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Chapter

Perovskite-Based Formulations as Rival Platinum Catalysts for NO\(_x\) Removal in Diesel Exhaust Aftertreatment

Jon Ander Onrubia-Calvo, Beñat Pereda-Ayo, Unai De-La-Torre and Juan Ramón González-Velasco

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\(_{0.5}\)CoO\(_3\)/Al\(_2\)O\(_3\) catalyst achieves NO\(_x\)-to-N\(_2\) 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 CO\(_2\), 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
aftertreatment systems to control pollutant emissions, especially those related to NO\textsubscript{x} and soot emission.

Current diesel engine exhaust treatment system can contain: (i) diesel oxidation catalyst (DOC); (ii) diesel particulate filter (DPF); (iii) NO\textsubscript{x} reduction catalyst; and (iv) ammonia slip catalyst (ASC) [3]. NO\textsubscript{x} storage and reduction (NSR) and selective catalytic reduction (SCR) technologies are the most promising approaches to control NO\textsubscript{x} emission [4]. NSR system, also known as lean NO\textsubscript{x} trap (LNT), operates cyclically under lean-rich periods with 1.5% Pt–15% BaO/Al\textsubscript{2}O\textsubscript{3} as model catalyst. On the other hand, NH\textsubscript{3}-SCR systems are based on the selectively catalyzed reduction of NO\textsubscript{x}-to-N\textsubscript{2} with externally added NH\textsubscript{3} (produced by hydrolysis of urea) in an oxygen-rich environment. Cu or Fe/zeolite catalysts are the model NH\textsubscript{3}-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 NH\textsubscript{3}-SCR systems is growing [6–9], because NSR systems generate NH\textsubscript{3} as byproduct during the short-rich period, whereas this compound is the usual selective reducing agent in the SCR technology. As a result, NO\textsubscript{x} removal efficiency of the hybrid system increases notably with a simultaneous decrease in the NH\textsubscript{3} slip. Hence, the combined 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/Al\textsubscript{2}O\textsubscript{3} 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 ABO\textsubscript{3} and/or A\textsubscript{2}BO\textsubscript{4} structure, where A is the larger cation located in the center edge of the structure and B is a smaller cation.

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

<table>
<thead>
<tr>
<th>Type of vehicle</th>
<th>Euro level\textsuperscript{1}</th>
<th>NO\textsubscript{x} emission limit</th>
<th>Year of implementation</th>
<th>Aftertreatment system composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy-duty engines</td>
<td>1–3/I–III</td>
<td>DOC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/III</td>
<td>5\textsuperscript{a}</td>
<td>2000</td>
<td>DOC + DPF</td>
</tr>
<tr>
<td></td>
<td>4/IV</td>
<td>3.5\textsuperscript{a}</td>
<td>2005</td>
<td>DOC + DPF</td>
</tr>
<tr>
<td></td>
<td>5/V</td>
<td>2\textsuperscript{a}</td>
<td>2008</td>
<td>DOC + DPF + DeNO\textsubscript{x}</td>
</tr>
<tr>
<td></td>
<td>6/VI</td>
<td>0.4/0.46\textsuperscript{a}</td>
<td>2014</td>
<td>DOC + DPF + DeNO\textsubscript{x} + ASC</td>
</tr>
<tr>
<td>Passengers vehicles</td>
<td>1–3/I–III</td>
<td>DOC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/III</td>
<td>0.5\textsuperscript{b}</td>
<td>2001</td>
<td>DOC + DPF</td>
</tr>
<tr>
<td></td>
<td>4/IV</td>
<td>0.25\textsuperscript{b}</td>
<td>2006</td>
<td>DOC + DPF</td>
</tr>
<tr>
<td></td>
<td>5/V</td>
<td>0.18\textsuperscript{b}</td>
<td>2011</td>
<td>DOC + DPF + DeNO\textsubscript{x}</td>
</tr>
<tr>
<td></td>
<td>6/VI</td>
<td>0.08\textsuperscript{b}</td>
<td>2015</td>
<td>DOC + DPF + DeNO\textsubscript{x} + ASC</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Type 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\textsuperscript{−1}).

\textsuperscript{2}Type approval test for LDVs is conducted on an engine dynamometer, and limits defined as mass emitted per unit of distance driven (g km\textsuperscript{−1}).

\textsuperscript{3}European Union heavy-duty engine emission standards are denoted by Roman numerals, while light-duty vehicle standards are denoted by Arabic numbers.
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\textsubscript{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 Ba 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\textsubscript{x} and soot combustion in diesel engines allowing their implementation in diesel particulate-NO\textsubscript{x} reduction filter (DPNR) [24–31]. Furthermore, NO\textsubscript{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\textsubscript{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\textsubscript{x} emission from diesel engines has gained special attention during the last decades, both in the selective catalytic reduction (SCR) and in the NO\textsubscript{x} storage and reduction (NSR) systems.

2.1 Selective catalytic reduction (SCR)

SCR technology consists in the selective reduction of NO\textsubscript{x} by different reducing agents (NH\textsubscript{3}, H\textsubscript{2} or HC) in a net oxidizing environment. The NH\textsubscript{3}-SCR alternative became as the most promising avenue for NO\textsubscript{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 NH\textsubscript{3} to stoichiometrically reduce NO\textsubscript{x} in an oxygen-rich environment. A urea tank is usually required for NH\textsubscript{3} 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 ($2\text{NH}_3 + \text{NO} + \text{NO}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$); 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$_2$O 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 DeNO$_x$ 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 (MnO$_x$/Al$_2$O$_3$ and V$_2$O$_5$/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 DeNO$_x$ 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$_3$, LaMn$_{0.95}$V$_{0.05}$O$_3$, and BiMnO$_3$ perovskites was analyzed [56–58]. Among them, BiMnO$_3$ perovskite achieved higher NH$_3$-SCR activity at lower temperatures. LaMnO$_3$/attapulgite [59] and Fe-containing perovskites [57, 60] (LaMn$_{0.95}$Fe$_{0.05}$O$_3$, LaCo$_{0.3}$Fe$_{0.7}$O$_3$, or La$_{0.8}$Sr$_{0.2}$Fe$_{1.2}$Rh$_2$O$_x$) 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
period, the NO is oxidized to NO₂ and then adsorbed over the catalyst in the form of nitrates and specially nitrates up to its saturation. Then, the stored NOₓ 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 NOₓ reduction and an alkaline or alkaline earth metal (e.g. K, Ba, Ca, and Sr) to promote NOₓ 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 NOₓ 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 NOₓ leak due
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 NOₓ during the lean period. NO-to-NO₂ oxidation is considered a primary step for NOₓ 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 surface facilitate the adsorption and dissociation of O₂.

\[
2(\text{—M—□—M—}) + \text{O}_2 \rightarrow 2(\text{—M—O—M—}) \quad (1)
\]

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

\[
\text{R} + (\text{—M—O—M—}) \rightarrow (\text{—R—O}) + (\text{—M—□—M—}) \quad (2)
\]
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, Sr$^{2+}$ seems to be the most promising cation for this approach.

Figure 3 shows the evolution of $\alpha$ desorbed oxygen species concentration and NO-to-NO$_2$ conversion at 300°C with degree of lanthanum substitution for Sr, for (a) La$_{1-x}$Sr$_x$CoO$_3$ and (b) La$_{1-x}$Sr$_x$MnO$_3$ perovskites (Figure 3a). Note that $\alpha$-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 $\alpha$ oxygen species and NO-to-NO$_2$ oxidation capacity for Co-based perovskites than for Mn ones. The evolution of NO-to-NO$_2$ 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$_{0.3}$CoO$_3$ tends to agglomerate under high temperatures required during the calcination step (Figure 4). Thus, low specific surface areas (around 20 m$^2$ g$^{-1}$) and an insufficient number of NO$_x$ storage sites [81, 82] 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 ZrTiO$_4$ with LaCoO$_3$ perovskite was found to reduce sintering of perovskite, which improves NO$_x$ storage capacity [83]. More recently, You et al. [84, 85] found that ceria-supported and Ce$_{0.75}$Zr$_{0.25}$O$_2$-supported LaCoO$_3$ perovskite achieved high NO$_x$ storage and reduction capacity even with low-specific surface area (below 50 m$^2$ g$^{-1}$). We analyzed the effect of incorporating increasing loadings of La$_{0.7}$Sr$_{0.3}$CoO$_3$ perovskite over a conventional alumina support [80], which inhibited crystal growth of
bulk perovskites (Figure 4). Hence, diffusion of intermediate compounds from oxidation to adsorption sites was facilitated. Among all prepared catalysts, 30% La$_{0.7}$Sr$_{0.3}$CoO$_3$/Al$_2$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% La$_{0.7}$Sr$_{0.3}$CoO$_3$/Al$_2$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 La$_{0.7}$Sr$_{0.3}$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% La$_{0.7}$Sr$_{0.3}$CoO$_3$/Al$_2$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% BaO/Al$_2$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$_x$ 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.
Furthermore, the amount of NO\textsubscript{x} released during the rich period denotes low stability of adsorbed species, which induces fast NO\textsubscript{x} release when the reductant is injected. Thus, NO\textsubscript{x} reduction, and as a consequence N\textsubscript{2} production, could be further promoted. The increase of the concentration and strength of NO\textsubscript{x} adsorption sites by controlling an adequate balance between NO oxidation capacity and NO\textsubscript{x} adsorption site concentration and strength at the surface [81, 82] could be an alternative to overcome observed limitations. Two alternatives have been explored: (i) incorporation of additional NO\textsubscript{x} adsorption sites [83–85, 98, 99] and (ii) modification of perovskite composition to alter the nature and surface concentration of NO\textsubscript{x} adsorption sites [86, 100, 101]. The reported results show that the increase in NO\textsubscript{x} adsorption site concentration promotes NO\textsubscript{x} storage capacity confirming that the gas/solid equilibrium between NO\textsubscript{2} and the available NO\textsubscript{x} adsorption sites is a key factor to maximize NSC; meanwhile, the higher strength of adsorber species favors NO\textsubscript{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\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} adsorbs NO\textsubscript{x} in the form of nitrites/nitrates over surface basic sites, such as La or Ba-terminated perovskite surface, segregated BaCO\textsubscript{3}, or alumina support during lean conditions. Then, adsorbed NO\textsubscript{x} is released and reduced over Pd and in lower extent perovskite sites to form nitrogen containing products, such as N\textsubscript{2}O, NH\textsubscript{3}, or N\textsubscript{2}. Furthermore, a slower reaction of the NH\textsubscript{3} formed with the stored nitrates leading to the selective formation of N\textsubscript{2} also takes place [66].

A critical aspect of NSR model catalyst (1.5% Pt–15% BaO/Al\textsubscript{2}O\textsubscript{3}) is the low sulfur resistance due to the formation of stable barium sulfate, which limits NO\textsubscript{x}
adsorption during lean conditions. Hodjati et al. [102] analyzed NO\textsubscript{x} storage performance of ABO\textsubscript{3} perovskite-type catalysts (with A = Ca, Sr, or Ba; and B = Sn, Zr, or Ti). Regarding A-site cations, the NO\textsubscript{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 BaSnO\textsubscript{3} formulation exhibited limited sulfur resistance. In this sense, a BaFeO\textsubscript{3} catalyst developed latter 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 SO\textsubscript{2}-pretreatment of a BaFe\textsubscript{1−x}Ti\textsubscript{x}O\textsubscript{3} catalyst (x = 0.1 or 0.2).

In the case of La-based perovskites, LaCo\textsubscript{0.92}Pt\textsubscript{0.08}O\textsubscript{3} maintained a high NO\textsubscript{x} removal efficiency after regeneration of a pre-sulfated sample [105]. La\textsubscript{0.7}Sr\textsubscript{0.3}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3} perovskite suffers from a drop in NO\textsubscript{x} removal efficiency after SO\textsubscript{2}-pretreatment of 6.4% [106]. Wang et al. [107] and Wen et al. [99] compared the sulfur and hydrothermal aging resistance of LaCo\textsubscript{0.92}Pt\textsubscript{0.08}O\textsubscript{3} and 0.3% Pt/(Al\textsubscript{2}O\textsubscript{3} + LaCoO\textsubscript{3}) catalysts, with respect to those shown by 1% Pt–16% Ba/Al\textsubscript{2}O\textsubscript{3} model formulation. These alternatives achieved NO\textsubscript{x}-to-N\textsubscript{2} 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\textsubscript{x} adsorption during oxidizing conditions. Furthermore, despite the fact that only a few works analyzed NO\textsubscript{x} removal during the short reducing period, our results summarized in this chapter remark the potential of perovskite-based materials for application in NO\textsubscript{x} storage and reduction (NSR) technology for NO\textsubscript{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 by product generation is the main disadvantages, whereas SCR systems require an urea system to provide NH\textsubscript{3} 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\textsubscript{x}-to-N\textsubscript{2} reduction and minimizing NH\textsubscript{3} 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/Al\textsubscript{2}O\textsubscript{3}), 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\textsubscript{x} (NO+NO\textsubscript{2}), N\textsubscript{2}O, and NH\textsubscript{3} concentration profiles determined by FTIR for the single-NSR and double NSR-SCR configurations at 300°C. The N\textsubscript{2} signal determined by mass spectroscopy is also included. NSR and SCR formulations correspond to 0.5% Pd–30% La\textsubscript{0.5}Ba\textsubscript{0.5}CoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} and 4% Cu/SAPO-34 catalysts, respectively.
The single-NSR system (Figure 6a) shows the typical NO\textsubscript{x} outlet concentration profile [112]. At the beginning of the lean period, practically all NO\textsubscript{x} fed are stored, and therefore, concentration of NO\textsubscript{x} at the reactor outlet is almost null. Then, as the length of the lean period increases, NO\textsubscript{x} adsorption sites become progressively saturated and NO\textsubscript{x} outlet concentration increases. In the subsequent rich period, H\textsubscript{2} injected releases the stored NO\textsubscript{x} release and reduces it to a mixture of N\textsubscript{2}, NH\textsubscript{3} and N\textsubscript{2}O [113]. During this period, the NH\textsubscript{3} outlet concentration peaks to almost 1000 ppm (Figure 6b). NO\textsubscript{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 NH\textsubscript{3} formed during regeneration of the NSR catalyst is adsorbed on acidic sites of SAPO-34, since concentration of NH\textsubscript{3} detected at the outlet of the combined NSR-SCR system is almost zero. Then, in the subsequent lean period, NO\textsubscript{x} slipping the NSR catalyst reacts with NH\textsubscript{3} previously adsorbed on the SCR, leading to further NO\textsubscript{x} reduction [114].

The evolution of N\textsubscript{2} 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 $N_2$, $NO_x$, 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$_2$O$_3$ (model catalyst) and 0.5% Pd–30% La$_{0.5}$Ba$_{0.5}$CoO$_3$/Al$_2$O$_3$ (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 $NO_x$ 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
moderate improvement of NO\textsubscript{x}-to-N\textsubscript{2} 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\textsubscript{x}-to-N\textsubscript{2} reduction efficiencies to that shown by the double configuration when the 1.5% Pt–15% BaO/Al\textsubscript{2}O\textsubscript{3} model NSR catalyst is used.

In summary, the positive impact of placing an SCR catalyst downstream the NSR catalyst is verified on NO\textsubscript{x} removal efficiency, with notable increase in N\textsubscript{2} production. In this sense, the mixed NSR-SCR system based on the 0.5% Pd–30% La\textsubscript{0.7}Sr\textsubscript{0.3}CoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst emerges as a promising alternative, only emitting 7% NH\textsubscript{3} at 200°C (slip of NH\textsubscript{3}), which disappears at higher temperatures achieving NH\textsubscript{3} 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\textsubscript{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\textsubscript{x} storage and reduction (NSR) and selective catalytic reduction with NH\textsubscript{3} (NH\textsubscript{3}-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, NH\textsubscript{3} 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, NH\textsubscript{3}-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 NH\textsubscript{3} 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., LaCoO\textsubscript{3} and LaMnO\textsubscript{3}) have shown excellent NO oxidation conversion, a primary step in the NO\textsubscript{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\textsubscript{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\textsubscript{0.7}Sr\textsubscript{0.3}CoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}), is demonstrated to overcome this limitation. Nonetheless, NO\textsubscript{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\textsubscript{0.7}Sr\textsubscript{0.3}CoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} shows similar or even higher NO\textsubscript{x} removal efficiencies than the conventional NSR model catalyst (1.5% Pt–15% BaO/Al\textsubscript{2}O\textsubscript{3}). 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-N$_2$ 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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