxidation.

Alternative compounds have been investigated for NH_3 -SCR technology, such as supported metal oxides ($\text{MnO}_x/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{activated carbon}$) [52–54], mixed oxides derived from hydrotalcite compounds such as Cu-Mg-Al [55], and perovskites oxides. Most of the catalytic studies related to the utilization of perovskite-type compositions in De NO_x technologies are based on La as A cation. However, few of them are related to NH_3 -SCR technology, being focused most of them on a great majority on H_2 -SCR and HC-SCR alternatives [3]. The NO_x removal efficiency of LaMnO_3 , $\text{LaMn}_{0.95}\text{V}_{0.05}\text{O}_3$, and BiMnO_3 perovskites was analyzed [56–58]. Among them, BiMnO_3 perovskite achieved higher NH_3 -SCR activity at lower temperatures. $\text{LaMnO}_3/\text{attapulguite}$ [59] and Fe-containing perovskites [57, 60] ($\text{LaMn}_{0.95}\text{Fe}_{0.05}\text{O}_3$, $\text{LaCo}_{0.3}\text{Fe}_{0.7}\text{O}_3$, or $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Rh}_x\text{O}_3$) were also analyzed. However, these formulations showed limited NO_x conversion (70–90%) or selectivity toward N_2 . Taking into account the results observed in **Figure 1**, these formulations still not represent a real alternative to current Cu/chabazite NH_3 -SCR catalysts.

2.2 NO_x storage and reduction (NSR)

The NSR concept, also known as lean NO_x trap (LNT), was pioneered by Toyota in the middle 1990s [61]. In this technology, the engine works predominantly feeding a fuel-lean mixture with periodical short-rich excursions. During the lean

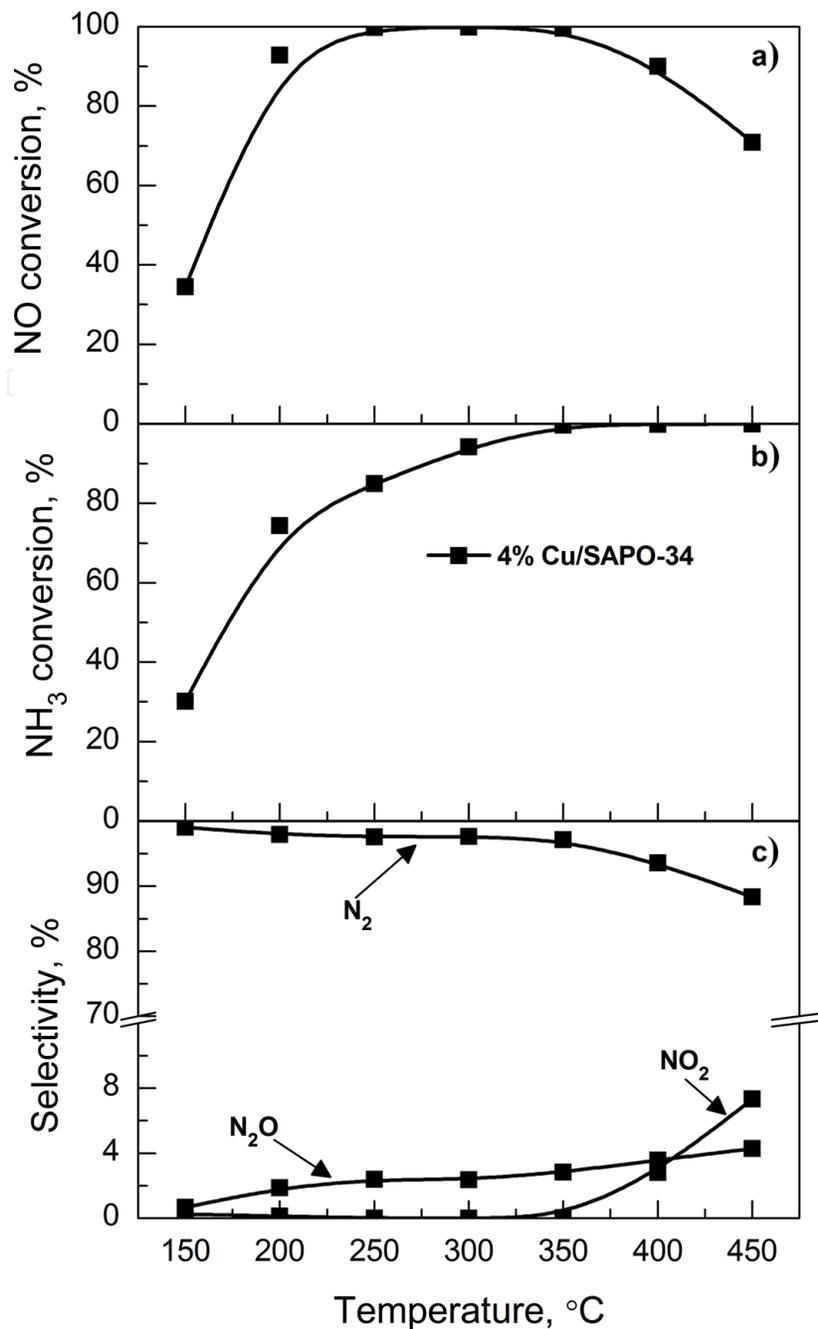


Figure 1. Evolution of NO conversion (a), ammonia conversion (b), and selectivity toward nitrogen, nitrogen dioxide, and nitrous oxide with reaction temperature, achieved with 4% Cu/SAPO-34 catalyst. Feed: 660 ppm NO, 660 ppm NH₃, 6% O₂, Ar to balance; W/F_{A0} = 222 (g cat.) h Mol⁻¹.

period, the NO is oxidized to NO₂ and then adsorbed over the catalyst in the form of nitrites and specially nitrates up to its saturation. Then, the stored NO_x should be released and reduced by a reductant, such as CO, H₂, or HC, during the short-rich period. The operational principle addressed the choice of NSR catalyst composition, which usually contains platinum group metals (e.g. Pt, Pd, and Rh) to activate NO oxidation and NO_x reduction and an alkaline or alkaline earth metal (e.g. K, Ba, Ca, and Sr) to promote NO_x adsorption during lean conditions. Both metals are well distributed over high-surface area materials as alumina, ceria, zirconia, or mixed oxides. A composition consisting of (1–2%) Pt/(10–15%) BaO/Al₂O₃ is widely accepted as the model NSR formulation [62–65]. **Figure 2** shows the typical NO_x storage and reduction operational principle on the NSR model catalyst [66].

LNT system shows some drawbacks derived from the operation principle and model formulation composition. On the one hand, LNT system shows NO_x leak due

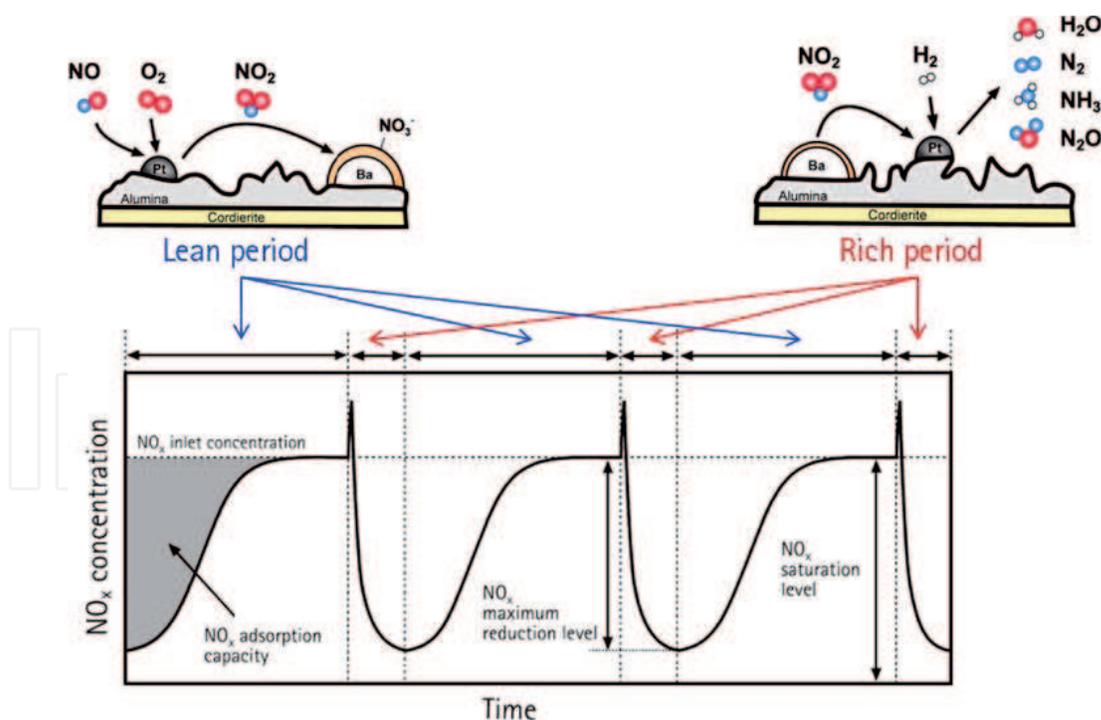
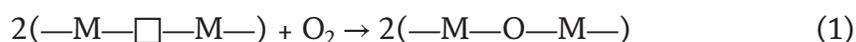


Figure 2. NO_x storage and reduction: mechanism (upper figure), NO_x outlet concentration during three consecutive lean-rich cycles (bottom figure).

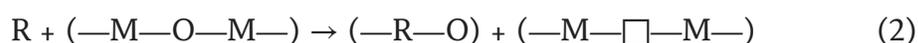
to the dynamic operation conditions under lean-rich conditions, and large amounts of N₂O and NH₃ can be also formed during rich period [67]. Furthermore, the catalyst requires high Pt loading to promote NO-to-NO₂ oxidation, which increases the cost and decreases thermal stability. Finally, the resistance to sulfur poisoning is also limited. Thus, the application of NSR technology is limited to light-duty vehicles with lean-burn engines using low-sulfur containing fuels [3].

During the last decades, modifications in composition of NSR model catalyst and new formulations such as perovskite-based materials have been explored with enhanced catalytic properties, strong deactivation resistance, and lower cost.

The application of perovskites to NSR application is mainly based on high capacity of this material to adsorb NO_x during the lean period. NO-to-NO₂ oxidation is considered a primary step for NO_x adsorption via nitrates in the model NSR catalyst, on which NO₂ adsorbs much faster than NO. With model NSR catalyst, this requires high Pt loads, which drastically increases the cost and limits the thermal stability [68, 69]. Many authors focused on development of perovskite-based formulations with high NO oxidation capacity as promising materials for use in automobile applications. In this sense, perovskite structures (ABO₃) such as LaCoO₃ and LaMnO₃ showed excellent performance on oxidation reactions [70, 71]. Choi et al. [72] reported that the catalytic oxidation activity is intimately connected to molecular and atomic interactions of oxygen with the oxide surface. Catalytic oxidation over metal oxides (M) is often rationalized in terms of a Mars-van Krevelen mechanism [73, 74], in which vacancies (□) in the oxide lattice facilitate the adsorption and dissociation of O₂.



Subsequent reaction with a reductant (R) reforms the vacancies to complete the catalytic cycle.



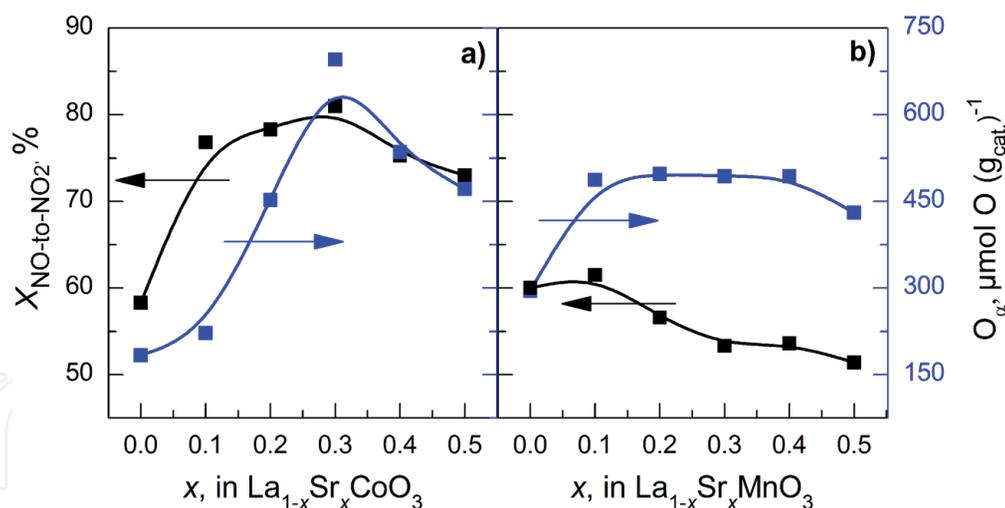


Figure 3. Evolution of α desorbed oxygen species and NO-to-NO₂ conversion at 300°C with lanthanum substitution degree for (a) La_{1-x}Sr_xCoO₃ and (b) La_{1-x}Sr_xMnO₃ perovskites (reprinted from Ref. [16] with permission of Elsevier).

As a result, perovskite activity for oxidation reactions seems to be related to a change in the oxidation state of B cation, active oxygen mobility, and ion vacancy defect [70]. The enhancement of oxidation activity of perovskite-based catalysts is usually attributed to a promotion of oxygen vacancy density [75–79]. In this sense, lanthanum partial substitution by other cations modifies the composition and alters the physico-chemical properties of perovskite, such as crystallinity, specific surface area, average crystal size, abundance of oxygen vacancies, and oxidation state of B cation. Among different cations, Sr²⁺ seems to be the most promising cation for this approach.

Figure 3 shows the evolution of α oxygen species concentration and NO-to-NO₂ conversion at 300°C with degree of lanthanum substitution by Sr, for (a) La_{1-x}Sr_xCoO₃ and (**Figure 3a**) La_{1-x}Sr_xMnO₃ perovskites (**Figure 3b**). Note that α -oxygen was assigned to the oxygen release from vacancies located very near to or on the surface [16].

As a general trend, Sr promotes in a higher degree the formation of α oxygen species and NO-to-NO₂ oxidation capacity for Co-based perovskites than for Mn ones. The evolution of NO-to-NO₂ conversion with lanthanum substitution degree confirms that the amount of oxygen vacancies is the key factor for this enhancement. As a result, Co-based perovskites show higher NO oxidation capacity, even above than Pt-based catalyst does [16]. These results confirm that perovskites can be considered as an excellent alternative for promotion NO oxidation reactions in automotive catalysis.

Nonetheless, La_{0.7}Sr_{0.3}CoO₃ tends to agglomerate under high temperatures required during the calcination step (**Figure 4**). Thus, low specific surface areas (around 20 m² g⁻¹) and an insufficient number of NO_x storage sites [80, 81] arise as main drawbacks of bulk perovskites. Two approaches have been proposed to overcome this limitation: synthesizing mesostructured perovskites via nanocasting and/or distribution of perovskite over high-surface area materials [12]. Mesoporous supports were tried in the past. In this sense, overlaying ZrTiO₄ with LaCoO₃ perovskite was found to reduce sintering of perovskite, which improves NO_x storage capacity [82]. More recently, You et al. [83, 84] found that ceria-supported and Ce_{0.75}Zr_{0.25}O₂-supported LaCoO₃ perovskite achieved high NO_x storage and reduction capacity even with low-specific surface area (below 50 m² g⁻¹). We analyzed the effect of incorporating increasing loadings of La_{0.7}Sr_{0.3}CoO₃ perovskite over a conventional alumina support [85], which inhibited crystal growth of

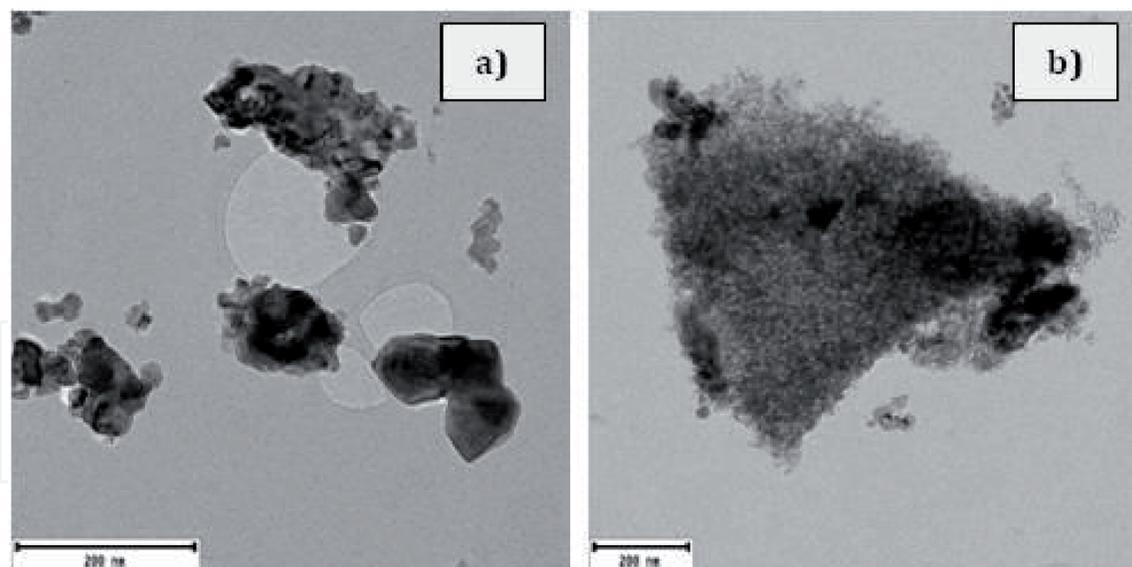


Figure 4. TEM images of: (a) $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ and (b) 30% $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3/\text{Al}_2\text{O}_3$ samples (reprinted from Ref. [85] with permission of Elsevier).

bulk perovskites (**Figure 4**). Hence, diffusion of intermediate compounds from oxidation to adsorption sites was facilitated. Among all prepared catalysts, 30% $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3/\text{Al}_2\text{O}_3$ sample achieved the most efficient use of perovskite phase due to the best balance between well-developed perovskite phase and NO oxidation and NO adsorption site distribution such as oxygen vacancies, structural La and Sr at the surface, and segregated SrCO_3 [86, 87].

However, NO_x reduction capacity of supported formulations is still limited (**Figure 5**). The incorporation of Pd is analyzed as a promising avenue to improve the NO_x reduction capacity of the 30% $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3/\text{Al}_2\text{O}_3$ catalyst. Two approaches can be used for the incorporation of palladium in the perovskite-based formulations via impregnation [88–90] and/or by doping the perovskite structure [86, 91, 92]. The former promotes palladium accessibility; meanwhile, the latter seems to prevent the metal from agglomeration during reduction steps [93, 94]. However, contradictory conclusions have been extracted about which of them is the optimum alternative [95, 96]. In a recent study, Zhao et al. [97] compared both Pd incorporation methods for $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ perovskite. In their study, NO_x adsorption during lean conditions and NO_x reduction to N_2 during rich period is significantly promoted after the incorporation of Pd, especially by impregnation method. The enhancement of the catalytic performance is related to a higher NO_x adsorption site regeneration and to a promotion of NO_x reduction rate by the palladium incorporation, respectively. In our previous work, we prepared several catalysts with increasing palladium contents (0.75, 1.5, and 3.0%) incorporated doping perovskite structure or by wetness impregnation over alumina-supported perovskite. They concluded that the 1.5% Pd–30% $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3/\text{Al}_2\text{O}_3$ sample shows the best balance between NO_x removal efficiency and minimum palladium content. The NO_x removal efficiency and nitrogen production are as high as 86.2 and 69.5%, respectively (**Figure 5**). DeNO_x activity of this formulation is similar or even higher than that achieved with the reference catalyst (1.5% Pt–15% $\text{BaO}/\text{Al}_2\text{O}_3$). Thus, the developed formulation revealed as a promising alternative to the NSR model catalyst for NO_x removal in the automotive application.

It is worth noting that proposed alternative showed a high NO_2 outlet concentration under oxidizing conditions [66]. This suggests that on these materials more amount of NO_2 is formed than the catalyst can adsorb during the lean period.

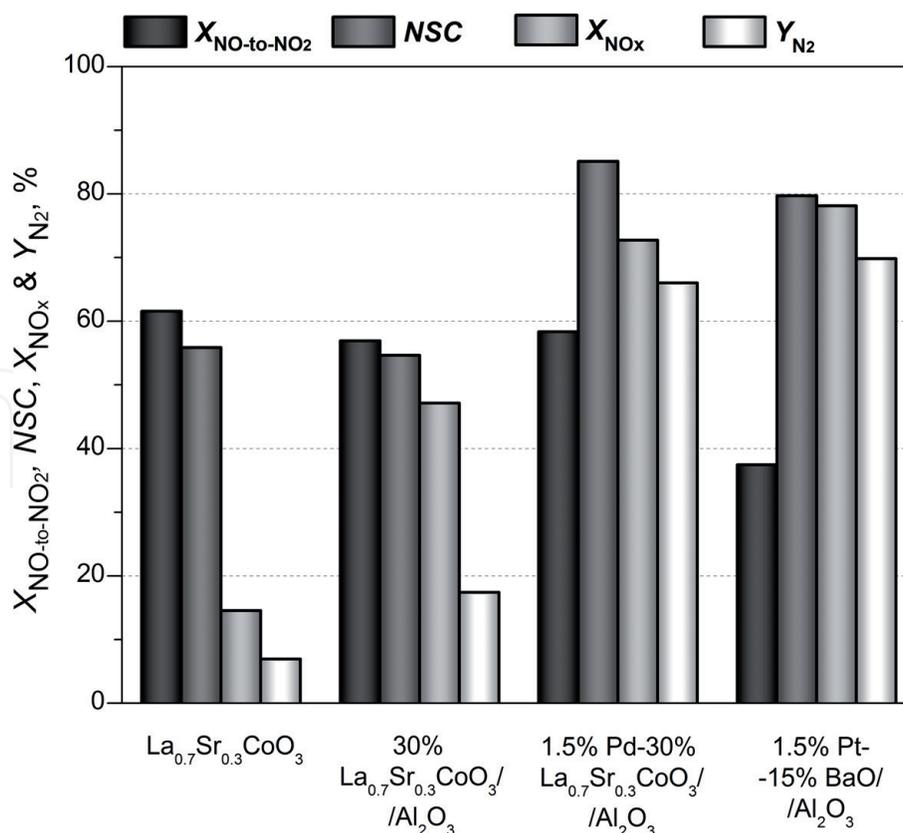


Figure 5. NO-to-NO₂ conversion (X_{NO-to-NO₂}, first column), NO_x storage capacity (NSC, second column), global NO_x conversion (X_{NO_x}, third column), and nitrogen production (Y_{N₂}, fourth column) at 400°C for perovskite-based formulations and NSR model catalyst. Feed: 500 ppm NO, 6% O₂ (lean)/3% H₂ (rich), Ar to balance; W/F_{A0} = 200 (g cat.) h Mol⁻¹.

Furthermore, the amount of NO_x released during the rich period denotes low stability of adsorbed species, which induces fast NO_x release when the reductant is injected. Thus, NO_x reduction, and as a consequence N₂ production, could be further promoted. The increase of the concentration and strength of NO_x adsorption sites by controlling an adequate balance between NO oxidation capacity and NO_x adsorption site concentration and strength at the surface [80, 81] could be an alternative to overcome observed limitations. Two alternatives have been explored: (i) incorporation of additional NO_x adsorption sites [82–84, 98, 99] and (ii) modification of perovskite composition to alter the nature and surface concentration of NO_x adsorption sites [86, 100, 101]. The reported results show that the increase in NO_x adsorption site concentration promotes NO_x storage capacity confirming that the gas/solid equilibrium between NO₂ and the available NO_x adsorption sites is a key factor to maximize NSC; meanwhile, the higher strength of adsorber species favors NO_x reduction efficiencies during short-rich period. Thus, both alternatives improved the catalytic behavior of the corresponding perovskite-based formulation. In our case, the selected approach was the modification of the perovskite composition by Ba doping instead of Sr doping. The developed formulation 0.5% Pd–30% La_{0.5}Ba_{0.5}CoO₃/Al₂O₃ adsorbs NO_x in the form of nitrites/nitrates over surface basic sites, such as La or Ba-terminated perovskite surface, segregated BaCO₃, or alumina support during lean conditions. Then, adsorbed NO_x is released and reduced over Pd and in lower extent perovskite sites to form nitrogen containing products, such as N₂O, NH₃, or N₂. Furthermore, a slower reaction of the NH₃ formed with the stored nitrates leading to the selective formation of N₂ also takes place [66].

A critical aspect of NSR model catalyst (1.5% Pt–15% BaO/Al₂O₃) is the low sulfur resistance due to the formation of stable barium sulfate, which limits NO_x

adsorption during lean conditions. Hodjati et al. [102] analyzed NO_x storage performance of ABO₃ perovskite-type catalysts (with A = Ca, Sr, or Ba; and B = Sn, Zr, or Ti). Regarding A-site cations, the NO_x storage capacity (NSC) followed the order Ba > Sr > Ca, whereas in the case of B cation, the order was Sn > Zr > Ti. Nevertheless, the BaSnO₃ formulation exhibited limited sulfur resistance. In this sense, a BaFeO₃ catalyst developed later by Xian et al. [87, 103, 104] showed a lower decrease of NSC after sulfating (about 11–12%). The incorporation of Ti improves sulfur resistance in a higher extent; activity decreased only 5.1% after SO₂-pretreatment of a BaFe_{1-x}Ti_xO₃ catalyst ($x = 0.1$ or 0.2).

In the case of La-based perovskites, LaCo_{0.92}Pt_{0.08}O₃ maintained a high NO_x removal efficiency after regeneration of a pre-sulfated sample [105]. La_{0.7}Sr_{0.3}Co_{0.8}Fe_{0.2}O₃ perovskite suffers from a drop in NO_x removal efficiency after SO₂-pretreatment of 6.4% [106]. Wang et al. [107] and Wen et al. [99] compared the sulfur and hydrothermal aging resistance of LaCo_{0.92}Pt_{0.08}O₃ and 0.3% Pt/(Al₂O₃ + LaCoO₃) catalysts, with respect to those shown by 1% Pt–16% Ba/Al₂O₃ model formulation. These alternatives achieved NO_x-to-N₂ reduction, sulfur resistance, regeneration, and durability similar or even higher than the model catalyst.

In summary, perovskite-based formulations achieve notable NO oxidation and NO_x adsorption during oxidizing conditions. Furthermore, despite the fact that only a few works analyzed NO_x removal during the short reducing period, our results summarized in this chapter remark the potential of perovskite-based materials for application in NO_x storage and reduction (NSR) technology for NO_x control in diesel and lean-burn engines. In fact, the excellent sulfur tolerance and hydrothermal resistance reported in previous work make these formulations even more promising alternative to Pt-based NSR model catalyst.

2.3 NSR-SCR combined system

As previously observed, stand-alone SCR and NSR systems have some disadvantages that hinder their extended application in both light-duty and heavy-duty vehicles. In the case of the NSR system the high cost, poor thermal stability due to the use of precious metals and undesired byproduct generation is the main disadvantages, whereas SCR systems require an urea system to provide NH₃ and additional device to avoid ammonia slip under transient vehicle operation. The coupling of NSR and SCR catalysts has been rapidly accepted as a potential solution, since its discovery by the Ford Motor company [9, 108]. Different catalytic formulations, system architectures, and operation control have been explored [7, 8, 50, 109, 110]. The systems based on model NSR formulation and Cu/chabazite-type zeolites emerge as the most efficient combination [111]. This hybrid technology has been demonstrated more efficient by maximizing NO_x-to-N₂ reduction and minimizing NH₃ slip with respect to the alone-NSR catalyst. Nevertheless, the most studied NSR formulation used in the combined NSR-SCR system has usually been the conventional Pt-based model catalyst (1.5% Pt–15% BaO/Al₂O₃), which transfers its high cost and limited hydrothermal stability to the hybrid configuration. Based on the results demonstrated by perovskite-based formulations in the single-NSR technology, their application in combined NSR-SCR systems is considered as an evolution of the current NSR-SCR architecture.

Figure 6 shows the NO_x (NO+NO₂), N₂O, and NH₃ concentration profiles determined by FTIR for the single-NSR and double NSR-SCR configurations at 300°C. The N₂ signal determined by mass spectroscopy is also included. NSR and SCR formulations correspond to 0.5% Pd–30% La_{0.5}Ba_{0.5}CoO₃/Al₂O₃ and 4% Cu/SAPO-34 catalysts, respectively.

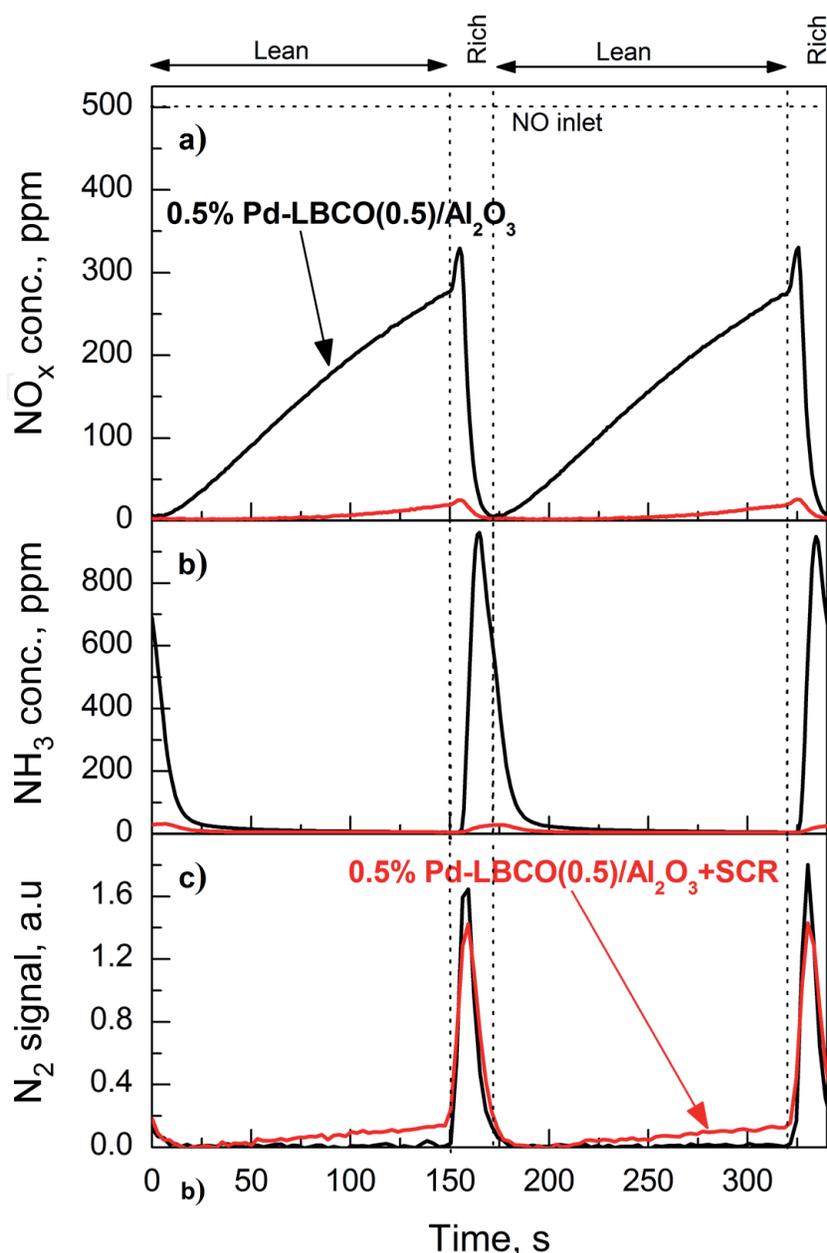


Figure 6. NO_x (NO + NO₂) and NH₃ outlet concentrations, and MS signal of N₂ for the single NSR and NSR-SCR configurations at 300°C. Feed: 500 ppm NO, 6% O₂/3% H₂, and Ar to balance; W/FA₀ = 200 (g h Mol⁻¹).

The single-NSR system (**Figure 6a**) shows the typical NO_x outlet concentration profile [112]. At the beginning of the lean period, practically all NO_x fed are stored, and therefore, concentration of NO_x at the reactor outlet is almost null. Then, as the length of the lean period increases, NO_x adsorption sites become progressively saturated and NO_x outlet concentration increases. In the subsequent rich period, H₂ injected releases the stored NO_x release and reduces it to a mixture of N₂, NH₃ and N₂O [113]. During this period, the NH₃ outlet concentration peaks to almost 1000 ppm (**Figure 6b**). NO_x outlet concentration (**Figure 6a**) decreases drastically when the system operates under the NSR-SCR double configuration. As can be observed in **Figure 6b**, most NH₃ formed during regeneration of the NSR catalyst is adsorbed on acidic sites of SAPO-34, since concentration of NH₃ detected at the outlet of the combined NSR-SCR system is almost zero. Then, in the subsequent lean period, NO_x slipping the NSR catalyst reacts with NH₃ previously adsorbed on the SCR, leading to further NO_x reduction [114].

The evolution of N₂ signal also confirms the existence of SCR reaction over the Cu/SAPO-34 catalyst (**Figure 6c**). When the operation is performed with alone-NSR

catalyst, formation of N_2 was only detected during the rich period, the signal being constant and negligible throughout the storage period. By contrast, when the reaction was carried out with the combined NSR-SCR system, N_2 formation was also detected during the storage period. At the beginning of this period, practically all NO_x fed are trapped in the NSR catalyst, and therefore, there is no available NO_x at the outlet gas stream to carry out the SCR reaction downstream. As a result, the N_2 signals at the exit of the NSR catalyst and at the outlet of the NSR-SCR are coincident. As the storage period proceeds, the NSR catalyst becomes saturated, and the gradual increase of NO_x concentration at intermediate stream that feeds the SCR catalyst activates its reduction with the NH_3 previously stored over the Cu/SAPO-34 catalyst to form the effluent N_2 [66].

Thus, the beneficial effect of placing an SCR catalyst downstream of the NSR is demonstrated. Hence, the catalytic behavior of different perovskite-based formulations was compared in a wider range of temperature using a H_2 concentration of 3% during the rich period. **Figure 7** quantifies the evolution of NO conversion and N_2 , NO_2 , and NH_3 productions at 200, 300, and 400°C, for single-NSR and combined NSR-SCR systems. The NSR formulation was varied between 1.5% Pt–15% BaO/ Al_2O_3 (model catalyst) and 0.5% Pd–30% $La_{0.5}Ba_{0.5}CoO_3/Al_2O_3$ (perovskite-based catalyst here formulated).

As a general trend, NO conversion improves with the NSR-SCR configuration irrespective of the NSR catalyst composition used. The implementation of the SCR catalyst in the hybrid configuration also improves production of N_2 , by consumption of NH_3 and NO_2 produced in the NSR catalyst. The improvement of NO_x removal efficiency up to 300°C is due to higher NH_3 production when the SCR catalyst is highly efficiency (200–300°C). In good agreement with this, NH_3 production at the outlet decreases significantly for the combined NSR-SCR systems [66]. However, above 300°C, the NH_3 production in the NSR catalyst decreases significantly due to the reaction of the NH_3 with the stored nitrate downstream ($3Ba(NO_3)_2 + 10NH_3 \rightarrow 3BaO + 8N_2 + 15H_2O$) of the NSR catalyst [65, 115]. Furthermore, NH_3 can be partially oxidized [113, 116], and thus, NH_3 generated is insufficient to reduce NO_x slipping the upstream NSR system. This explains the

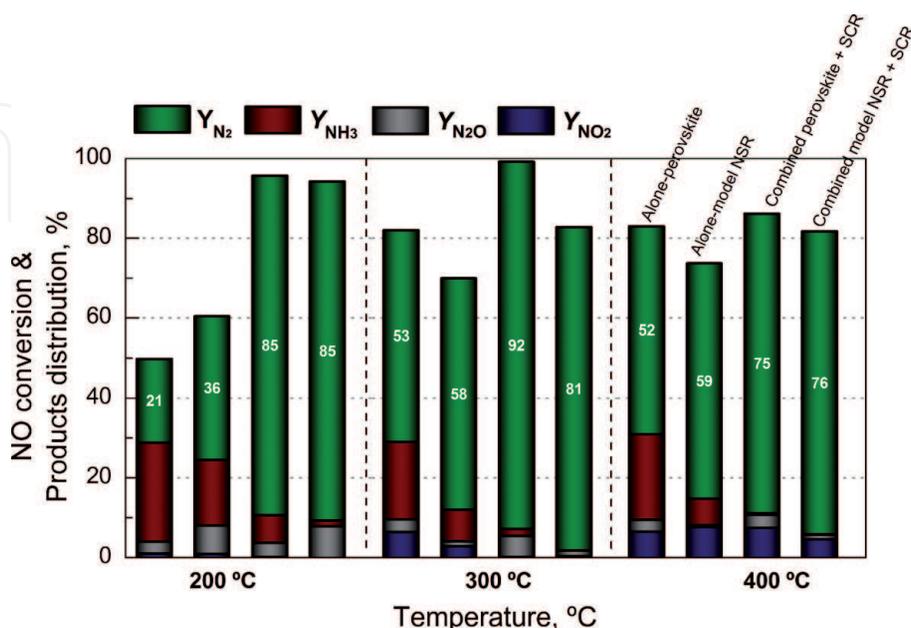


Figure 7. Global conversion of NO (X_{NO}) and product distribution at 200, 300, and 400°C for single-NSR and combined NSR-SCR systems, based on 0.5% Pd–30% $La_{0.5}Ba_{0.5}CoO_3/Al_2O_3$ (perovs.) and 1.5% Pt–15% BaO/ Al_2O_3 (model) as NSR catalysts.

moderate improvement of NO_x-to-N₂ reduction for the NSR-SCR double configuration with respect to the single-NSR system at high temperature.

Both configurations show high NO conversion and nitrogen production in the whole temperature range. Specifically, perovskite-based system shows a maximum NO conversion of 99% and a nitrogen production of 92% at 300°C. Indeed, perovskite-based combined NSR-SCR system shows similar or even higher NO_x-to-N₂ reduction efficiencies to that shown by the double configuration when the 1.5% Pt–15% BaO/Al₂O₃ model NSR catalyst is used.

In summary, the positive impact of placing an SCR catalyst downstream the NSR catalyst is verified on NO_x removal efficiency, with notable increase in N₂ production. In this sense, the mixed NSR-SCR system based on the 0.5% Pd–30% La_{0.5}Ba_{0.5}CoO₃/Al₂O₃ catalyst emerges as a promising alternative, only emitting 7% NH₃ at 200°C (slip of NH₃), which disappears at higher temperatures achieving NH₃ total elimination. This can be considered as a promising starting point for the implementation of these types of oxides in coupled NSR-SCR configurations.

2.4 Outlook and concluding remarks

NO_x emission removal from lean-burn and diesel engine exhaust gases remains as a technological challenge. To overcome this environmental pollution issue, two main alternatives have been explored during the last decades: NO_x storage and reduction (NSR) and selective catalytic reduction with NH₃ (NH₃-SCR). These alternatives show some limitations that limit their extensive application. In the case of NSR system, some NO can slip without being totally converted, and also, NH₃ generated during the rich period can slip as byproduct in the effluent. Furthermore, the catalyst requires high Pt loadings, which limit the cost and thermal stability. On the other hand, NH₃-SCR system requires the urea feeding system, which increases the cost and requires an extra volume of the system. Moreover, the latter shows lower NO conversion at low temperatures and allows NH₃ slip. As a result, combined NSR-SCR configurations have been explored as an evolution of previous stand-alone technologies. In fact, this hybrid alternative increases the temperature operational window, promotes NO conversion, and avoids the need of urea feeding system. However, up to now, only a conventional Pt-based NSR formulation has been explored in coupled NSR-SCR configurations.

In recent years, efforts have been focused on designing a new generation of NSR catalysts with improved oxidation, adsorption, and reduction capacities. Furthermore, these new materials should be low cost and achieve long hydrothermal stability and high sulfur resistance. Perovskites have gained attention during the recent years as a potential solution. La-based formulations (i.e., LaCoO₃ and LaMnO₃) have shown excellent NO oxidation conversion, a primary step in the NO_x adsorption during lean conditions. In fact, Sr doping further promotes the NO oxidation activity of these formulations, which is closely related to the generation of oxygen vacancies favoring oxygen mobility. However, NO_x storage and reduction efficiencies are limited for bulk perovskites due to a low exposed surface area derived from the drastic calcination protocols required during the synthesis process. Supporting perovskite over high surface area materials, e.g., alumina (30% La_{0.7}Sr_{0.3}CoO₃/Al₂O₃), is demonstrated to overcome this limitation. Nonetheless, NO_x reduction at low and intermediate temperatures is still limited. The incorporation of low Pd contents over supported perovskite by wetness impregnation emerges as an efficient solution. In fact, 1.5% Pd–30% La_{0.7}Sr_{0.3}CoO₃/Al₂O₃ shows similar or even higher NO_x removal efficiencies than the conventional NSR model catalyst (1.5% Pt–15% BaO/Al₂O₃). The activity enhancement showed by perovskite-based formulations motivates their implementation in combined

NSR-SCR systems, which as an alternative to further improve the NO_x removal efficiency of the stand-alone NSR and stand-alone SCR systems. The preliminary results are very promising since NO_x-to-N₂ reduction above 90% has been achieved with significant lower noble metal content than platinum in the model catalyst.

Improving the exhaust aftertreatment systems is considered as a critical point in the current vehicle development. In upcoming years, research should be focus on better understanding the mechanism over perovskite-based formulation, especially during regeneration period. Moreover, the NO_x trapping efficiency and NO_x reduction of the adsorbed NO_x can be further promoted. To the best of the authors' knowledge, no studies have been published related to the application of this type of materials to the combined NSR-SCR system. Thus, the room improvement is huge for this application, such as exploring different catalyst architectures (i.e., segmented zones or dual layer monoliths), optimizing precious metal loading, and dispersion. The construction of detailed kinetic model and modeling a full-scale operation will allow to develop a suitable aftertreatment system for automobile application.

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