Selective Catalytic Reduction of NO\textsubscript{x} over Perovskite-Based Catalysts Using C\textsubscript{x}H\textsubscript{y}(O\textsubscript{2}), H\textsubscript{2} and CO as Reducing Agents—A Review of the Latest Developments

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Abstract: Selective catalytic reduction (SCR) is probably the most widespread process for limiting NO\textsubscript{x} emissions under lean conditions (O\textsubscript{2} excess) and, in addition to the currently used NH\textsubscript{3} or urea as a reducing agent, many other alternative reductants could be more promising, such as C\textsubscript{x}H\textsubscript{y}/C\textsubscript{x}H\textsubscript{y}O\textsubscript{2}, H\textsubscript{2} and CO. Different catalysts have been used thus far for NO\textsubscript{x} abatement from mobile (automotive) and stationary (fossil fuel combustion plants) sources, however, perovskites demand considerable attention, partly due to their versatility to combine and incorporate various chemical elements in their lattice that favor deNO\textsubscript{x} catalysis. In this work, the C\textsubscript{x}H\textsubscript{y}/C\textsubscript{x}H\textsubscript{y}O\textsubscript{2}, H\textsubscript{2}, and CO SCR of NO\textsubscript{x} on perovskite-based catalysts is reviewed, with particular emphasis on the role of the reducing agent nature and perovskite composition. An effort has also been made to further discuss the correlation between the physicochemical properties of the perovskite-based catalysts and their deNO\textsubscript{x} activity. Proposed kinetic models are presented as well, that delve deeper into deNO\textsubscript{x} mechanisms over perovskite-based catalysts and potentially pave the way for further improving their deNO\textsubscript{x} efficiency.

Keywords: NO\textsubscript{x}; perovskites; CO-SCR; H\textsubscript{2}-SCR; hydrocarbon-SCR

1. Introduction

DeNO\textsubscript{x}—general remarks: The number of automobiles worldwide is constantly increasing, leading to the emission of CO, NO\textsubscript{x} (x = 1, 2), hydrocarbons (HCs), and particulate matter (PM) in the atmosphere a major environmental problem of ever-increasing impact [1–4]. Similarly, increased energy demand for industry, home heating, etc., produced by stationary facilities, and still mainly based on fossil fuels, exacerbates the problem of air pollution in relation to these contaminants. Therefore, the regulations for emissions from stationary and mobile sources have become stringent while numerous technologies have been evolved in order to curb atmospheric pollution [1,2]. In general, heterogeneous catalysis for tackling environmental issues has been widely adopted as a low-cost, highly efficient, and selective technology for mitigating undesirable air pollutants that accompany energy production processes [5]. The prevalent heterocatalytic control technology of NO\textsubscript{x} emissions (in excess of O\textsubscript{2} in the gas stream) is called selective catalytic reduction (SCR); it is an end-of-pipe, after-treatment, process that selectively reduces NO\textsubscript{x} emissions by means of different reducing agents such as NH\textsubscript{3}, urea, CO, H\textsubscript{2}, or HC/C\textsubscript{x}H\textsubscript{y}O\textsubscript{2}, using an appropriate catalyst [1,6–14]. Although NH\textsubscript{3} and urea is currently the preferred choice for
the SCR of NO\textsubscript{x} applications in stationary power and chemical plants [6], reducing agents such as H\textsubscript{2}, light hydrocarbons, and CO have recently attracted intense interest, among other reasons, due to the fact that these components usually coexist in the exhaust gases [4,5,7–15].

Dispersed on mixed oxides, typically γ-Al\textsubscript{2}O\textsubscript{3}-(CeO\textsubscript{2}, La\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, BaO, etc.) supports, noble metals such as Rh, Pd, Ir, and Pt have been demonstrated as the most efficient and tolerant to steam-induced lattice distortion and sulfur poisoning catalysts for the control of CO, HCs and NO\textsubscript{x} emissions [15–25] and successfully applied for years in three-way catalytic converters (TWCs) technology [2]. However, despite intensive research efforts, such noble metal catalyst formulations, although very efficient in controlling emissions of stoichiometric gasoline engines (TWC conditions), have not been yet as effective as required for the control of non-stoichiometric engines emissions in order to be applicable in the case of lean-burn gasoline and diesel engines or in stationary fossil fuel combustion processes [1,7,13]. Bearing in mind that the use of precious metals is also associated with high costs and relatively poor stability, i.e., a propensity to particle agglomeration in the case of hot spots that often occur under real driving conditions (although means and methodologies for stabilizing dispersed catalyst nanoparticles against sintering have recently been discovered [26–30]), significant efforts have been put to the development and use of alternatives such as perovskite derived catalysts, due to their unique physicochemical properties, low cost, and favorable heat stability [31–37].

**Perovskite materials and their consideration in catalytic processes:** Perovskites is a class of oxides that has the structural formula ABO\textsubscript{3} and an ideal crystalline structure described as cubic from the Pm\textsubscript{3}m space group, as shown in Figure 1a. On the other hand, oxides with the structural formula A\textsubscript{2}BO\textsubscript{4}, which are composed of alternated ABO\textsubscript{3} and AO layers (Figure 1b), have quite similar properties to ABO\textsubscript{3} perovskites and are often called perovskite-like oxides [32]. Both oxide types are called hereinafter perovskites. In the structure of the perovskites, A is a large cation 12-fold coordinated with oxygen ions and located on the edge of the octahedron, while B is a smaller cation, six-fold coordinated with O\textsuperscript{2–} and located in the center of the octahedron (Figure 1a). The tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ should lie within $0.75 < t < 1.0$ in order to ensure perovskite matrix structure stability [32]. The A cation in the perovskite matrix can be an alkaline, alkaline earth, or lanthanide element, while the B cation can be an element from the 3d, 4d, or 5d configuration metals [32–44].

Perovskites are capable of partially substituting cations of A and/or B-sites by other cations with different or same valences (i.e., $A_{1-x}A'_{x}B_{1-x}B'_{x}O_{3±\delta}$) to adjust their redox, bulk, and surface properties [38]. That said, with an appropriate combination of $A'$ and $B'$ metals the catalytic activity of a desired reaction can be readily tuned by modifying the perovskite chemical formula [33]. Indeed, besides their high thermal stability perovskites are characterized by some additional properties that make them favorable or even unique materials for several practical applications. For example, their high mixed electronic and ionic (O\textsuperscript{2–}) conductivity makes them almost irreplaceable in electrocatalysis and solid oxide fuel cells (SOFCs) technology [34,45,46]; their intrinsic redox properties and oxygen ions mobility makes them beneficial materials in many heterocatalytic reaction systems, due to the sought after strong electronic metal–support interactions and oxygen ions back-spillover phenomena that accompany their use. The easily adjusted acid–base properties of perovskites are also key factors that make them favorable for regulating the activity and or selectivity of many catalytic reactions, including deNO\textsubscript{x} [1,2,31–42]. It is also worth noting that the additional ability of partially substituting A and B-sites by other cations (i.e., $A_{1-x}A'_{x}B_{1-x}B'_{x}O_{3±\delta}$), can provide a variety of ($A$, $A'$, B and B' nature)-affected active sites for catalysis. For example, if La and a first series transition metal are selected for the A and B-site, respectively, high activity for NO reduction by CO can be achieved [43]. When lower valence ions are added in the A-site, which is typically occupied by a lanthanide, alkali, or alkaline earth [32,33,38–44], structural defects, as well as lattice distortion, can be seen, leading to an improvement in terms of catalytic behavior of B cation and lattice O\textsubscript{2}\textsuperscript{−} mobility [47,48]. To illustrate this point doping with Ba\textsuperscript{2+}, Sr\textsuperscript{2+}, Rb\textsuperscript{1+}, and Cs\textsuperscript{1+} can result
in the formation of structural deficiencies (i.e., anionic vacancies) and an alteration in the oxidation state of the cations enhancing the perovskite’s catalytic performance.

Figure 1. Ideal models of perovskite oxides with ABO$_3$ and A$_2$BO$_4$ structure. The red dot represents the substitution of an A-site cation by a foreign one; the blue square represents the oxygen vacancies. The oxygen symbol is not shown in the A$_2$BO$_4$ structure for simplification. Reproduced with permission from Ref. [32]. Copyright 2014, ACS.

An additional advantageous concept concerning the use of perovskite materials as metal catalyst nanoparticles supports is the so-called “redox exsolution”, discovered over the last decade [49], which opened new horizons and opportunities to heterogeneous catalysts design. Pioneers in the field, Nishihata et al. [50], used a Pd–perovskite catalyst to control automotive emissions and proved that the advanced electro-catalytic properties and high durability of this class of materials can be attributed to the utilization of metal nanoparticles exsolved from perovskite oxide lattices. The authors found that Pd can reversibly move into and out of the lattice of the perovskite while undergoing oxidation and reduction (as is usually the case in exhaust gas). This movement of Pd particles seemed to inhibit the growth of Pd nanoparticles and consequently led to improved catalytic activity for long-term use. However, despite the mounting interest in this method, a thorough understanding of how the perovskite supports and driving forces are combined is still lacking [51].

The focus of the present review: The aforementioned issues, and the fact that, to the best of our knowledge, there is no other literature report that focuses exclusively on the SCR of NO$_x$ emphasizing these three types of reducing agents (i.e., C$_x$H$_y$/C$_x$H$_y$O$_z$, H$_2$, CO), we have gathered herein, exhaustively, recent relevant literature results on the subject, which are thoroughly and comparatively discussed in order to shed light on current developments and new perspectives.

2. Perovskite-Catalyzed SCR of NO$_x$

Among the first to use perovskites in the SCR of NO$_x$ was Buciuman et al. [47] who ascertained the superiority of the Sr-containing sample from a series of La$_{0.8}$A$_{0.2}$MnO$_3$ perovskites (A = Cs, K, Ba, Sr) studied. He et al. [52] reported a strong dependence between the degree of x substitution and catalytic activity of a La$_{1-x}$Sr$_x$MO$_3$ (M = Co$_{0.77}$Bi$_{0.20}$Pd$_{0.03}$) perovskite under three-way catalysis (TWC) conditions, and Zhu et al. [53] showed a promising performance of La$_{2-x}$Sr$_x$CuO$_4$ perovskites for the simultaneous removal of NO and CO under similar conditions. Fino et al. [54] proposed La$_{1.8}$K$_{0.2}$Cu$_{0.9}$V$_{0.1}$O$_4$ as the best formulation for the simultaneous removal of NO$_x$ and diesel particulate. In
addition, considerable attention was paid to Cu-doped perovskites for the NO reduction by CO [43,55–59]. Noteworthy works have been carried out by Gisenti et al. [59] and Zhang et al. [43] who prepared B-site-Cu-doped perovskite catalysts to study the NO reduction by CO. With respect to A-site substitution, Ce, was thought to be the superior promoter as O$_2$ desorption and reducibility seemed to increase after Ce was added into the perovskite structure, although excess amounts of Ce can result in the degradation of the perovskite structure compromising the catalytic performance of the material [60–64].

As we will see in the following sections, the reduction of NO using CO as a reducing agent on perovskite catalysts has been extensively studied under conditions of absence of O$_2$ but very limited under conditions of excess O$_2$ (i.e., SCR). However, the use of hydrogen as a reducing agent of NO$_x$ under excess O$_2$ conditions (H$_2$-SCR) has been thoroughly studied providing encouraging results [65–67].

On the other hand, historically, the use of hydrocarbons as reducing agents for SCR of NO$_x$ (C$_x$H$_y$-SCR) in O$_2$-rich atmospheres has been investigated since the pioneering reports of Sato et al. [68]. In general, C$_3$H$_6$, C$_3$H$_8$, and CH$_4$ are considered the most common reducing agents in the C$_x$H$_y$-SCR reaction in lean conditions [48,69,70]. Nevertheless, even though C$_x$H$_y$-SCR holds great promise, it is associated with poor activity in low-temperature domains. In this regard, O$_2$-containing hydrocarbons (i.e., preferentially O$_2$-rich C$_x$H$_y$O$_z$) can be chosen as reducing agents to tackle this low-temperature inefficiency. Kucherov et al. [71] pioneered the use of ethanol as an effective reducing agent for NO reduction over Cu-ZSM-5 zeolites. The C$_2$H$_5$OH-SCR process was also investigated by Uksu et al. [72] and Wu et al. [73] over Ag/Al$_2$O$_3$ catalysts. The latter group reported the superiority of enolic species over acetate species in generating —CN/—NCO species and resultantly promoting the activity. However, the narrow temperature window in terms of activity, which is related to these non-perovskite-type materials, is still observed compromising the catalytic activity of the catalysts. To this end, Wang et al. [74] synthesized perovskite-based catalysts to test their activity in the C$_2$H$_5$O$_2$-SCR process under lean-burn conditions with methanol as the reducing agent.

A detailed analysis of the literature on the perovskites-catalyzed reduction of NO$_x$ using hydrocarbons, hydrogen, or carbon monoxide as reducing agents follows. It is divided into three distinct chapters based on the means of reduction used. At the end of each chapter, a summary table is included that presents, in a comparative manner, the literature analyzed in each of the chapters.

2.1. Perovskite Catalysts in C$_2$H$_5$/C$_2$H$_6$O$_2$-SCR of NO$_x$

Wang et al. [74] investigated the SCR of NO by methanol (CH$_3$OH) using a LaFe$_{0.8}$Cu$_{0.2}$O$_3$ perovskite. The results were compared with those obtained on a Ag/Al$_2$O$_3$ reference catalyst, which is widely used in deNO$_x$ applications. The said perovskite catalyst was prepared by a conventional citric acid (CA) complexation method, while the Ag/Al$_2$O$_3$ sample was prepared by wet impregnation. Furthermore, a high-surface-area nanoscale perovskite structure was produced by adapting the reactive grinding method (RG), which is a synthesis approach that is commonly used in metallurgy. The SCR activity tests were carried out in a tubular fixed bed quartz microreactor with a GHSV = 63,000 h$^{-1}$. The feed mixture comprised of 1000 ppm NO, 3000 ppm CH$_3$OH, 8% O$_2$, and He as balance gas. The catalyst physicochemical properties were explored by carrying out NO$_{ads}$ + O$_{2ads}$ TPD, XRD, H$_2$-TPR, H$_2$ physisorption, and isotopic exchange experiments. The LaFe$_{0.8}$Cu$_{0.2}$O$_3$ sample modified using the RG method outperformed the other tested catalysts in terms of both NO conversion and N$_2$ yield (Figure 2). Specifically, NO conversion of LaFe$_{0.8}$Cu$_{0.2}$O$_3$/RG was almost 95% at 450 °C while N$_2$ yield was approximately 93% as shown in Figures 2 and 3; the latter figure also shows the perovskite sites on which the CH$_3$OH, O$_2$, and NO reactants are activated. The increased catalytic performance of LaFe$_{0.8}$Cu$_{0.2}$O$_3$/RG was attributed to the higher surface area and subsequently to the increased number of surface-active sites available (Figure 3). Furthermore, a promoting effect regarding the formation of surface bounded O$_2$ species was observed, probably due to the increased number of active redox
sites resulting from the decrease in crystal domain size. The second-best catalyst was LaFe$_{0.8}$Cu$_{0.2}$O$_3$/CA whereas the Cu-free LaFeO$_3$/CA catalyst was third in activity order, offering maximum conversions that slightly exceeded 80% at the highest temperature (600 °C) investigated (Figure 2). The conventional Ag/Al$_2$O$_3$ catalyst performed poorly (close to inactive) for the entire temperature range under investigation (Figure 2).

Figure 2. NO conversion performance versus temperature over different catalysts during the CH$_3$OH-SCR of NO$_x$. Reaction conditions: 1000 ppm NO, 3000 ppm CH$_3$OH, and 8% O$_2$. Reproduced with permission from Ref. [74]. Copyright 2019, Elsevier.

Figure 3. The deNO$_x$ activity of LaFe$_{0.8}$Cu$_{0.2}$O$_3$ perovskite in comparison to that of Ag/Al$_2$O$_3$ catalyst during CH$_3$OH-SCR of NO$_x$. The sites for methanol, O$_2$, and NO adsorption/activation on the perovskite are also indicated. Reproduced with permission from Ref. [74]. Copyright 2019, Elsevier.
The deNO\textsubscript{x} performance of the catalysts was also investigated in the presence of CO\textsubscript{2} and H\textsubscript{2}O in the reaction feed with the results showing an activity decrease of only ca. 10% in the presence of CO\textsubscript{2} in the feed and a more profound decrease (ca. 20%) in the presence of H\textsubscript{2}O. Nevertheless, these inhibition effects were fully reversible when both CO\textsubscript{2} and H\textsubscript{2}O were removed from the feed stream. Performing in situ DRIFTS studies the authors demonstrated the formation of methoxy species (−O−CH\textsubscript{3}) over Cu-containing samples. The presence of formohydroxamic acid and carboxylate was assigned to the reaction between the adNO\textsubscript{x} nitrate/nitrite species detected on the surface of the Cu/Gr catalyst with the said methoxy species. With respect to the reference Ag/Al\textsubscript{2}O\textsubscript{3} catalyst, a continuous accumulation of nitrate species over the alumina surface was noticed, upon which dehydration of methanol unequivocally ensued. This fact explained the absence of enolic intermediate of SCR over this conventional catalyst (Ag/Al\textsubscript{2}O\textsubscript{3}). The authors also proposed a reaction mechanism for LaFe\textsubscript{0.8}O\textsubscript{3} supported by DFT calculations; the crucial step to producing N\textsubscript{2} over this type of catalyst is C−N bond coupling along with the first H transfer (1.455 eV at the highest energy barrier) \[74\].

Teng et al. \[75\] conducted a joint experimental and theoretical study and proposed a system that combined enriching coal bed methane (CBM) with solar energy and SCR of NO\textsubscript{x}. The basic approach was that the enriched CBM could be used as a reducing agent in SCR with a La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} perovskite catalyst. Catalytic performance results showed that the CH\textsubscript{4}-SCR system exhibited the highest NO conversion (80%) with recorded outlet NO concentrations below 20 mg·m\textsuperscript{-3}. Regarding the numerical simulations, the Navier–Stokes equations were used with the hypothesis that density difference, caused by a temperature gradient, was the key parameter. The authors argued that the temperature gradient, caused by the exploitation of solar energy, can enrich CBM and subsequently more CH\textsubscript{4} can be accumulated at the zone at increased temperature. In this regard, when the temperature difference was 150, the number of enriching units was estimated to be 200, which corresponded to a final CH\textsubscript{4} mole fraction of 0.8.

The same group \[76\] used CH\textsubscript{4} as a reductant to study the SCR of NO, though this time over an a-Al\textsubscript{2}O\textsubscript{3}-supported La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} perovskite-type catalyst. The precursor was prepared by a conventional sol–gel method, while the supported La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}/a-Al\textsubscript{2}O\textsubscript{3} catalyst was synthesized by a co-impregnation method. The perovskite structure of La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}/a-Al\textsubscript{2}O\textsubscript{3} was corroborated by XRD and SEM analysis. The inlet flue gas in the fixed bed reactor contained excess methane (CH\textsubscript{4}/NO = 1.2:1000 ppm NO, 1200 ppm CH\textsubscript{4}, 0–10% of O\textsubscript{2} and N\textsubscript{2} as carrier gas) to facilitate NO reduction, where the effect of temperature (600–900 °C) and resident time (\(\tau = 1.0\) s, 1.6 s, 2.2 s) was evaluated. It was shown that, in the absence of O\textsubscript{2}, methane can effectively convert NO (i.e., above 90%) over the La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}/a-Al\textsubscript{2}O\textsubscript{3}. On the other hand, in the presence of O\textsubscript{2}, the NO conversion was positively correlated with resident time. A positive correlation was also observed between NO conversion and temperature when the O\textsubscript{2} content ranged from 0% to 3%. Furthermore, at high reaction temperatures, moderate O\textsubscript{2} concentration was found to promote the NO reduction by filling the O\textsubscript{2} vacancies in the lattice. Interestingly, the supported catalyst had a decent performance for the broadest range of O\textsubscript{2} concentrations, while it outreached 90% of NO conversion when the O\textsubscript{2} concentration ranged from 4% to 6%. The authors concluded that the optimal experimental condition was: 2.2 s of residence time, 4–6% of O\textsubscript{2} concentration in feed gas, and 800 °C of reaction temperature.

Giroir-Fendler et al. \[77\] evaluated the catalytic activity of LaMnO\textsubscript{3} and partially substituted La\textsubscript{0.8}A\textsubscript{0.2}MnO\textsubscript{3} (A = K, Sr) perovskites for the SCR of NO using decane (C\textsubscript{10}H\textsubscript{22}) as reductant, as well as NO oxidation and C\textsubscript{10}H\textsubscript{22} oxidation. A 2 wt% Pt/SiO\textsubscript{2} sample was also used as a reference catalyst for comparison. The perovskite materials were synthesized by a complexation route. The gas mixture comprised of 400 ppm(v) NO, 240 ppm(v) C\textsubscript{10}H\textsubscript{22}, 1.5 vol% H\textsubscript{2}O, and 9 vol% O\textsubscript{2} (WGHSV = 36,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}) resembling a diesel exhaust gas, and the light-off behavior of the catalytic systems was acquired in the temperature range 100 to 500 °C (Figure 4). With respect to the ref. \[2\] wt% Pt/SiO\textsubscript{2} catalyst, 50% conversion was achieved at 180 °C which was 50 °C higher compared to the corresponding
temperature shown during the C_{10}H_{22} oxidation experiments (Figure 4A). The presence of NO did not affect the oxidation of C_{10}H_{22} when the La_{0.8}Sr_{0.2}MnO_{3} catalyst was used (Figure 4B). Catalytic tests in the absence of NO at 190 °C provided a similar T_{50} value. Interestingly, C_{10}H_{22} conversion for both Pt/SiO_{2} and La_{0.8}Sr_{0.2}MnO_{3} catalysts reached 100% at 200 °C (Figure 4).

![Figure 4](image_url). Reactant (C_{10}H_{22}) conversion and product (N_{2}, N_{2}O, NO_{2}) yields for Pt/SiO_{2} (A) and La_{0.8}Sr_{0.2}MnO_{3} (B) catalysts (feed gas: 400 ppm NO, 240 ppm C_{10}H_{22}, 1.5 vol% H_{2}O, and 9 vol% O_{2}). Reproduced with permission from Ref. [77]. Copyright 2014, Elsevier.

A closer look at the behavior of Pt/SiO_{2} catalyst under SCR conditions (Figure 4A) shows that both reduction of NO to N_{2}O and C_{10}H_{22} oxidation initiated at the same temperature, while the maximum N_{2}O yield (i.e., 65%) was obtained at 195 °C when the conversion of C_{10}H_{22} was 100%. The amount of N_{2} produced was lower compared to that of N_{2}O, both reaching maximum yields of 18% and 65%, respectively, at ~200 °C. Exceeding 200 °C, N_{2} and N_{2}O yields dropped, though, NO conversion to NO_{2} showed an increasing trend and reached a maximum of 37% at 370 °C. The maximum NO_{2} yield was lower and shifted to higher temperatures when NO oxidation took place in the absence of C_{10}H_{22}. In addition, the NO_{2} yield was below the thermodynamic equilibrium curve even at the highest temperature of 500 °C reached (Figure 4A). The La_{0.8}Sr_{0.2}MnO_{3} catalyst showed a relatively different catalytic behavior than Pt/SiO_{2}. A less competitive relationship between NO and C_{10}H_{22} was observed for temperatures lower than 200 °C, and thereby NO conversion was not favored toward C_{10}H_{22} oxidation. The maximum values of N_{2} and N_{2}O yields (almost 13%) at 210 °C were obtained when the conversion of C_{10}H_{22} was 100%. NO_{2} production started at 200 °C and reached a maximum value of 50% at 290 °C. Regarding the maximum yield of NO_{2}, it was lower compared to that of the NO oxidation experiment in the absence of C_{10}H_{22}, however, it was recorded at almost the same temperature ca. 285–290 °C. The fact that the NO/C_{10}H_{22} system exhibited lower maximum NO_{2} yield was ascribed to the parallel oxidation reactions of C_{10}H_{22} and NO over different redox systems (Mn^{3+}/Mn^{2+} and/or Mn^{4+}/Mn^{3+}). The said redox systems were considered as the active species participating in the Mars–van Krevelen mechanism, which is a widely accepted mechanism for hydrocarbons oxidation using mixed oxide catalysts [78,79]. The perovskite (La_{0.8}Sr_{0.2}MnO_{3} catalyst) showed better NO → NO_{2} oxidation activity and thus allowed a closer approximation of the thermodynamic equilibrium of this reaction compared to the Pt-based catalyst (Figure 4). Finally, the authors concluded...
that the La$_{0.8}$Sr$_{0.2}$MnO$_3$ perovskite could be a promising alternative, noble metal-free catalyst for NO$_x$ emission control (Figure 5). Table 1 synopsizes the main literature studies analyzed in Section 2.1.

**Figure 5.** Comparison of the maximum N$_2$, N$_2$O, NO$_2$ yields, and NO conversions and the corresponding temperatures these maxima appeared at for the C$_{10}$H$_{22}$-SCR of NO$_x$ over a noble metal-based catalyst and a noble metal-free perovskite catalyst. Reproduced with permission from ref. [77]. Copyright 2014, Elsevier.

**Table 1.** Perovskite-catalyzed H$_x$C$_y$(O$_z$)-SCR of NO$_x$ representative studies.

| Catalyst | NO (%) | HC (%) | O$_2$ (%) | Other (%) | WGSV (mL·g$^{-1}$·h$^{-1}$) | X$_{NO}$ (%) at T (°C) | S$_{N2}$ (%) | Ref. |
|----------|--------|--------|-----------|-----------|-----------------------------|------------------------|-------------|-----|
| LaFe$_2$Cu$_2$O$_5$-RG | 0.1 | 0.3 (CH$_3$OH) | 8 | - | 30,000 | >90 | >430 | n/a | [74] |
| LaFe$_2$Cu$_2$O$_5$-CA | 0.1 | 0.3 (CH$_3$OH) | 8 | - | 30,000 | >90 | >475 | n/a | [74] |
| LaFeO$_3$-CA | 0.1 | 0.3 (CH$_3$OH) | 8 | - | 30,000 | >80 | >575 | n/a | [74] |
| La$_2$Sr$_2$MnO$_3$/α-Al$_2$O$_3$ | 0.1 | 0.12 (CH$_4$) | 0 | - | 1636 h$^{-1}$ (GHSV) | >90 | >875 | n/a | [76] |
| La$_2$Sr$_2$MnO$_3$/α-Al$_2$O$_3$ | 0.1 | 0.12 (CH$_4$) | 5 | - | 1636 h$^{-1}$ (GHSV) | 96 | 800 | n/a | [76] |
| La$_2$Sr$_2$MnO$_3$ | 0.4 | 0.24 (C$_{10}$H$_{22}$) | 9 | 1.5 (H$_2$O) | 36,000 | 20–65 | 200–275 | 13 (max at 210°C) | [77] |

Conventional, supported on oxide supports NM catalysts

| Catalyst | NO (%) | HC (%) | O$_2$ (%) | Other (%) | WGSV (mL·g$^{-1}$·h$^{-1}$) | X$_{NO}$ (%) at T (°C) | S$_{N2}$ (%) | Ref. |
|----------|--------|--------|-----------|-----------|-----------------------------|------------------------|-------------|-----|
| 2wt%Pt/SiO$_2$ | 0.4 | 0.24 (C$_{10}$H$_{22}$) | 9 | 1.5 (H$_2$O) | 36,000 | >90 | 200–250 | 18 (max at 200°C) | [77] |
| 0.5wt%Pt/α-Al$_2$O$_3$ | 0.1 | 0.1 (C$_3$H$_6$) | 5 | - | 180,000 * | >50 | 300–400 | 40 (at 300°C) | [7] |
| 0.5wt%Pt/0.6wt%Na/α-Al$_2$O$_3$ | 0.1 | 0.1 (C$_3$H$_6$) | 5 | - | 53,485 * | >50 | 225–375 | 75 (at 225°C) | [7] |

* The same contact time of the reactants with the catalyst active sites was imposed in these two cases by adjusting WGSV.

2.2. Perovskite Catalysts in H$_2$-SCR of NO$_x$

Efstathiou and co-workers [9] using a ceramic method prepared a La$_{0.2}$Sr$_{0.2}$Ce$_{0.1}$FeO$_3$ solid in which the major crystal phases detected by XRD were LaFeO$_3$ and SrFeO$_3$–x perovskite structures and the oxidic phases CeO$_2$ and Fe$_2$O$_3$ (i.e., not a pure perovskite but a mixed oxide material). The material was used as support for the preparation of a 1 wt% Pt content catalyst, by wet impregnation (1 wt% Pt/La$_{0.2}$Sr$_{0.2}$Ce$_{0.1}$FeO$_3$), while counterpart catalysts, namely 1 wt% Pt content Pt/CeO$_2$, Pt/Fe$_2$O$_3$, and Pt/SiO$_2$, were also prepared.
for the sake of comparison. The H₂-SCR deNOₓ performance of the Pt/La₀.7Sr₀.2Ce₀.1FeO₃ catalyst, using a 0.25% NO/1% H₂/5% O₂/balance He at a WGSHSV of 40,000 mL·g⁻¹·h⁻¹ (GHSV = 80,000 h⁻¹), found to transcend that of the other tested catalysts: a maximum NO conversion of 83% with a N₂-selectivity as high as 93% was achieved at 150 °C; corresponding maximum values for Pt/SiO₂, Pt/CeO₂, and Pt/Fe₂O₃ catalysts were X_NO = 82%/S_N₂ = 65% (at 120 °C), X_NO = 82%/S_N₂ = 43% (at 150 °C), and X_NO = 16%/S_N₂ = 5% (at 200 °C), respectively. Notably, for the optimal Pt/La₀.7Sr₀.2Ce₀.1FeO₃ catalyst, the addition of 5% H₂O in the feed stream at 140 °C resulted in some widening of the operating temperature window with considerable NO conversion and N₂-selectivity values, while no degradation effects were observed on its stability for 20 h time-on-stream.

Luo et al. [80] prepared, via a sol–gel method, a series of LaNi₁₋ₓFeₓO₃ (x = 0.0, 0.2, 0.4, 0.7, 1.0) perovskites to study the SCR of NOₓ by H₂ at temperatures between 200 and 400 °C in a fixed bed reactor (500 mg catalyst) using a 500 ppm NO, 3.5 vol% H₂, 8 vol% O₂ (balance N₂) gas feed composition with a total flow rate of 600 mL min⁻¹. Sulfur-aging and regeneration treatments were also involved in their study. They found that Fe-doping of the base LaNiO₃ perovskite results in a better NOₓ removal (Figure 6), and high structural stability.

Figure 6. Effect of temperature on NOₓ conversion efficiency of LaNi₁₋ₓFeₓO₃ perovskite catalysts during H₂-SCR of NOₓ. Reproduced with permission from Ref. [80]. Copyright 2014, Elsevier.

H₂-TPR analysis showed that partial substitution of Ni by Fe results in better reducibility of nickel particles (Ni³⁺ → Ni²⁺), which in turn play a critical role in promoting NO-SCR. The perovskite LaNi₀.6Fe₀.4O₃ with the best reducibility characteristics was the best overall in deNOₓ performance (Figure 6). Regarding perovskite stability, N₂ physiosorption and SEM analysis showed that the partial substitution of nickel with appropriate amounts of Fe can lead to enhanced surface area as well as thermal stability. Finally, the bulk LaNiO₃ and LaNi₀.6Fe₀.4O₃ were tested toward their sulfur resistance and regeneration ability. Results showed that the presence of SO₂ resulted in lower NOₓ conversion in both cases. However, both samples were capable of being regenerated after 12-h long H₂ treatment. XPS results (Figure 7) suggested the predominance of sulfate species formed on the active nickel components, whereas the addition of Fe significantly affected the sulfation process, leading to enhanced sulfur resistance.
Using a cost-effective solution combustion synthesis (SCS) method, Furfori et al. [81] prepared a series of perovskites and Pd-promoted (via wet impregnation) perovskite-type catalysts belonging to the LaFeO$_3$ group in order to evaluate their catalytic performance and decipher H$_2$-SCR of NO$_x$ mechanisms in the absence and presence of O$_2$. The synthesized catalysts were La$_{0.8}$Sr$_{0.2}$FeO$_3$, Pd/La$_{0.8}$Sr$_{0.2}$FeO$_3$, La$_{0.8}$Sr$_{0.2}$Fe$_{0.9}$Pd$_{0.1}$O$_3$, La$_{0.8}$Sr$_{0.2}$Ce$_{0.1}$FeO$_3$, Pd/La$_{0.8}$Sr$_{0.2}$Ce$_{0.1}$FeO$_3$, La$_{0.8}$Sr$_{0.2}$Ce$_{0.1}$Fe$_{0.9}$Pd$_{0.1}$O$_3$, and bulk LaFeO$_3$; Figure 8 shows a field emission scanning electron micrograph of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sample appearing as a very foamy structure, a structure that was found to be representative of all perovskites prepared by the SCS method with a specific surface area, ~10 m$^2$·g$^{-1}$ on average. The catalytic tests performed in a fixed bed reactor at the temperature range of 25–400 °C, using a gas feed consisted of 1000 ppm NO, 4000 or 10,000 ppm H$_2$, 0 or 5% O$_2$, balance He, at WGHSV = 180,000, 270,000 and 360,000 mL·g$^{-1}$·h$^{-1}$ (GHSV = 20,000, 30,000, and 40,000 h$^{-1}$). In the absence of O$_2$ in the feed stream, the most promising catalyst that outperformed all other catalysts was found to be La$_{0.8}$Sr$_{0.2}$Fe$_{0.9}$Pd$_{0.1}$O$_3$ (Figure 9), which was then further studied in the presence of 5% O$_2$ at three different WGHSV, and at a higher H$_2$ concentration in the feed (10,000 ppm). Up to 75% NO conversion toward N$_2$ at a temperature as low as 125 °C for WGHSV = 180,000 mL·g$^{-1}$·h$^{-1}$ was achieved. For the highest space velocity value, the maximum NO conversion to N$_2$ was reduced to ~55% while the corresponding temperature was shifted to a value ~10 °C higher. As the temperature increased, the selectivity to N$_2$ gradually decreased due to the favorable formation of N$_2$O and NO$_2$, a behavior typical of SCR processes. Regarding the deNO$_x$ reaction mechanism, H$_2$-TPR and other characterization results allowed the authors to conclude that both the availability of oxygen vacancies (suitable for NO adsorption) and the reducibility of
the B-sites play a critical role in the catalytic activity of the perovskites. Finally, the authors stated that the results, although promising, do not yet meet industry demands.

Figure 8. Field emission SEM micrograph of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ catalyst crystals. Reproduced with permission from Ref. [81]. Copyright 2010, Elsevier.

Figure 9. Comparison of the NO conversion light-off performance of all synthesized perovskite-type catalysts under 1000 ppmv NO, 4000 ppmv H$_2$, 0% O$_2$, balance He, WGHSV = 180,000 mL·g$^{-1}$·h$^{-1}$ feed conditions. Reproduced with permission from Ref. [81]. Copyright 2010, Elsevier.

Mondragon Rodriguez and Saruhan [67] studied the effect of Fe/Co-ratio on the phase composition of LaFe$_{0.95-x}$Co$_x$Pd$_{0.05}$O$_3$ ($x = 0.475, 0.4, 0.3$) perovskite catalysts and then evaluated their behavior with respect to H$_2$-SCR of NO$_x$. The catalysts under consideration were prepared by the so-called citrate method. Three different feed stream composition protocols were adopted during catalyst evaluation tests in a tubular fixed bed reactor
operated at 1 bar. In the first one the feed gas comprised of 0.072% NO, 5% O\textsubscript{2}, 1% H\textsubscript{2}, He balance. The second experimental protocol included the addition of 7.2% H\textsubscript{2}O and 7.2% CO\textsubscript{2} to the mixture (0.072% NO, 5% O\textsubscript{2}, 1% H\textsubscript{2}, 7.2% H\textsubscript{2}O), while the third one included the addition of 0.25% CO instead of H\textsubscript{2}O, and CO\textsubscript{2} (0.072% NO, 5% O\textsubscript{2}, 1% H\textsubscript{2}, 0.25% CO). The WGHSV in all experiments was kept at 55,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1} and the reaction temperature ranged from 50 to 400 °C. All tested samples were characterized using the TPR, EDS, FESEM, XPS, XRD, and DSC techniques. Results from the first experimental protocol suggested that LaFe\textsubscript{0.475}Co\textsubscript{0.475}Pd\textsubscript{0.05}O\textsubscript{3} and LaFe\textsubscript{0.65}Co\textsubscript{0.3}Pd\textsubscript{0.05}O\textsubscript{3} exhibited the best (i.e., 79% NO conversion at 180–230 °C) and second-best (i.e., 74% NO conversion at 200 °C) catalytic performance, respectively. Representative field emission SEM images of these two materials are depicted in Figure 10.

Figure 10. SEM images of the perovskite surface LFC\textsubscript{(0.3)}-Pd (a) and LFC\textsubscript{(0.475)}-Pd (b) after calcination in air at 900 °C/3 h. Reproduced with permission from Ref. [67]. Copyright 2010, Elsevier.

Figure 11a shows that the NO\textsubscript{x} conversion of LaFe\textsubscript{0.475}Co\textsubscript{0.475}Pd\textsubscript{0.05}O\textsubscript{3} and LaFe\textsubscript{0.65}Co\textsubscript{0.3}Pd\textsubscript{0.05}O\textsubscript{3} followed a typical volcano-type behavior [67], indicating the existence of competing redox reactions which might entail the dissociation of NO into adsorbed N and O species, as also proposed by Burch and Coleman [82] upon investigating the H\textsubscript{2}-SCR of NO\textsubscript{x} over platinum group metal catalysts dispersed on traditional oxide supports. The optimum operating temperature was between 200 °C and 250 °C (Figure 11a). By decreasing the Co-content of the La-containing perovskites, the selectivity of N\textsubscript{2} shifted to higher temperatures (Figure 11b). Nevertheless, LaFe\textsubscript{0.475}Co\textsubscript{0.475}Pd\textsubscript{0.05}O\textsubscript{3} was found to produce slightly more N\textsubscript{2}O (35 ppm) between 160 °C and 240 °C, in comparison to LaFe\textsubscript{0.65}Co\textsubscript{0.3}Pd\textsubscript{0.05}O\textsubscript{3}. Interestingly the latter catalyst reduced less NO\textsubscript{x} compared to LaFe\textsubscript{0.475}Co\textsubscript{0.475}Pd\textsubscript{0.05}O\textsubscript{3} suggesting that either Co or Co-species can promote the development of active sites, which participate in the NO\textsubscript{x} reduction. Additionally, with respect to the bimetallic particles (i.e., Co and Pd), they may be involved in NO-dissociation and chemisorption, N\textsubscript{2}O formation, and H\textsubscript{2}-chemisorption. The authors also examined the effect of CO\textsubscript{2} and H\textsubscript{2}O given that they are always involved in the exhausts of any combustion engine and can affect the catalyst performance during the H\textsubscript{2}-SCR of NO\textsubscript{x} reaction. Results from the second series of these catalytic tests showed that the NO conversion dropped when the Co amount in the structure of the perovskite decreased, whereas N\textsubscript{2} selectivity remained constant. When the temperature was lower than 250 °C the NO\textsubscript{x} reduction performance decreased, while above 250 °C the NO\textsubscript{x} conversion was maintained. Competitive adsorption of H\textsubscript{2}O and NO molecules on the active sites of the perovskite was observed, affecting the NO\textsubscript{x} conversion, and increasing the formation of N\textsubscript{2}O. In addition, as the temperature increased above 250 °C lower amounts of N\textsubscript{2}O were produced over the LaFe\textsubscript{0.65}Co\textsubscript{0.3}Pd\textsubscript{0.05}O\textsubscript{3} sample [67]. The results from the experiments involving CO\textsubscript{2} and H\textsubscript{2}O in the feed gas indicated that H\textsubscript{2}O molecules can easily dissociate at increased temperatures on the catalyst surface, facilitating the formation of adsorbed H
species, which may eventually lead to higher concentrations of N adsorbed species via the reaction $\text{NO}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{OH}_{\text{ads}}$ as also proposed by Dhainaut et al. [83] upon studying the H$_2$-SCR of NO$_x$ on Pd/LaCoO$_3$ catalysts. Resultantly, more molecular N$_2$ was formed due to the reaction between two neighboring chemisorbed N atoms on the surface of the LaFe$_{0.65}$Co$_{0.3}$Pd$_{0.05}$O$_3$. The reason why these reactions occurred on catalyst Pd, Pd-Fe, or/and Pd-Co-surface was that the Pd-free sample exhibited no activity for the H$_2$-SCR of NO$_x$ reaction. Agreeing with Dhainaut et al. [83], the authors stated that the physicochemical properties of Pd were strongly affected by its interaction with La [67]. On the other hand, the LaFe$_{0.475}$Co$_{0.475}$Pd$_{0.05}$O$_3$ catalyst displayed improved NO$_x$ conversion in the presence of H$_2$O vapor in the feed. Results suggested that 20% more NO$_x$ was reduced for the H$_2$O-containing mixture in comparison to that or H$_2$O-free mixture (dry conditions) at 350 °C [67]. Decreased amount of N$_2$O was also observed with H$_2$O vapor in the reaction that took place below 250 °C, while at higher temperatures N$_2$O formation was almost constant. Under these conditions, H$_2$O was more likely to be dissociated on the LaFe$_{0.475}$Co$_{0.475}$Pd$_{0.05}$O$_3$ surface promoting the formation of molecular N$_2$ and lowering the chance of N$_2$O formation. The authors suggested that the improved N$_2$ selectivity of Pd-La perovskites was probably assigned to the existence of alloy compounds (e.g., Pd$_3$La) as was also reported by others [66,84]. The effect of CO in the feed was also examined in the third experimental protocol and it was found that both the N$_2$ selectivity and the NO$_x$ conversion for LaFe$_{0.475}$Co$_{0.475}$Pd$_{0.05}$O$_3$ and LaFe$_{0.65}$Co$_{0.3}$Pd$_{0.05}$O$_3$ perovskites were negatively affected by CO presence [67]. LaFe$_{0.475}$Co$_{0.475}$Pd$_{0.05}$O$_3$ exhibited higher N$_2$ selectivity compared to that of LaFe$_{0.65}$Co$_{0.3}$Pd$_{0.05}$O$_3$ reaching 54% at 180 °C and 46% as the temperature ranged from 210 to 290 °C. Increasing the Fe-content led to decreased NO$_x$ reduction performance for temperatures above 225 °C. Regarding the LaFe$_{0.65}$Co$_{0.3}$Pd$_{0.05}$O$_3$ catalyst, lower N$_2$-formation rates were observed while the maximum value of N$_2$ selectivity was 34% at 237 °C. A 10% decrease was noticed at higher temperatures (i.e., 340 °C) because of the relatively high N$_2$O concentration formed. Results suggested that higher Co-content in the catalyst, resulted in the formation of perovskite phase, as corroborated by in situ XRD measurements. Another conclusion made was that the new intermetallic phases, which can be formed between the metallic Fe, Pd, and Co perovskite components, were more resistant to CO poisoning.

![Figure 11](image-url)

Figure 11. NO$_x$ conversion (a) and N$_2$-selectivity (b) of LaFe$_{0.475}$Co$_{0.475}$Pd$_{0.05}$O$_3$ and LaFe$_{0.65}$Co$_{0.3}$Pd$_{0.05}$O$_3$ perovskite catalysts. The samples were calcined at 900 °C in air for 3 h. Reproduced with permission from Ref. [67]. Copyright 2010, Elsevier.

Mondragon Rodriquez et al. [85] have also prepared, via a co-precipitation method, two different perovskite-based catalysts, namely BaTi$_{0.95}$Pd$_{0.05}$O$_3$ and Pd/BaTiO$_3$, to evaluate their catalytic performance in the H$_2$-SCR of NO$_x$ reaction. Four experimental protocols were adopted in the study to decipher the effects of H$_2$O, CO$_2$, and CO co-feed, the WGHSV
employed, as well as the calcination temperature of the materials during preparation. H$_2$-TPR, XPS, SEM, TEM, and XRD measurements were adopted for the characterization of the materials under consideration. A TEM image of the BaTi$_{0.95}$Pd$_{0.05}$O$_3$ perovskite calcined at 700 °C is shown in Figure 12a. Interestingly, a low Pd-content was found by the EDX-point measurements in the matrix (Figure 12a, arrow), while from Figure 12b qualitatively noticeable Pd-peaks were detected at various sites of the material. EF-TEM analysis was also applied to elucidate the presence of Pd particles before and after reduction pretreatment (Figures 12a and 13b). That said, images using exclusively electrons of a specific energy loss were tracked via an imaging filter. In particular, Figure 13b showed the elemental distribution of Pd, which was calcined in air. Even though the reduction pretreatment was postponed in this sample, many Pd-containing particles were detected in the mapped image. On the other hand, from Figure 13a these particles were hardly visible, while their chemical nature was hardly identified. It was also reported that both Pd-containing perovskite phases and Pd-oxides may be present. Following exposure to the electron beam during the reduction of PdO metallic Pd can also be formed. Besides this vagueness, it was obvious that Pd-rich nanoparticles were present in the catalyst. The catalytic results showed that the use of a high calcination temperature deteriorates the deNO$_x$ activity of the BaTi$_{0.95}$Pd$_{0.05}$O$_3$ perovskite: the calcined at 500 °C BaTi$_{0.95}$Pd$_{0.05}$O$_3$ catalyst exhibited higher NO conversion (ca. 90%) than that calcined at 900 °C, due to the lower surface area (53% lower) of the latter [85]. However, with respect to the N$_2$ selectivity, no significant effects resulted. Under the use of a very high WGSV (1.61 × 10$^6$ mL·g$^{-1}$·h$^{-1}$), the authors reported maximum NO conversions of 50% at 250 °C and 70% at 200 °C for BaTi$_{0.95}$Pd$_{0.05}$O$_3$ and Pd/BaTiO$_3$ catalysts, respectively (Table 2). Considering the high space velocity of these catalytic tests, NO$_x$ conversions were decent. In general, Pd/BaTiO$_3$ catalyst outperformed the BaTi$_{0.95}$Pd$_{0.05}$O$_3$ catalyst in terms of catalytic activity below 250 °C, though more N$_2$O was formed (Figure 14). On the other hand, above 250 °C the BaTi$_{0.95}$Pd$_{0.05}$O$_3$ sample exhibited higher NO$_x$ conversion compared to the Pd/BaTiO$_3$ catalyst. It was also found [85] that the addition of CO in the feed afflicted the NO$_x$ conversion, particularly in the temperature range of 160–195 °C. The authors argued that the negative effect of the presence of CO was smaller in comparison to the results presented in the literature. They also highlighted the oxidation potential of Pd which can promote the chemical adsorption of CO on Pd-containing surfaces below 200 °C. However, below this temperature, CO adsorption probably competed with NO$_x$ reduction for occupying the same active sites. Above 200 °C, higher rates of CO oxidation were observed, though they still blocked the active sites of the catalyst compromising the NO$_x$ reduction process. On this basis, small NO$_x$ reduction levels were achieved in the presence of CO, while increased N$_2$O formation rates were found between 160 and 195 °C. Finally, the conversion of NO$_x$ was further decreased upon increasing the temperature while with respect to N$_2$ selectivity a medium fluctuation was reported. The appearance of two maxima of the NO$_x$ conversion obtained between 150 and 200 °C during the NO$_x$ reduction in the presence of CO was not interpretable from the available data. In the presence of CO$_2$ and H$_2$O, the catalyst maintained 58.7% of NO$_x$ conversion for temperatures between 160 and 195 °C. Above 230 °C, maximum NO$_x$ conversion (ca. 71.5%) was recorded, however, a further increase led to an inverse correlation between temperature and conversion. A beneficial effect on the catalytic performance of BaTi$_{0.95}$Pd$_{0.05}$O$_3$/900 (calcined at 900 °C) was reported for temperatures between 195 and 270 °C, suggesting slightly decreased N$_2$O formation in this temperature range. A positive effect by the addition of CO$_2$ and H$_2$O on NO conversion was also found for the BaTi$_{0.95}$Pd$_{0.05}$O$_3$/900 catalyst. Nevertheless, below 200 °C, the presence of H$_2$O resulted in a complex mechanism with antagonistic reactions, (i.e., N$_2$O and N$_2$ formation versus NO$_x$ reduction), however above 200 °C the conversion of NO$_x$ was improved. This behavior was attributed to the co-adsorption of CO$_2$ and H$_2$O during the NO$_x$ reduction. Moreover, above this temperature H$_2$O dissociation and H$_2$O adsorption may be involved in the NO$_x$ reduction mechanism [85].
Figure 12. TEM of the BaTi$_{0.85}$Pd$_{0.05}$O$_3$ calcined up to 700 °C/3 h (in air): (a) a minute part of an agglomerate, (b) EDS spectrum of matrix area encircled in image a, regions containing the Pd–K and Pd–L X-ray diffractions are scaled up to provide a visible Pd-signal. Reproduced with permission from Ref. [85]. Copyright 2010, Elsevier.

Figure 13. TEM of BaTi$_{0.95}$Pd$_{0.05}$O$_3$ calcined up to 700 °C/3 h (in air), (a) image of a zero-loss filtered bright field (10 eV slit width), and (b) image of Pd elemental map using the 3-window method (i.e., 60 s/window, 20 eV slit width, slit centered at 315 eV, 325 eV, and 410 eV). Reproduced with permission from Ref. [85]. Copyright 2010, Elsevier.
In order to highlight the benefits that can be achieved for the H₂-SCR of NOₓ using perovskite-type catalysts, i.e., perovskites and/or perovskites promoted by very low noble metal (NM) loadings, in Table 2 we present comparative representative results obtained using perovskite-based catalysts and conventional supported noble metal catalysts. It can be concluded that perovskite-based catalysts are highly active and significantly selective toward N₂ at temperatures typically below 200 °C; the achievements on these catalysts are well compared to those obtained using the more expensive NM-based conventional catalysts, typically containing higher NM loadings.

Table 2. Comparative presentation of the achievements obtained for H₂-SCR of NOₓ by using representative perovskite-based catalysts and conventional-type noble metal catalysts.

| Catalyst | NO (%) | H₂ (%) | O₂ (%) | Other (%) | WGHSV (g⁻¹ h⁻¹) | N₂O (%) at T (°C) max. | S N₂ (%) | Ref. |
|----------|--------|--------|--------|-----------|----------------|---------------------|--------|-----|
| Perovskite and NM/perovskite catalysts | | | | | | | | |
| LaFe₀.₆₅Co₀.₃Pd₀.₀₅O₃ | 0.072 | 1 | 5 | 7.2 (H₂O) + 7.2 (CO₂) | 55,400 | >50 (max. 57) | 200–250 | 75 (at 200 °C) [67] |
| LaFe₀.₄₇₅Co₀.₄₇₅Pd₀.₀₅O₃ | 0.072 | 1 | 5 | 7.2 (H₂O) + 7.2 (CO₂) | 55,400 | >50 (max. 85) | 175–300 | 75 (at 200 °C) [67] |
| La₀.₈Sr₀.₂Fe₀.₉Pd₀.₁O₃ | 0.045 | 0.8 | 5 | 1.61 x 10⁶ | >50 (max. 55) | 150–150 | 68 (at 200 °C) [85] |
| BaTi₀.₉₅Pd₀.₀₅O₃ | 0.045 | 0.8 | 5 | 1.61 x 10⁶ | >50 (max. 55) | 125–250 | 60 (at 200 °C) [85] |
| 0.3%Pt/La₀.₇Sr₀.₂Ce₀.₁FeO₃ | 0.25 | 1 | 5 | 40,000 | >50 (max. 83) | 125–225 | 93 (at 170 °C) [9] |
| 0.1%Pt/La₀.₅Ce₀.₅MnO₃ | 0.25 | 1 | 5 | 40,000 | >50 (max. 83) | 125–175 | 78 (at 150 °C) [86] |
| Conventional, supported on oxide supports, NM catalysts | | | | | | | | |
| 1%Pt/SiO₂ | 0.072 | 1 | 5 | 7.2 (H₂O) + 7.2 (CO₂) | 55,400 | >50 (max. 80) | 100–175 | 51 (at 125 °C) [67] |
| 1%Pt/Al₂O₃ | 0.05 | 0.2 | 6 | 120,000 | 50 | 150 | 30 | [82] |
| 1%Pt/SiO₂ | 0.05 | 0.2 | 6 | 120,000 | >50 (max. 80) | 100–175 | 51 (at 125 °C) [67] |
| 0.1%Pt/MnO₂ | 0.25 | 1 | 5 | 5(H₂O) | 40,000 | >50 (max. 95) | 80–250 | 75 (at 200 °C) [86] |
| 0.1%Pt/Al₂O₃-(10%TiO₂) | 0.25 | 1 | 5 | 5(H₂O) | 40,000 | >50 (max. 95) | 80–250 | 75 (at 200 °C) [86] |

2.3. Perovskite Catalysts in CO-SCR of NO$_x$

It is worth noting that our literature search on the perovskites-catalyzed selective (i.e., at excess O$_2$ conditions) reduction of NO$_x$ by CO was virtually fruitless as we managed to unearth only one publication [90]. On the contrary, and to our surprise, many reports were found on the reduction of NO by CO in the absence of O$_2$. The former unexplained lack of interest can be partly understood by the fact that the management of CO as an externally supplied reducing agent (as is normally followed in the case of NH$_3$-, HCs-, or H$_2$-SCR processes) is difficult due to the extremely dangerous nature of this molecule. However, it should be noted that in many practical combustion processes CO is contained in a high concentration in the exhaust gases together with excess O$_2$ [13,87,89]. Therefore, it would be of great interest to exploit its existence in the exhaust gases to reduce the coexisting NO$_x$ (i.e., CO-SCR of NO$_x$) regardless of the fact that its external supply is not desirable. In the following lines we first analyze the report that was found to be directly related to the CO-SCR of NO$_x$ (i.e., the presence of excess O$_2$) on perovskite-based catalysts, and then, due to the importance of the topic, we consciously choose to deviate slightly from the title of the present review by analyzing the literature on reduction of NO by CO over perovskites even in the absence of O$_2$.

Qin et al. [90] investigated the effect of ceria-content in La$_x$Ce$_{1-x}$FeO$_3$ ($x = 0.2, 0.4, 0.6, 0.8, 1$) perovskite catalysts on improving SO$_2$ resistance for catalytic reduction of NO with CO in the presence of O$_2$. Specifically, the feed gas was comprised of 400 ppm NO/500 ppm CO/3% O$_2$/3% H$_2$O (100 ppm SO$_2$) balance N$_2$ at a GHSV of 24,000 h$^{-1}$, and the temperature range of catalytic tests was 100–500 °C. The perovskites were characterized by SO$_2$-TPD, CO−TPR, XRD, and XPS measurements. In the absence of H$_2$O, O$_2$, and SO$_2$ in the feed (NO + CO reaction) results suggested better catalytic performance with respect to both NO conversion (Figure 15a) and N$_2$−selectivity (Figure 15b) of LaFeO$_3$ catalyst. To investigate the effect of SO$_2$ in the NO conversion activity of the perovskites 100 ppm of SO$_2$ was added into the NO + CO feed after 30 min of operation and the transient experiments were kept running for a total of 300 min time-on-stream (Figure 15c). Obviously, the existence of SO$_2$ inhibits the catalytic activity of all perovskites but to a different degree. La$_{0.6}$Ce$_{0.4}$FeO$_3$ was less inhibited in the presence of SO$_2$ highlighting the beneficial effect of substituting La by Ce in the A-sites of the perovskite on its resistance to SO$_2$-poisoning. It is also apparent that exceeding La substitution by Ce in the perovskite is detrimental to both activity (Figure 14a) and SO$_2$-poisoning resistance (Figure 15c). The authors also evaluated the materials at CO-SCR conditions, i.e., in the presence of excess O$_2$ and co-presence of H$_2$O and SO$_2$ (Figure 15d). The La$_{0.6}$Ce$_{0.4}$FeO$_3$ perovskite which was found to be optimal in the previous sets of experiments was again optimal in this case in particular at high temperature, however, no results for nitrogen-containing products are available in order to see its N$_2$-selectivity behavior as well; actually, at high temperatures, the NO$_2$ production via the NO + O$_2$ reaction is favored. Based on their characterization results, the authors conclude that the optimal La$_{0.6}$Ce$_{0.4}$FeO$_3$ catalyst retains its original structure during the reaction, and the specific redox properties of Ce in its structure are the cause of its superior activity and SO$_2$ tolerance performance [90].

We now turn our attention to works that report on the performance of perovskite materials during the reduction of NO by CO in the absence of O$_2$. Wu et al. [91] employed a sol−gel method to prepare LaM$_{0.5}$Mn$_{0.5}$O$_3$ (M = Cu, Co, Fe, Ni, Cr) perovskite catalysts in order to evaluate the effect of partial substitution on B-site of this series of catalysts in NO reduction by CO in the absence of O$_2$ but using excess H$_2$O (10%) in the feed: 10% CO/5% NO/He balance (i.e., excess CO) and occasionally 10% H$_2$O and 1000 ppm SO$_2$. A variety of WGHSVs ranging from 60,000 to 600,000 mL·g$^{-1}$·h$^{-1}$ were employed, and 72 h time-on-stream stability tests at 250 °C were also conducted. The study includes materials characterization by XPS, ICP-AES, O$_2$-TPD, H$_2$−TPR, XRD, BET, and in situ DRIFTS measurements. It was demonstrated that the NO reduction performance of the perovskites clearly improved via the partial substitution of the B-sites by the aforementioned elements, following the order LaCu$_{0.5}$Mn$_{0.5}$O$_3$ > LaCr$_{0.5}$Mn$_{0.5}$O$_3$ > LaNi$_{0.5}$Mn$_{0.5}$O$_3$ > LaCo$_{0.5}$Mn$_{0.5}$O$_3$. 

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LaFe$_{0.5}$Mn$_{0.5}$O$_3$ > LaMnO$_3$. LaCu$_{0.5}$Mn$_{0.5}$O$_3$ catalyst displayed the best catalytic behavior with complete removal of NO at 300 °C and 100% selectivity toward N$_2$. On the other hand, the bare LaMnO$_3$ displayed the worst behavior in terms of both NO conversion and N$_2$-selectivity compared to other Cu-modified perovskites. The authors also examined the stability of the catalysts by carrying out 72-h time-on-stream stability tests at 750 °C. Results indicated that the NO conversion of LaMnO$_3$ dropped from 22.2 to 10.3% whereas the NO conversion of LaCu$_{0.5}$Mn$_{0.5}$O$_3$ was barely affected (i.e., 63.8 to 59.3%). The recycle catalytic capacity for 10 cycles was also conducted using the bare LaMnO$_3$ and the optimal LaCu$_{0.5}$Mn$_{0.5}$O$_3$ catalysts. A gradual decrease of the catalytic performance was reported for both catalysts, however, the degree of degradation was less significant for the Cu-containing catalyst, highlighting once again the positive role of Cu addition. XRD supportive measurements during these experiments also corroborated the superiority of LaCu$_{0.5}$Mn$_{0.5}$O$_3$ over LaMnO$_3$, by showing that the crystallinity of LaCu$_{0.5}$Mn$_{0.5}$O$_3$ was less affected (i.e., Cu addition hindered the decrease of crystallinity in the bulk phase) in comparison to that of the bulk phase during the cycles. Moreover, XPS analysis illustrated the existence of constant electron binding energy for the Cu-containing sample during the cycles, indicating an invariant valence state of Mn and La species under the reaction conditions [91]. On the other hand, it was also clear that the LaMnO$_3$ sample was less resistant to the reaction atmosphere. The effect of WGHSV (i.e., 60,000–600,000 mL·g$^{-1}$·h$^{-1}$) was also studied for these two catalysts showing a gradual shift of the NO conversion profiles to higher temperatures upon increasing space velocity for both catalysts.

**Figure 15.** NO conversion over La$_x$Ce$_{1-x}$FeO$_3$ perovskites during the NO reduction by CO: NO conversion versus temperature from 100 to 500 °C (a), and corresponding N$_2$-selectivities (b) using 400 ppm NO/500 ppm CO/He balance at 1 bar and GHSV of 24,000 h$^{-1}$; NO conversion versus time of La$_x$Ce$_{1-x}$FeO$_3$ catalysts at 500 °C with 100 ppm SO$_2$ in the feed (c); NO conversion versus temperature of La$_x$Ce$_{1-x}$FeO$_3$ catalysts in CO + NO reaction with the addition of 100 ppm SO$_2$, 3% O$_2$ and 3 vol.% H$_2$O in the feed (d). (1): LaFeO$_3$, (2): La$_{0.8}$Ce$_{0.2}$FeO$_3$, (3): La$_{0.6}$Ce$_{0.4}$FeO$_3$, (4): La$_{0.4}$Ce$_{0.6}$FeO$_3$, (5): La$_{0.2}$Ce$_{0.8}$FeO$_3$, and (6): CeO$_2$. Reproduced with permission from Ref. [90]. Copyright 2016, Elsevier.
The sulfur and H$_2$O resistance capacity of the optimal LaCu$_{0.5}$Mn$_{0.5}$O$_3$ catalyst was also probed during time-on-stream experiments at a constant temperature in which 10% H$_2$O or 1000 ppm SO$_2$ or even 10% H$_2$O + 1000 ppm SO$_2$ was co-fed with the flowing NO + CO gas mixture (Figure 16) [91]. As can be seen, the addition of H$_2$O led to an about 16% drop in NO conversion which then maintained approximately constant. When H$_2$O was removed from the feed, the catalytic performance was only partially restored. The effects of inhibition/recovery on catalytic behavior due to the introduction/removal of SO$_2$ into the feed stream were qualitatively similar to those of H$_2$O but more pronounced, and become even more intense when both SO$_2$ and H$_2$O are fed (Figure 16). An increase of the temperature from 300 to 400 °C was needed to lead to a complete restoration of catalytic activity after removal of the inhibitors from the feed stream, regardless of their identity. That said, this Cu-containing perovskite catalyst could be considered a fairly good sulfur and H$_2$O resistant material. In situ DRIFTS experiments enabled the authors to suggest an Eley–Rideal reaction mechanism (Figure 17) which adequately describes their findings. As shown in Figure 17, introducing NO and CO at ambient temperature can lead to the attachment of NO molecules onto the perovskite, covering the active sites indicated in the figure. Therefore, some nitrates and nitrate-like species may be formed on the perovskite’s surface inhibiting the adsorption of CO molecules. Below 200 °C, the adsorbed NO species may react with CO to form N$_2$, N$_2$O, and CO$_2$, as corroborated by both in situ DRIFTS measurements and catalytic runs under a real reaction atmosphere. Above 200 °C, the desorption, dissociation, and conversion of NO species can be observed to form N$_2$O and N$_2$ (i.e., NO → [N] + [O], NO + [N] → N$_2$O, [N] + [N] → N$_2$).

The sulfur and H$_2$O resistance capacity of the optimal LaCu$_{0.5}$Mn$_{0.5}$O$_3$ catalyst was also probed during time-on-stream experiments at a constant temperature in which 10% H$_2$O or 1000 ppm SO$_2$ or even 10% H$_2$O + 1000 ppm SO$_2$ was co-fed with the flowing NO + CO gas mixture (Figure 16) [91]. As can be seen, the addition of H$_2$O led to an about 16% drop in NO conversion which then maintained approximately constant. When H$_2$O was removed from the feed, the catalytic performance was only partially restored. The effects of inhibition/recovery on catalytic behavior due to the introduction/removal of SO$_2$ into the feed stream were qualitatively similar to those of H$_2$O but more pronounced, and become even more intense when both SO$_2$ and H$_2$O are fed (Figure 16). An increase of the temperature from 300 to 400 °C was needed to lead to a complete restoration of catalytic activity after removal of the inhibitors from the feed stream, regardless of their identity. That said, this Cu-containing perovskite catalyst could be considered a fairly good sulfur and H$_2$O resistant material. In situ DRIFTS experiments enabled the authors to suggest an Eley–Rideal reaction mechanism (Figure 17) which adequately describes their findings. As shown in Figure 17, introducing NO and CO at ambient temperature can lead to the attachment of NO molecules onto the perovskite, covering the active sites indicated in the figure. Therefore, some nitrates and nitrate-like species may be formed on the perovskite’s surface inhibiting the adsorption of CO molecules. Below 200 °C, the adsorbed NO species may react with CO to form N$_2$, N$_2$O, and CO$_2$, as corroborated by both in situ DRIFTS measurements and catalytic runs under a real reaction atmosphere. Above 200 °C, the desorption, dissociation, and conversion of NO species can be observed to form N$_2$O and N$_2$ (i.e., NO → [N] + [O], NO + [N] → N$_2$O, [N] + [N] → N$_2$).
Figure 16. The NO conversions over LaCu_{0.5}Mn_{0.5}O_3 catalyst upon adding different reaction inhibiting substances (10% H_2O/1000 ppm SO_2 and 10 % H_2O + 1000 ppm SO_2) in the NO + CO reactor feed stream. Reproduced with permission from Ref. [91]. Copyright 2020, Elsevier.

Figure 17. The mechanism of catalytic reduction NO by CO on LaCu_{0.5}Mn_{0.5}O_3 perovskites. Reproduced with permission from Ref. [91]. Copyright 2020, Elsevier.

In a different study, using the same preparation method (sol–gel) the research group also prepared a LaCu_{0.25}Co_{0.75}O_3 (LCC) perovskite to study the effect of calcination temperature (250, 500, 750, and 1000 °C) on its catalytic performance for NO + CO reaction tested in a feed composition of 10% CO/5% NO/Ar balance at WGSV = 60,000 mL·g^{-1}·h^{-1} and temperature range between 100–600 °C [92]. Regarding the NO and CO conversion efficiency, the LCC-750 > LCC-500 > LCC-250 > LCC-1000 sequence was found, with the outperformed LCC-750 sample to achieve complete NO and 50% CO conversions at ~350 °C, and 100% selectivity toward N_2 at ~400 °C. The authors concluded that the ratio of Cu^+/Cu^2+ and Co^{2+}/(Co^{2+} + Co^{3+}), the reducibility, and amount of oxygen deficiencies were the key points for the enhancement catalytic behavior observed. Indeed, maximum values of all these ratios and properties were measured on the outperformed LCR-750 catalyst (Figure 18).
Figure 18. The surface element distribution of LCC-x (x = 250, 500, 750 and 1000 °C) perovskites calcined at different temperatures. O’ and O” are bulk and chemically absorbed oxygen, respectively; O’ is connected with the redox capacity of the catalysts, and the proportion of O” is closely linked to the quantity of oxygen deficiency in catalysts. Data were taken with permission from Ref. [92]. Copyright 2019, Elsevier.

In yet another study, the same group reported the effect of B-site partial substitution of a La$_{0.8}$Ce$_{0.2}$M$_{0.25}$Co$_{0.75}$O$_3$ (M = Fe, Mn, Cu) perovskite on NO reduction by CO [93]. The preparation method and reaction conditions used were similar as above. It was found that the addition of all Fe, Mn, and Cu on the bare La$_{0.8}$Ce$_{0.2}$CoO$_3$ perovskite was beneficial to its NO reduction activity; however, the Cu-substituted La$_{0.8}$Ce$_{0.2}$Cu$_{0.25}$Co$_{0.75}$O$_3$ perovskite outperformed all the other samples on both activity and N$_2$ selectivity. In terms of maximum achievements, the Cu-substituted perovskite showed 100% NO conversion, 50% CO conversion, and 99% N$_2$ selectivity at ~300 °C. This catalyst has also been found to be substantially more stable in 48-h time-on-stream performance; a slight (82% → 80.3%) compared to a significant (58.8% → 43.6%) degradation of NO conversion activity was recorded for La$_{0.8}$Ce$_{0.2}$Cu$_{0.25}$Co$_{0.75}$O$_3$ and La$_{0.8}$Ce$_{0.2}$CoO$_3$, respectively. The performance superiority of La$_{0.8}$Ce$_{0.2}$Cu$_{0.25}$Co$_{0.75}$O$_3$ was attributed to the enhanced amount of O$_2$ vacancies, texture properties, and reducibility, while the NO + CO reaction kinetics appeared to comply with the Eley–Rideal mechanism [93].

Moreover, the same group also studied a series of LaNi$_{0.5}$M$_{0.5}$O$_3$ (M = Co, Mn, Cu) perovskites using again a NO + CO feed with excess CO (i.e., 5% NO/10% CO/85% He at WGHSV = 36,000 mL·g$^{-1}$·h$^{-1}$) [94]. Results illustrated that the partial (50 mol%) substitution of Ni with Co, Mn, or Cu in LaNiO$_3$ had in all cases a positive effect on its catalytic activity, with Cu-substituted LaNi$_{0.5}$Cu$_{0.5}$O$_3$ perovskite outperforming all others in N$_2$
selectivity at temperatures > 250 °C. In situ DRIFTS experiments enabled the authors to propose a Langmuir–Hinshelwood mechanism for the NO reduction by CO on this series of perovskites as schematically shown in Figure 19, exemplified for LaNi₀.₅Cu₀.₅O₃ perovskite [94]. According to the mechanism, at low temperatures (50–150 °C) NO is preferentially adsorbed on the active sites of the perovskite surface forming nitrates, which can be gradually desorbed and react with gaseous CO forming small amounts of N₂O, N₂, and CO₂. In the temperature region 150–250 °C, Cu²⁺ is reduced to Cu⁺ providing sites for CO chemisorption that produce some carbonate and carboxylate species. At the same time, surface oxygen vacancies can activate NO dissociative adsorption and facilitate N₂O decomposition. The as derived dissociative products can further react with adsorbed CO forming CO₂ and N₂O. For high temperatures (ca. 250 °C and higher) chemisorbed O species began to desorb regenerating oxygen vacancy sites. The increased availability of the latter sites further facilitates NO and N₂O dissociation. Then Cu²⁺ sites can be regenerated via Ni³⁺ + Cu⁺ ↔ Ni²⁺ + Cu²⁺, and Cu⁺ also can be oxidized by N₂O to Cu²⁺ leading to N₂O conversion toward N₂ (Figure 19) [94].

Figure 19. Reaction mechanism for the catalytic reduction of NO by CO on LaNi₀.₅Cu₀.₅O₃ perovskites. Reproduced with permission from Ref. [94]. Copyright 2019, Elsevier.
Tarjomannejad et al. [95] prepared via a sol–gel method LaMn$_{1-x}$Fe$_x$O$_3$ (x = 0, 0.3, 0.5, 0.7, 1) and La$_{0.8}$Mn$_{0.2}$Mn$_{0.3}$Fe$_{0.7}$O$_3$ (M = Ce, Ba, Cs, Sr) perovskites to evaluate their performance in catalytic reduction of NO by CO under a 3000 ppm NO/3000 ppm CO/Ar balance gas feed at a WGHSV = 12,000 mL·g$^{-1}$·h$^{-1}$ in the temperature range between 150 and 500 °C. The catalysts under consideration were characterized using SEM, H$_2$-TPR, XPS, BET, and XRD techniques. Results showed that the LaMn$_{0.3}$Fe$_{0.7}$O$_3$ catalyst exhibited the highest catalytic activity when compared to the other catalysts of the LaMn$_{1-x}$Fe$_x$O$_3$ group. In particular, the catalytic activity of this group followed the order LaMn$_{0.3}$Fe$_{0.7}$O$_3$ < LaFeO$_3$ < LaMn$_{0.3}$Fe$_{0.5}$O$_3$ < LaMn$_{0.5}$Fe$_{0.5}$O$_3$ < LaMn$_{0.3}$Fe$_{0.7}$O$_3$. It was reported that the partial substitution of Mn by Fe in the perovskite led to the formation of O$_{2}$ vacancies promoting the catalyst’s reducibility. The introduction of a small amount of Ce, Sr, Cs into the A-site of the perovskite had a beneficial effect on catalytic performance. In contrast, partial substitution of La by Ba compromised the catalyst’s activity. On this basis the catalytic activity followed the order La$_{0.8}$Ba$_{0.2}$Mn$_{0.3}$Fe$_{0.7}$O$_3$ < LaMn$_{0.3}$Fe$_{0.7}$O$_3$ < La$_{0.8}$Cs$_{0.2}$Mn$_{0.3}$O$_3$ < La$_{0.8}$Sr$_{0.2}$Mn$_{0.3}$Fe$_{0.7}$O$_3$. The authors concluded that the enhanced activity of the best and second-best catalyst (obtained by substitution of La by Ce$^{4+}$ and Sr$^{2+}$ in the A-site) was due to the induced chances in the reducibility of B-site cations, Mn$^{4+}$/Mn$^{3+}$, and Fe$^{4+}$/Fe$^{3+}$ ratios, and increase the O$_{ads}$/O$_{latt}$ ratio, factors that increase the number of structural defects in the perovskite structure. In an additional publication of the research group [35], LaCu$_{0.7}$Ba$_{0.3}$O$_3$ (B = Mn, Fe, Co) perovskites were synthesized and comparatively evaluated in NO + CO reaction using stoichiometric conditions (3000 ppm NO/3000 ppm CO/Ar balance at WGHSV = 12,000 mL·g$^{-1}$·h$^{-1}$ and temperatures between 100 and 450 °C). The catalytic activity for the LaFe$_{0.5}$Mn$_{0.5}$O$_3$ group followed the order LaFeCo < LaFe < LaFeCu < LaFeMn. The catalytic activity for the LaMn$_{0.3}$Mn$_{0.7}$O$_3$ group followed the order LaMn < LaMnCo < LaMnFe < LaMnCu. Among all the samples tested (both series) the optimal behavior overall was that of LaMn$_{0.3}$Cu$_{0.7}$O$_3$. It was associated with a synergistic interaction between Mn and Cu, higher reducibility at low temperatures, and an increased number of structural defects. The authors also examined three different mechanisms for the NO reduction by CO. Among them, the Langmuir–Hinshelwood model was found to be more suitable for describing the kinetic data obtained. More specifically, the proposed mechanism is that described by the following reaction steps (R.1)–(R.6), which is similar to that reported for noble metal catalyzed NO + CO reaction [97,98].

\[
\begin{align*}
\text{NO} + \ast & \rightarrow \text{NO}^* \\
\text{CO} + \ast & \rightarrow \text{CO}^* \\
\text{NO}^* + \ast & \rightarrow \text{N}^* + \text{O}^* \\
\text{N}^* + \ast & \rightarrow \text{N}_2 + 2\ast \\
\text{N}^* + \text{NO}^* & \rightarrow \text{N}_2\text{O} + 2\ast \\
\text{CO}^* + \text{O}^* & \rightarrow \text{CO}_2 + 2\ast
\end{align*}
\]

De Lima et al. [99] prepared LaFe$_{1-x}$Co$_x$O$_3$ perovskites, namely LaFeO$_3$ and LaFe$_{0.6}$Co$_{0.4}$O$_3$, synthesized either conventionally (by the citrate method) or using a nanocasting method; the latter leads to materials constituted by more than 97 wt% of perovskite phase and by agglomerates smaller than 100 nm constituted by crystallites of about 6 nm (Figure 20). As a result, the nanocast perovskites had about 10 times larger specific surface areas compared
to the conventional perovskites (e.g., 49.3 and 30.5 vs. 5.6 and 3.6 m$^2$/g for the nanocast and conventional LaFeO$_3$ and LaFe$_{0.6}$Co$_{0.4}$O$_3$ perovskites, respectively). These materials were comparatively evaluated in the reduction of NO by CO. Figure 21 shows the results of this comparison. Obviously, the nanocast perovskites are significantly more active than their conventional counterparts, and as the authors conclude this is mainly due to the higher specific surface area of the former and the consequent higher number of accessible active sites exposed to the reactants.

*Figure 20.* TEM images of LaFeO$_3$ (a) and LaFe$_{0.6}$Co$_{0.4}$O$_3$ (b) prepared by a nanocast method. Reproduced with permission from Ref. [99]. Copyright 2009, Elsevier.

Finally, aiming at three-way catalysis (TWC), Glisenti et al. [59] prepared largely Cu-doped LaCo$_{1-x}$Cu$_x$O$_3$ (x = 0, 0.1, 0.3, and 0.5) perovskites by means of the citrate method and tested these materials in model reactions involved in TWC (i.e., NO + CO and CO + O$_2$) as well as at simulated automotive exhaust conditions. Regarding the NO + CO model reaction the feed gas composition comprised of 4% CO/4% NO/Ar balance at 1 bar with a WGSHe = 150,000 mL·g$^{-1}$·h$^{-1}$. The catalysts under consideration were characterized by a variety of techniques. XRD results corroborated for a stable perovskite phase holding a rhombohedral geometry with the crystallite size to be decreased upon increasing the copper amount. XPS results suggested that the addition of Cu caused the decrease of Co(III) → Co(II) → Co(0) reduction temperatures, as a result of H$_2$ activation. This H$_2$ activation can be assigned to the surface segregated Cu clusters and to the increased O$_2$ mobility because of the formation of vacancies. Regarding the catalytic performance of the materials in NO reduction by CO, it has been shown that the introduction of Cu into the LaCoO$_3$ structure was beneficial as almost complete NO and CO conversions were achieved at 400 °C. Specifically, the catalytic activity of the samples followed the order LaCoO$_3$ < LaCo$_{0.9}$Cu$_{0.1}$O$_3$ < LaCo$_{0.7}$Cu$_{0.3}$O$_3$ < LaCo$_{0.5}$Cu$_{0.5}$O$_3$. That is the perovskite with the highest Cu doping outperformed the other samples (Figure 22); notably, N$_2$ was the main N-containing reaction product [59].
Figure 21. Temperature profiles for the conversion of NO to N\(_2\) (○, ●) and CO to CO\(_2\) (△, ▲) on: (a) uncast LaFeO\(_3\) (○, △) and nanocast LaFeO\(_3\) (●, ▲). Inset: conversion of NO to N\(_2\) (○) and CO to CO\(_2\) (△) without any catalyst; (b) uncast LaFe\(_{0.6}\)Co\(_{0.4}\)O\(_3\) (○, △) and nanocast LaFe\(_{0.6}\)Co\(_{0.4}\)O\(_3\) (●, ▲). Reproduced with permission from Ref. [99]. Copyright 2009, Elsevier.
Figure 22. CO (a) and NO (b) conversion as a function of temperature on LaCo$_{0.5}$Cu$_{0.5}$O$_3$, LaCo$_{0.7}$Cu$_{0.3}$O$_3$, LaCo$_{0.9}$Cu$_{0.1}$O$_3$, and LaCoO$_3$ perovskites. Conditions: 4% NO/4% CO/balance He at 1 bar; WGHSV = 150,000 mL·g$^{-1}$·h$^{-1}$. Reproduced with permission from Ref. [59]. Copyright 2016, Elsevier.

As in the previous sections, we constructed Table 3 here, comparing the aforementioned results (and some additional ones) from the literature on NO reduction by CO using perovskite catalysts, even though, as mentioned at the beginning of the section, literature on the selective catalytic reduction (i.e., in excess of O$_2$) of NO$_x$ by CO is rather rare. For comparison, the table also includes some representative results on the titled reaction catalyzed by NM-based catalysts.
Table 3. Representative literature for NO reduction by CO over perovskites and on transitional noble metal catalysts.

| Catalyst | Reaction Conditions | Achievements | Ref. |
|----------|---------------------|--------------|------|
|          | NO (%) | CO (%) | O₂ (%) | Other (%) | WGSHEV (mL/g·h) | XNO (%) | at T (°C) | max. SN₂ (%) |
| Perovskite catalysts | | | | | | | | |
| La₀.₆Ce₀.₄FeO₃ (a) | 0.04 | 0.05 | - | - | 24,000 h⁻¹ (GHSV) | >50 (max. 88) | 350–500 | 90 (at 350) | [90] |
| La₀.₆Ce₀.₄FeO₃ (a) | 0.04 | 0.05 | - | 0.01 (SO₂) | 24,000 h⁻¹ (GHSV) | 76 | 500 | n/a | [90] |
| La₀.₆Ce₀.₄FeO₃ (a) | 0.04 | 0.05 | 3 | 0.01 (SO₂) + 3 (H₂O) | 24,000 h⁻¹ (GHSV) | >50 (max. 74) | 350–500 | n/a | [90] |
| LaₐCu₀.₅Mn₀.₅O₃ (b) | 5 | 10 | - | - | 60,000 | 100 | 300–600 | 100 | [91] |
| LaₐCu₀.₂₅Co₀.₇₅O₃ (c) | -750 | 5 | 10 | - | 60,000 | 100 | 290–600 | 100 | [92] |
| Laₐ₀.₈Ce₀.₂Cu₀.₂₅Co₀.₇₅O₃ (d) | 5 | 10 | - | - | 60,000 | 100 | 300–600 | 100 | [93] |
| LaₐNi₀.₅Cu₀.₅O₃ (e) | 5 | 10 | - | - | 36,000 | 100 | 375–500 | 100 (at 450 °C) | [94] |
| LaₐMn₂₃Fe₇O₃₋₁₊O₃ (f) | 0.3 | 0.3 | - | - | 12,000 h⁻¹ (GHSV) | 90–100 | 390–450 | 90–100 | [95] |
| Laₐ₀.₆Co₀.₄Fe₃Mn₀.₃O₃ (g) | 0.3 | 0.3 | - | - | 12,000 h⁻¹ (GHSV) | 90–100 | 340–450 | 90–96 | [95] |
| Laₐ₀.₈Co₀.₂₅Fe₇Mn₀.₃O₃ (h) | 0.3 | 0.3 | - | - | 12,000 h⁻¹ (GHSV) | 90–100 | 420–450 | 90–98 | [95] |
| LaₐₐFe₈₃Mn₇₃O₃₋₁₋₇O₃ (i) | 0.3 | 0.3 | - | - | 12,000 h⁻¹ (GHSV) | 90–100 | 400–450 | 90–98 | [95] |
| LaFe₃O₇-nanocast | 0.5 | 0.5 | - | - | 30,000 | 100 | 375–700 | 100 | [99] |
| LaFe₃O₇-uncast | 0.5 | 0.5 | - | - | 30,000 | 100 | 600–700 | 100 | [99] |
| Laₐ₀.₆Co₀.₄O₂-nanocast | 0.5 | 0.5 | - | - | 30,000 | 100 | 550–700 | 100 | [99] |
| LaFe₃O₇-Co₉O₃-uncast | 0.5 | 0.5 | - | - | 30,000 | 100 | 650–700 | 100 | [99] |
| Laₐ₀.₈Co₉O₃ (l) | 4 | 4 | - | - | 150,000 | 95 | 400 | n/a | [59] |
| LaₐₐCu₀.₅Co₀.₅O₃ (l) | 0.3 | 0.3 | - | - | 12,000 h⁻¹ (GHSV) | >90 | 360–450 | n/a | [35] |
| LaₐₐSn₀.₃₃Cu₀.₇₇Mn₀.₃O₃ (l) | 0.3 | 0.3 | - | - | 12,000 h⁻¹ (GHSV) | >90 | 320–450 | n/a | [35] |
| Laₐ₀.₆Ce₀.₄FeO₃ (m) | 2 | 2 | - | - | 30,000 | >90 | 330–500 | n/a | [64] |
| LaMnO₃ (r); LaFeO₃ (r) | 2 | 2 | - | - | 30,000 | >90 | 420–500 | n/a | [100] |
| LaMnO₃ (n) | 2 | 2 | - | - | 30,000 | >90 | 510–570 | 100 | [101] |
Table 3. Cont.

| Catalyst | Reaction Conditions | Achievements | Ref. |
|----------|---------------------|--------------|------|
|          | NO (%) | CO (%) | O₂ (%) | Other (%) | WGS (mL/g·h) | X₇NO (%) | at T (°C) | max. S₅N₂ (%) |
| Conventional, supported on oxide supports, NM catalysts |
| 0.5wt%Pt/γ-Al₂O₃ | 0.05 | 0.4 | 5 | - | 120,000 | 26 | 250 | 80 | [87] |
| 0.5wt%Pd/γ-Al₂O₃ | 0.05 | 0.4 | 5 | - | 120,000 | 13 | 180 | 62 | [87] |
| 0.5wt%Pt(9.7%Rb)/γ-Al₂O₃ | 0.1 | 0.1 | - | - | 600,000 | >90 | 320−500 | 100 (at 350 °C) | [102] |
| 0.5wt%Rh/γ-Al₂O₃ | 0.1 | 0.1 | - | - | 600,000 | >90 | 250−500 | 100 (at 300 °C) | [102] |

(a) The optimal from a series of LaₓCe₁−ₓFeO₃ (x = 0.2, 0.4, 0.6, 0.8, 1) perovskites investigated. (b) The optimal from a series of LaₓM₀.5MnₓO₃ (M = Cu, Co, Fe, Ni, Cr) perovskites investigated. (c) The optimal from a series of B-site partially substituted LaₓCu₀.5CoₓMn₀.5O₃ (M = Fe, Mn, Cu) perovskites investigated. (d) The optimal from a series of LaNiₓM₂O₃ (M = Co, Mn, Cu) perovskites investigated. (e) The optimal from a series of LaCuₓMnₓO₃ (M = Ce, Ba, Cs, Sr) perovskites investigated. (f) The optimal from a series of LaMnₓFeₓO₃ (M = Fe, Mn, Co) perovskites investigated. (g) The optimal from a series of LaNiₓM₂O₃ (M = Co, Mn, Cu) perovskites investigated. (h) The optimal from a series of LaMnₓFeₓO₃ (M = Fe, Mn, Co) perovskites investigated. (i) The optimal from a series of LaMnₓFeₓO₃ (M = Fe, Mn, Co) perovskites investigated. (j) The optimal from a series of LaCuₓMnₓO₃ (M = Cu, Co, Fe, Ni) perovskites investigated. (k) The optimal from a series of LaCuₓMnₓO₃ (M = Ni, Mn, Co) perovskites investigated. (l) The optimal from a series of LaCuₓMnₓO₃ (M = Fe, Mn, Co) perovskites investigated. (m) The optimal from a series of LaCuₓMnₓO₃ (M = Fe, Mn, Co) perovskites investigated. * Materials prepared by a microemulsion method in the reverse (r) state. (o) The optimal from a series of LaₓSr₁−ₓMnO₃ perovskites investigated.
3. General Outcomes and Future Perspectives

This work reviews the literature that concerns the use of perovskites and perovskite-based catalysts in the selective catalytic reduction (SCR) of NO\textsubscript{x} with different than the typically used NH\textsubscript{3} or urea reducing agents, i.e., C\textsubscript{x}H\textsubscript{y}/C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}, H\textsubscript{2}, and CO. The main purpose of this undertaking is to present the state-of-the-art in the field, which could help industry and academia become aware of new possibilities and perspectives in order to meet future requirements in addressing NO\textsubscript{x} emissions.

The urgency of developing efficient approaches for NO\textsubscript{x} emission control in order to meet increasingly stringent environmental requirements is widely accepted. Significant downsides are associated with low NO\textsubscript{x} concentration and excess oxygen in the exhaust gas, conditions under which the competitive role of dioxygen in the oxidation of reducing agents to the detriment of NO\textsubscript{x} reducing reactions to harmless N\textsubscript{2} is major. During SCR of NO\textsubscript{x}, several catalysts and conditions can also favor N\textsubscript{2}O production which has undesirable high global warming potential and is also the main current cause of ozone depletion in the stratosphere. To this date N\textsubscript{2}O emissions are not actually regulated by the EU, however, this matter will definitely be of future interest. That said the development of selective catalytic systems to reduce NO\textsubscript{x} emissions while using low-cost, non-noble metal-containing, catalytic systems is of great importance. Perovskite-based catalysts appear to be potential candidates for this purpose.

The easiness of substituting A and B-sites in ABO\textsubscript{3} and A\textsubscript{2}BO\textsubscript{4} perovskite formulas with rare earth metals, alkali, or alkaline earth elements (at A-sites), and transition metals from the 3d, 4d, or 5d configuration (at B-sites), endows them with a variety of different active sites capable of facilitating the adsorption of the reactants on different sites, thus eliminating the catalytic rate inhibitory competitive adsorption of reactants on the same sites.

Several papers have been published on perovskite-catalyzed C\textsubscript{x}H\textsubscript{y}/C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}-, H\textsubscript{2}-, and CO-SCR of NO\textsubscript{x}. Most of these involved H\textsubscript{2}-SCR, a few C\textsubscript{x}H\textsubscript{y}/C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}-SCR, and almost none CO-SCR. Representative cases of these works were analyzed in detail in this review and the achievements were presented comparatively in three comprehensive tables at the end of each respective section. For the sake of further convenience of comparison, the tables also include some results from NM-based catalysts applied under similar SCR conditions.

General conclusions that can be drawn and the corresponding perspectives are as follows:

- The SCR of NO\textsubscript{x} behavior of perovskites (both in activity and N\textsubscript{2}-selectivity) is comparable, if not better (especially at low temperatures) to that of NM-based catalysts. Their time-on-stream stability and SO\textsubscript{2} tolerance are also remarkable.
- The partial replacement of A and/or B-sites with other suitable elements allows a significant improvement and controlled optimization of their SCR performance. For example, partially substituted with Cu perovskites were found to be significantly more active in comparison with the bare sample, due to the additional effect of the advantageous in catalysis Cu\textsuperscript{2+}/Cu\textsuperscript{+} redox couple.
- Preparation methods capable of providing perovskites with a larger specific surface area are particularly advantageous due to the increased number of accessible active sites exposed to the reaction mixture. The typical specific surface of perovskites produced by traditional methods ranges between 5 and 20 m\textsuperscript{2}·g\textsuperscript{-1}. Advanced or modified classical methods have been reported which can raise these values by two or even three times resulting in a significant catalytic benefit during SCR of NO\textsubscript{x}. 
Currently, significant efforts have been put to synthesize perovskites with surface areas as high as 100 m²·g⁻¹.

- Extensive characterizations of the synthesized perovskite materials that were frequently applied allowed the researchers to better understand the reaction pathways, the nature, and the role of the active sites, thus extracting relatively reliable morphology–activity correlations. However, apart from the in situ DRIFTS studies, no other operando techniques such as in situ XRD and in situ TEM were found to have been applied to the studies included herein. In light of such shortcomings, the frequent borrowing of reaction mechanisms from those proposed for analogous NM-based systems is justified. However, the use of perovskites in the SCR process is more likely to introduce new, easier reaction pathways that need to be in-depth understood in order to proceed with a coordinated optimization of perovskite composition for the SCR of NOₓ. At the same time, DFT calculations that are generally missing from the documents included herein can be particularly helpful in the above objectives.

- On the other hand, modern approaches in catalysis have emerged following the pioneering work of the Hamada team [50] on what is now described as “exsolution” that offers new perspectives on the use of perovskites. The creation of different kinds of alloy or metal particles at nano or even atomic sizes on the surface of perovskites may provide the chance of tailoring the local surface properties and metal–support interactions, leading to enhanced performance. The active interfaces generated by the exsolution process can also result in higher activity and stability for this type of catalyst. The method could provide effective solutions in the field of SCR of NOₓ as well. Due to the recency of the discovery, applications focused on the specific topic of this review have not yet been found (the work of Hamada and co-workers was implemented in TWC conditions). We could assume that the exsolution concept will be an intense research approach in the coming years on NOₓ abatement under lean conditions.

It is obvious from the above that there is significant free space and many degrees of freedom for object research, which can bring significant environmental benefits and value. Perovskites as materials show unique handling properties and tailoring them through their composition could optimize SCR of NOₓ. They are thermally stable, rather tolerant of poisons, and above all seem to work adequately with all possible reducing agents considered herein.

The specialized properties of perovskites, such as multiple types of active centers including surface oxygen vacancies, as well as labile lattice oxygen and mobile O²⁻ ions are particularly useful in catalysis. According to recent discoveries, these properties can play multiple roles as reaction promoters and as stabilizers of dispersed catalyst nanoparticles providing catalysts with high anti-sintering characteristics [26–30].

Even though the total exclusion of precious metals in catalytic processes seems unrealistic in the short run, combined use of both may provide substantial technological advantages. Based on the significant research carried out in this field, it can be argued that perovskites can serve as suitable active supports for precious metals, allowing both the reduction of noble metal loadings and the extension of their lifetime, bearing in mind the issues mentioned in the above paragraph.

As has been shown, the deNOₓ efficacy of perovskites is remarkable for all the reducing agents considered herein. This provides additional practical benefits and alternatives. We believe that the involvement of perovskites in SCR of NOₓ could further expand the Environmental Catalysis Society’s potential for a cleaner environment, although catalysis has virtually unlimited outlets. More efforts are needed in fundamental and application studies for deNOₓ processes catalyzed by perovskites to fully enhance their potential in the field—there is ample open space for promising research and development on the subject.

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**Abbreviations**

- **BET** Brunauer, Emmett and Teller
- **CBM** Coal Bed Methane
- **DFT** Density Functional Theory
- **DLS** Dynamic Light Scattering
- **DRIFTS** Diffuse Reflectance Infrared Fourier Transform Spectroscopy
- **DSC** Differential Scanning Calorimetry
- **EDS** Energy-Dispersive X-ray Spectroscopy
- **EF-TEM** Energy Filtering Transmission Electron Microscopy
- **FE-SEM** Field Emission Scanning Electron Microscopy
- **FTIR** Fourier Transform Infrared Spectroscopy
- **HCs** Hydrocarbons
- **ICP-AES** Inductively Coupled Plasma Atomic Emission Spectroscopy
- **ICP-OES** Inductively Coupled Plasma Optical Emission Spectroscopy
- **PM** Particulate Matter
- **SCR** Selective Catalytic Reduction
- **SEM** Scanning Electron Microscopy
- **TEM** Transmission Electron Microscopy
- **TPD** Temperature-Programmed Desorption
- **TPR** Temperature-Programmed Reduction
- **TWC** Three-Way Catalysts
- **WGHSV** Weight-basis Gas Hourly Space Velocity
- **XRD** X-ray Diffraction
- **XPS** X-ray Photoelectron Spectroscopy

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