

De-NO_x IN PEROVSKITE-TYPE MATERIALS

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ABSTRACT

Perovskite-type oxides have shown excellent catalytic properties, especially in the depollution of exhaust gases. These solids have a well-defined but also highly flexible crystalline structure represented by the general formula ABO_3 , where A: a cation of rare-earth, alkaline earth, alkali or ions with a large ionic radius and B a transition metal cation. By partial substitutions on A- and/or B-sites is possible a large variety of compounds with different compositions and features i.e. hosting of B cations in mixed oxidation states, generation of structural defects and oxygen vacancies. Such wide compositional flexibility is of great importance for heterogeneous catalysis as it is responsible for hard modifications of the catalytic properties of the material including the dissociative properties over NO_x.

INTRODUCTION

The fossil fuel derived power generation is producing emissions of environmentally unacceptable compounds. Such exhausts from mobile (automobiles, marine) and stationary sources i.e. power plants contain CO, NO_x and hydrocarbons. The conversion of these pollutants to CO₂, N₂ and H₂O using catalysts is a challenge. In the last decades several approaches including catalytic methods for denitrification of emissions have been studied and the results have been published in a number of papers and reviews [1, 2]. Nearly all known categories of catalysts have been tested: metal and metal-supported catalysts, monocrystals and mixed phases, oxides and mixed oxides, zeolites and heteropolyacids, alloys and amorphous alloys, membrane and monolithic catalysts, etc. Each case follows a different strategy due to the different ways of NO removal reactions.

In this work examples and an outline over perovskite application in catalytic de-NO_x methods is reported in particular H₂ and or CH₄ selective catalytic reduction.

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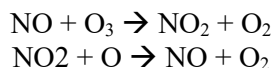
NO_x EMISSIONS

In EU air pollution emitted from sources such as traffic, industry and households is still above internationally agreed limits in many European countries, according to data published in June 2012 by European Environmental Agency (EEA). The accompanying report from the European Environment Agency (EEA) confirms an initial assessment published earlier in 2012, showing 12 EU Member States exceeded limits under the National Emissions Ceilings (NEC) Directive in 2010. This finding confirms an earlier assessment report [3]. According to EEA report:

- The reductions of NO_x from this sector over the last two decades have been lower than originally anticipated. This is partly because transport has grown more than expected, and partly because the real-world emissions from diesel vehicles are higher than those estimated when the vehicle emission limit standards were set.
- Spain was the only Member State to report exceeding three of its four emission ceilings (NO_x, NMVOC, NH₃), followed by Germany (NO_x, NMVOC) and Finland (NO_x, NH₃) with two exceedances each.

The EU also has emissions ceilings under the NEC Directive, one being the sum of the individual Member States' ceilings for each pollutant, while the second is a stricter, specific ceiling for the EU as a whole. Of these, the two EU ceilings for NO_x were both exceeded, albeit the first by only a small margin.

The NO_x play a crucial role in atmospheric chemistry by catalyzing ozone destruction via the following reactions:



These reactions are largely responsible for the ozone depletion [4]. Another adverse effect of NO_x is its contribution to acidification of ecosystems through acid rain and causing biological death of lakes and rivers.

According to biological studies NO acts as an essential messenger, responsible for the transmission of necessary information for i) the white blood cells to attack and destroy tumor cells and ii) to the neurotransmitters to dilate the blood vessels [5, 6]. On the other hand, the biologically active NO has a poisonous effect on the in vivo enzyme-catalyzed transformation of the amino acid, arginine. Inhaled NO is responsible for provoking both lung infections and respiratory allergies like bronchitis, pneumonia, etc. [7].

DENITRIFICATION OF GASEOUS EMISSIONS

From a thermodynamic point of view, the NO molecule is unstable even at 298 K and 1 atm. However the reaction is spin forbidden, and NO is kinetically stable. Thus, the high thermal stability of nitric oxide is due to its high energy of dissociation (153.3 kcal/mol) and to corresponding extremely low decomposition rates.

Additionally the reaction kinetics can not be influenced by pressure variations but reactions such as NO oxidation, its decomposition to N₂O and dimerization are. In the presence of a reductant, reactions lead to a strong decrease in the Gibbs free energy values. This explains that catalytic methods are used in NO_x abatement. Research in catalytic de-NO_x is extensive, and can be divided into four major paths of activities based on automobile and stationary sources.

- NO decomposition
- NO_x reduction by CO
- De-NO_x by H₂ and NH₃
- Selective catalytic reduction (SCR) of NO by H₂ or NH₃ or hydrocarbons (HC).

Extensive literature exists in all four de-NO_x paths [4]. Perovskite-type oxides have been investigated for catalytic converter applications in the aforementioned paths since the early 1970s [8]. However the more recent and the one with great potential and practical application is the SCR. NH₃-SCR is currently applied as state of art depollution technology in stationary sources but still with drawbacks. Of particular and more recent scientific interest is the H₂ and or HC selective catalytic reduction of NO as both exist in the exhaust or can be easily introduced in small amount needed [9, 10, 11].

PEROVSKITES

The term *perovskite*, was first introduced to describe the oxides CaTiO₃, a mineral that is named after a Russian mineralogist, Count Lev Aleksevich von Perovski. It was discovered in 1839 in the Achmatovsk Mine in the Nazyamskie Mountains of Southern Ural Mountains by Gustav Rose. Since then considerable attention has been drawn to the perovskite type oxides.

Perovskite, is now extensively referring to oxides with ABO₃ structure, and also to the oxides with A₂BO₄ structure. Perovskite solids have a well-defined but also highly flexible crystalline structure of the general formula ABO₃, where A: a cation of rare-earth, alkaline earth, alkali or ions with a large ionic radius and B a transition metal cation. In this structure, the B cation is 6-fold coordinated and the A cation is 12-fold coordinated with the oxygen anions. In some cases, carbides, nitrides, halides, and hydrides also have the ABO₃ structure but practically perovskite refers to the oxides compounds. By partial substitutions on A- and/or B-sites is possible a large variety of compounds with different compositions and features can be generated i.e. hosting of B cations in mixed oxidation states, generation of structural defects and oxygen vacancies. As the size of the elements vary across the periodic table it is impossible to maintain a cubic structure for all elements and still keep realistic bond lengths creating distortions (cation displacements, distortion or tilts of octahedra) hindering the structure from collapsing. This unique property of wide compositional flexibility is of great

importance for heterogeneous catalysis. It is responsible for hard modifications of the catalytic properties of the material including the dissociative ability over NO_x. As a measure of the deviation from the ideal situation, Goldschmidt [12.] introduced equation:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}, \quad (0.75 < t < 1.0)$$

For an ideal perovskite t is unity, but is also found for lower t -values. The ideal cubic perovskite structure appears in a few cases for t -values very close to 1 and at high temperatures. In most cases, different distortions of the perovskite structure appear.

Catalytic de-NO_x reactions require multifunctional catalysts with appropriate solid state, surface, and morphological properties. This is because in complex reactions systems such as H₂/NO/O₂ or HC/NO/O₂ and in most cases in the presence of H₂O the catalyst is required to have:

- ✓ ability for redox circles over the catalyst active sites
- ✓ availability of oxygen species
- ✓ adsorption / activation of NO
- ✓ activation of reducing agent (RA) e.g. HC, H₂
- ✓ selectivity in oxidation of activated RA species by activated NO_x species.

The broad diversity of properties that perovskite compounds exhibit is derived from flexibility in:

- *Composition*; as the great majority of the metallic elements of the Periodic Table are known to be stable in a perovskite type oxide structure or form multicomponent perovskites by partial substitution of cations in positions A and B,
- *Structure*; distorted structures with mixed oxidation states, structural defects and oxygen vacancies
- *Synthesis and nano/micro structural features*; nanoparticles, surface area, high thermal stability etc

Thus perovskite-type mixed metal oxides can be engineered to show excellent catalytic properties, in de-NO_x. Therefore they are considered as great candidates for substituting noble metals in catalytic materials for gas after treatment. However it has been observed that they can coexist with noble metals (e.g. Pt) in such catalytic systems by performing in a synergistic way i.e. as reactive supports. The catalytic de-NO_x performance in terms of activity and N₂ selectivity is enhanced even with lower noble metal loading for the catalyst.

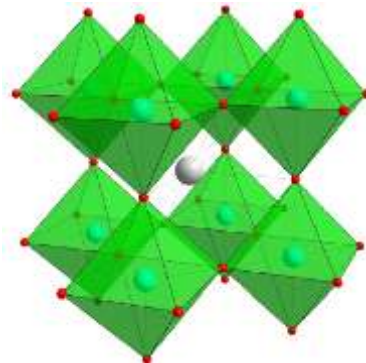


Figure 1. ABO₃ structure (Red: O, White: A, Green: B)

Table 1. The main characteristics of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ solids prepared by the ceramic and surfactant methods (Data from [11]).

Properties	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ Perovskite	
	LSF-1 (ceramic method)	LSF-2 (surfactant method)
BET (m^2/g)	3	33
XRD phases		
Main:	LaFeO_3 , SrFeO_{3-x} [13]	LaFeO_3 , SrFeO_{3-x}
Traces:	$\text{La}(\text{OH})_3$, Fe_2O_3 , LaSrFeO_4 , $\text{SrFe}_{12}\text{O}_{19}$	
% Fe phases (Mössbauer, 20K)	53% LaFeO_3 22% Fe_2O_3 25% SrFeO_{3-x} (14% Fe^{3+} , 11% Fe^{5+}), [52]	38% LaFeO_3 36% Fe_2O_3 26% SrFeO_{3-x}
XPS composition original	$\text{La}_{0.08}\text{Sr}_{0.02}\text{Fe}_{0.12}\text{O}_{0.78}$ $\text{O}_a:\text{O}_b:\text{O}_c^* = 1.61:1.41:1$ $\text{La}_a:\text{La}_b^* = 1.27$ $\text{Sr}_a:\text{Sr}_b:\text{Sr}_c^* = 2.7:1.36:1$	$\text{La}_{0.09}\text{Sr}_{0.02}\text{Fe}_{0.14}\text{O}_{0.75}$ $\text{O}_a:\text{O}_b^* = 0.61$ $\text{La}_a:\text{La}_b^* = 2.2$ $\text{Sr}_a:\text{Sr}_b^* = 0.41$
Ar^+ sputtered	$\text{La}_{0.1}\text{Sr}_{0.015}\text{Fe}_{0.21}\text{O}_{0.67}$ $\text{O}_a:\text{O}_b:\text{O}_c^* = 7.8:4:1$ $\text{La}_a:\text{La}_b^* = 2.7$ $\text{Sr}_a:\text{Sr}_b:\text{Sr}_c^* = 1.22:2.38:1$	$\text{La}_{0.14}\text{Sr}_{0.03}\text{Fe}_{0.2}\text{O}_{0.63}$ $\text{O}_a:\text{O}_b^* = 3.27$ $\text{Sr}_a:\text{Sr}_b^* = 0.51$

*: subscripts a,b,c denote different chemical oxidation states of the elements.

Perovskites LaCoO_3 , $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_{3-d}$, have been suggested as potential NO_x abatement catalyst for automobile exhaust control [14, 15]. The partial substitution of lanthanum and manganese to form mixed oxides $\text{La}_{1-x}\text{A}_x\text{Mn}_{1-y}\text{B}_y\text{O}_3$ and its effect on the catalytic activity was investigated. La^{3+} has been partially replaced by A^+ , A^{2+} , or A^{4+} ions in order to obtain Mn ions in various oxidation states or to create O₂ vacancies in the lattice, which can dissociate NO.

$\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ showed more selective NO reduction than LaMnO_3 [16]. Mn^{3+} was also partially substituted by other catalytically active transition metals, such as Cu^{2+} , leading to much higher activity for the CO + NO reaction [17].

The effect of preparation method

In a $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ perovskite oxide A site substitution stabilized iron in various oxidation states even in the unusual 5+ state [10]. The same material $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ prepared by an alternative method resulted in very different structural features (Table 1) in terms of surface area and crystallinity and consequently different catalytic behavior in CH₄ SCR and H₂ SCR. Details of the preparation procedure can be found elsewhere [11].

These two mixed oxides tested towards the NO/H₂/O₂ and NO/CH₄/O₂ lean-deNO_x reactions in the 200-450 °C range also in the presence of water. Significant differences in the composition of the bulk phases and the surface chemical states of

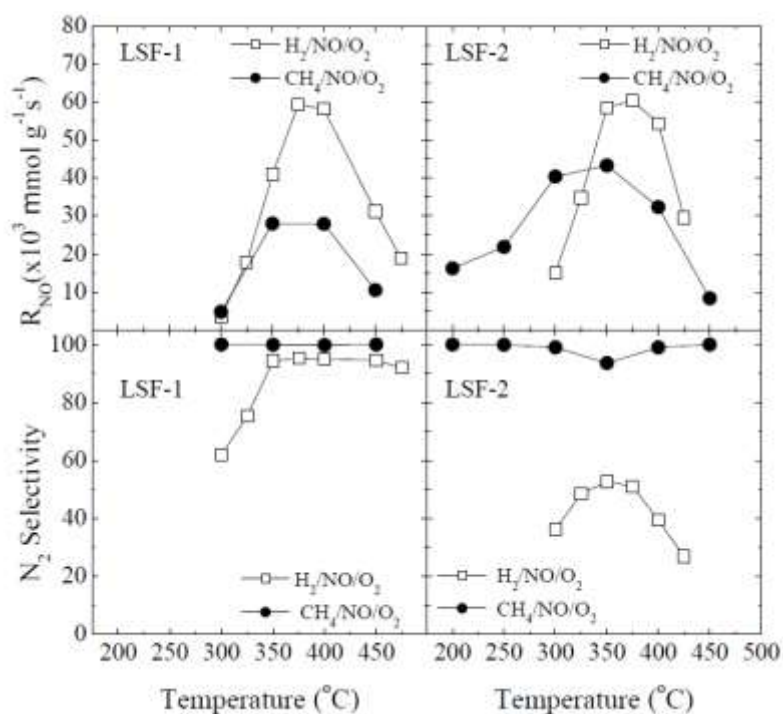


Figure 2. Temperature profiles of the rates of NO conversion and N₂ selectivity of the CH₄/NO/O₂ “lean-deNO_x” reaction (●) and H₂/NO/O₂ “lean-deNO_x” reaction (□) for LSF-1 and LSF-2 solids.

Reaction conditions:

CH₄=0.67 mol%, NO=0.5 mol%, O₂=5 mol%, W=0.5 g, GHSV=12000 h⁻¹

H₂=1 mol%, NO=0.5 mol%, O₂=10 mol%, W=0.5 g, GHSV=40000 h⁻¹

Fe, Sr and La were revealed among the two solids. The main crystal phases detected were perovskites LaFeO₃ and SrFeO_{3-x}, and α-Fe₂O₃.

For the CH₄ lean-deNO_x reaction at 350 °C, the La_{0.8}Sr_{0.2}FeO_{3-x} solid composition (LSF-2) prepared by the surfactant method exhibited an increase by 55% in the rate of NO conversion and by 30% in the rate of N₂ formation (per gram basis) as compared to the solid prepared by the ceramic method (LSF-1). An opposite relative catalytic activity behavior was observed for the two solids when tested towards the H₂ de-NO_x reaction. At 375 °C (maximum activity observed) the solid prepared by the ceramic method (LSF-1) exhibited an increase by 83% in the rate of N₂ formation as compared to the solid prepared by the surfactant method (LSF-2). The activity towards N₂ formation in H₂ de-NO_x reaction is greatly increased when charge disproportionation of iron species is observed, as in the case of the solid prepared by the ceramic method.

A perovskite-type phase of SrFe^{3+,5+}O_{3±0.5} containing iron in mixed oxidation states 3+ and 5+ was found for LSF-1. This phase shows impressive adsorptive and catalytic properties towards de-NO_x using CH₄ and H₂ due to their extensive ability for oxygen reversible adsorption. For the moment, the drawback of such materials is their low surface area due to the high temperatures employed during preparation

via the ceramic method. The wet chemical method employed organic gelating agents, although result in an increase of the surface area (a tenfold increase), seem to expose or form less active sites for the present CH₄ and H₂ de-NO_x reactions than the solid prepared by the ceramic method. No SrFe^{3+,5+}O_{3±0.5} phase was found. The prospect of developing such solids containing unusual mixed oxidation states is highly beneficial for the catalytic de-NO_x. It seems that the catalytic activity is much strongly affected by the “quality” of the catalytic surface, e.g. “site reactivity” rather than size of the area itself. Of course from a catalytic point of view interesting would be the preparation of catalytic materials with controlled high surface area and on the same token tailored mixed valence phases. It was suggested that the mobility of surface lattice oxygen, the concentration of oxygen vacant sites, and the mixed valences of metal cations present in the La_{0.8}Sr_{0.2}FeO_{3-x} solid were the main parameters that largely influenced the catalytic behavior observed over these two solids. These parameters influenced by the preparation method used.

The case of Pt over a perovskite support

Incorporating noble metals into a perovskite structure can stabilize the noble metal against sintering, reaction with the support, or volatilization. It was found that the perovskite La_{0.5}Ce_{0.5}MnO₃ exhibited a relatively low catalytic activity but the addition of 0.1 wt% Pt resulted in a catalyst showing high activity and N₂ selectivity for the H₂-SCR [10]. This was attributed to the oxygen vacancy sites of the support located next to the small Pt clusters that could provide the means for the formation of adsorbed NO with the N atom located on the Pt metal and the O atom on the oxygen vacancy.

Similar effect of Pt dispersion over a perovskite have been reported for a 0.1% Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ for the H₂ SCR. An overall excellent performance is observed in terms of activity, selectivity and stability has been reported for the case of 0.1% Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ [11].

A 0.1 wt% Pt supported on La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ solid (mixed oxide containing LaFeO₃, SrFeO_{3-x}, CeO₂, and Fe₂O₃ phases) has been studied for the NO/H₂/O₂ reaction in the 100–400°C range. For a critical comparison, 0.1 wt% Pt was supported on SiO₂, CeO₂, and Fe₂O₃ and tested under the same reaction conditions. For the Pt/ La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ catalyst a maximum in the NO conversion (83%) has been observed at 150°C with a N₂ selectivity value of 93%, while for the Pt/SiO₂ catalyst at 120°C (82% conversion) with a N₂ selectivity value of 65% using a GHSV of 80,000 h⁻¹.

Low N₂ selectivity values, were obtained with the Pt/CeO₂ and Pt/Fe₂O₃ catalysts. For the Pt/ La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ catalyst, addition of 5% H₂O in the feed stream at 140°C resulted in a widening of the operating temperature window with appreciable NO conversion and no negative effect on the stability of the catalyst during 20 h on stream. In addition, a remarkable N₂ yield (93%) after 20 h on 0.25% NO/1% H₂/5% O₂/5% H₂O/He gas stream at 140°C has been observed. Remarkable N₂ selectivity values in the range of 80–90% have also been observed in the 100–200°C low-temperature range either in the absence or in the presence of

water in the feed stream. A maximum specific integral reaction rate of $443.5 \mu\text{mol N}_2/\text{s g}$ of Pt metal was measured at 160°C during reaction with a $0.25\% \text{ NO}/1\% \text{ H}_2/5\% \text{ O}_2/5\% \text{ H}_2\text{O}/\text{He}$ gas mixture. This value is higher by 90% than the corresponding one observed on the $0.1 \text{ wt}\% \text{ Pt}/\text{SiO}_2$ catalyst at 120°C and it is the highest value ever reported for the reaction at hand in the $100\text{--}200^\circ\text{C}$ low-temperature range on Pt-based catalysts. A TOF value of $13.4 \times 10^{-2} \text{ s}^{-1}$ for N_2 formation was calculated at 110°C for the $\text{Pt}/\text{La}_{0.7}\text{Sr}_{0.2}\text{Ce}_{0.1}\text{FeO}_3$ catalyst. Temperature-programmed desorption (TPD) of NO and transient titration experiments of the catalyst surface following $\text{NO}/\text{H}_2/\text{O}_2$ reaction have revealed important information concerning the amount and chemical composition of active and inactive (spectator) adsorbed N-containing species present under reaction conditions.

The remarkable catalytic behavior of $0.1 \text{ wt}\% \text{ Pt}/\text{La}_{0.7}\text{Sr}_{0.2}\text{Ce}_{0.1}\text{FeO}_3$ toward $\text{NO}/\text{H}_2/\text{O}_2$ reaction is suggested to be due to various direct and indirect influences of support composition, in particular of the $\text{SrFeO}_{3\pm X}$ mixed valence phase. However the causes for this superior activity rely on various findings:

- Strongly bound adsorbed states of NO_x
- Variable degree of NO sorption and activation over the surface of the catalyst
- The rate of oxidation of H_2 to form H_2O

All these factors found to differentiate from Pt/SiO_2 catalyst explaining the different and superior behavior of Pt/perovskite catalyst.

CONCLUDING REMARKS

Perovskites can perform as de- NO_x catalysts either as oxides/mixed oxides but even more efficiently in combination with noble metals surpassing the state of the art catalysts. This explicit behavior is attributed to synergistic surface phenomena among the perovskite phases and the noble metal.

In the literature, the establishment and precise knowledge of the relationships between solid-state properties and catalytic performance of perovskites is an open issue. Such a tool would be crucial for design and tailoring efficient catalysts.

NO molecule has the electron configuration $(\sigma_g^2)(\sigma_u^2)(\sigma_g, \pi_u)(\pi_g^1)$. NO has an unpaired electron in its $2\pi^*$ orbital and amphoteric bonding for NO on a surface is considered. NO can either donate its electron to the surface (like CO) or it can accept electron density from the surface into the half-filled $2\pi^*$ orbital, and therefore show a very wide variety of chemistry on surface.

The solid surface serves as a template providing electronic orbitals of the proper energy and symmetry for the bonding of reagents and intermediates. There is a proven close relationship between the electronic configuration of the transition metal ion (M) of the B site in a perovskite and its catalytic activity:

- *NO decomposition follows the decreasing order of the binding energy of surface oxygen / B–O bond covalency [18, 19]*

- Activity is determined by the cations of the transition metals at high temperature and by the rare earth ions at low temperature. [20]
- Twin-peak patterns in catalytic activity profiles resemble the twin-pattern which is found on going from d^0 to d^{10} cations in the change in the crystal field stabilization energy caused by the change in the coordination of surface M^{3+} cations upon oxygen adsorption [21]
- A volcano-type dependence between the activity for CO oxidation and the e^- configuration of the transition metal [18, 22, 23]
- In oxygen reduction reaction critical influences of the σ^* orbital and metal–O covalency on the competition between O_2^{2-}/OH^- displacement and OH^- regeneration on surface transition-metal ions as the rate-limiting steps of the reaction [24].

However in multicomponent reaction systems such as $H_2/NO/O_2$ or $HC/NO/O_2$ and in most cases in the presence of H_2O several factors may interact.

But for perovskite materials tuning surface electronic structure features such as transition-metal e_g filling and covalency is feasible. This is a promising strategy in developing highly active non-noble-metal-containing oxide catalysts or even high performance supported noble metal catalyst of low %wt loading. Within this context it is anticipated that further investigations will expand the catalytic perspectives of this magnificent class of materials.

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