

Article

NO_x Storage and Reduction (NSR) Performance of Sr-Doped LaCoO₃ Perovskite Prepared by Glycine-Assisted Solution Combustion

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Abstract: Here, we successfully synthesized Sr-doped perovskite-type oxides of La_{1-x}Sr_xCo_{1-λ}O_{3-δ}, “LSX” (x = 0, 0.1, 0.3, 0.5, 0.7), using the glycine-assisted solution combustion method. The effect of strontium doping on the catalyst structure, NO to NO₂ conversion, NO_x adsorption and storage, and NO_x reduction performance were investigated. The physicochemical properties of the catalysts were studied by XRD, SEM-EDS, N₂ adsorption–desorption, FTIR, H₂-TPR, O₂-TPD, and XPS techniques. The NSR performance of LaCoO₃ perovskite was improved after Sr doping. Specifically, the perovskite with 50% of Sr doping (LS5 sample) exhibited excellent NO_x storage capacity within a wide temperature range (200–400 °C), and excellent stability after hydrothermal and sulfur poisoning. It also displayed the highest NO_x adsorption–storage capacity (NAC: 1889 μmol/g; NSC: 1048 μmol/g) at 300 °C. This superior performance of the LS5 catalyst can be attributed to its superior reducibility, better NO oxidation capacity, increased surface Co²⁺ concentration, and, in particular, its generation of more oxygen vacancies. FTIR results further revealed that the LSX catalysts primarily store NO_x through the “nitrate route”. During the lean–rich cycle tests, we observed an average NO_x conversion rate of over 50% in the temperature range of 200–300 °C, with a maximum conversion rate of 61% achieved at 250 °C.

Keywords: perovskite oxides; NO_x storage and reduction; strontium doping



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1. Introduction

Nitrogen oxides (NO_x) are considered to be significant air pollutants generated in diverse combustion processes. Researchers have explored and recognized NO_x storage and reduction (NSR) [1] and selective catalytic reduction (SCR) [2] as effective methods for removing NO_x from exhaust emissions. NSR catalysts typically consist of active components such as noble metals (Pt, Pd, Rh) [3,4], storage components such as alkali or alkaline earth metals, and supports such as Al₂O₃ or CeO₂ [5,6]. A representative catalyst commonly employed in NO_x storage and reduction (NSR) systems is Pt-BaO/Al₂O₃. The operation of this catalyst involves alternating cycles of lean and rich conditions. Specifically, in the lean phase, the platinum (Pt) active sites facilitate the oxidation of NO to NO₂. Following this conversion, the resulting NO₂ species are subsequently stored as nitrates and nitrites on the barium oxide (BaO) sites [7]. In the rich phase, the oxidation of NO_x occurs, followed by its reduction to N₂ through the catalytic action of a reducing agent [8,9]. However, the use of Pt-based catalysts is limited due to their high cost, low activity at low temperatures [10], susceptibility to sintering at high temperatures, and poor resistance to sulfur [11]. Therefore, there is an urgent need to develop NSR catalysts with excellent low-temperature activity.

Perovskite (ABO_3) catalysts have been widely employed in environmental catalysis due to their low cost, superior thermal stability, and catalytic activity [12]. Alkali or alkaline earth metals have the potential to act as substitutes for the A-site, while transition metals can replace the B-site in perovskite catalysts. Incorporation of alkali or alkaline earth metal dopants plays a vital role in controlling the performance of perovskite catalysts by facilitating the creation of more oxygen vacancies and stabilizing the perovskite structure. The study conducted by Ueda et al. [13] revealed that the incorporation of Ba^{2+} ions amounting to 30% into La^{3+} -based perovskite ($LaFe_{0.97}Pd_{0.03}O_3$) remarkably tripled the capacity for NO_x storage. Similarly, Panunzi et al. [14] synthesized lanthanum strontium ferrite (LSFPt), and investigated how the oxygen vacancy content and the catalyst surface activity were enhanced in combined Sr substitution at the A-site and Pt doping at the B-site of lanthanum ferrites, leading to a substantial improvement in the activity and stability of methane oxidation. Concomitantly, Ji et al. [15] proposed that Sr dopants played a crucial role in enhancing the performance of catalysts during low-temperature reduction. Moreover, substitution of La with Sr in perovskite compounds like $LaCoO_3$ and $LaMnO_3$ exhibited enhanced oxidation activity, effectively converting NO to NO_2 [16,17]. Thus, Sr doping at the A site in perovskite catalysts yields improved NO oxidation performance and thermal stability.

NSR for environmental catalysis is known to have various drawbacks associated with thermal aging and sulfur poisoning [18,19]. The catalytic materials are typically exposed to high temperature, resulting in sintering of active sites/promoters/catalytic support materials and loss of specific surface area (SSA) and functionality [20]. Furthermore, since acidic $NO_2(g)$ and $SO_2(g)$ adsorbates compete for similar adsorption sites on the catalyst surface, SO_x species gradually accumulate over the NO_x -storage components and form more stable sulfides, diminishing the NSC of the catalyst [21]. Therefore, the ABO_3 surface chemistry and composition of catalytic materials need to be tuned at the nanoscale to improve their NSC, thermal stability, and resistance to sulfur neutrality.

In this study, we aimed to enhance the NO_x storage and reduction performance of $LaCoO_3$ catalysts by Sr doping at the A-site. The solution combustion method was employed to prepare the oxide materials. This method is attractive and simple [22], as it produces pure, uniform, and crystalline products with the desired composition and structure. In this study, we employed a rational design strategy and optimized the synthesis process, leading to the successful synthesis of perovskite-type catalysts. Specifically, $La_{1-x}Sr_xCo_{1-\lambda}O_{3-\delta}$ ($x = 0, 0.1, 0.3, 0.5, 0.7$) catalysts were synthesized via the glycine-assisted solution combustion method. Our research focused on elucidating the influence of Sr doping on the NSR performance. Additionally, Infrared Spectroscopy (FTIR) was employed to analyze the NO_x storage route on the catalyst surface.

2. Experimental

2.1. Catalyst Preparation

The perovskite-type catalysts $La_{1-x}Sr_xCoO_3$ ($x = 0, 0.1, 0.3, 0.5, 0.7$) were synthesized using the glycine-assisted solution combustion method, denoted as LSX ($X = 0, 1, 3, 5, 7$). The theoretical value of $(La + Sr)/Co$ is set to 1:1. A precise amount of $La(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 4H_2O$, and $Sr(NO_3)_2 \cdot 4H_2O$ was dissolved in deionized water. Following the addition of glycine ($G/N = 1.6$) to the mixture of nitrates, the resulting solution was stirred at ambient temperature for a duration of 2 h. Subsequently, the solution underwent evaporation under constant stirring at $80\text{ }^\circ\text{C}$ until a viscous gel with a distinctive purple hue was obtained. The gel was combusted in an oven at $200\text{ }^\circ\text{C}$. After the reaction was completed, the fluffy flocculent product was ground to a powder and calcined in a muffle furnace at $700\text{ }^\circ\text{C}$ for 4 h.

2.2. Catalysts Characterization

X-ray diffraction (XRD) patterns of the samples were obtained using the German D8 advance. The radiation source used was Cu K α . A scanning range of 10 to 90° was employed, with a scanning speed of 6° per minute.

The specific surface area, pore volume, and size of the samples were measured at −196 °C through utilization of an ASAP 2020 automated specific surface area and porosity analyzer. In preparation for the assessment, all samples were subjected to a 6 h vacuum degassing process at 300 °C to eliminate any adsorbed species. The surface areas of the samples were determined by employing the Brumauer–Emmett–Teller (BET) technique.

The surface morphology and microstructure of the specimens were examined utilizing a Quanta FEG 250 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany). The applied working voltage was 10 kV, and a thin layer of gold was deposited on the specimens for 60 s prior to the scanning process.

The infrared spectra (FTIR) of the specimens were recorded with a Bruker tensor 27 infrared spectrometer (Bruker, Saarbrücken, Germany) located in Germany. The spectra were acquired by conducting 16 scans at a resolution of 4 cm^{−1}. Prior to the analysis, the specimens were mixed with dry KBr in a ratio of 1:100 and subsequently compressed into tablets using a tablet press under a pressure of 10 MPa.

Using a quartz tube reactor equipped with a TCD (thermal conductivity detector) (Lunan Ruihong Chemical, Zaozhuang, China), we conducted temperature-programmed reduction with H₂ (H₂-TPR) measurements. The catalysts, weighing 0.05 g, were progressively heated from ambient temperature to 900 °C in the presence of a 5 vol.% H₂/N₂ mixture. The heating rate was set at 10 °C per minute, while maintaining a total flow rate of 30 mL/min.

O₂ temperature-programmed desorption (O₂-TPD) tests were conducted to observe the dynamic process of oxygen adsorption and desorption on perovskite. A quartz tube reactor with a capacity of approximately 150 mg of catalyst sample was utilized. The sample was subjected to a purification procedure involving a 30 min purge using a mixture of 10 vol% O₂ in N₂ flow (50 mL/min) at a temperature of 500 °C. Following the purification step, the sample was cooled to 50 °C and underwent an additional 30 min purge with N₂ flow (50 mL/min) to eliminate any residual adsorbed oxygen. Subsequently, a gradual heating process was conducted from 50 to 900 °C at a heating rate of 10 °C/min under a N₂ flow (30 mL/min), while simultaneously monitoring the released oxygen employing a TCD. Integration of the resulting TPD curves facilitated the determination of the quantities of oxygen species present.

By employing the Thermo Scientific X-ray photoelectron spectrometer (Bruker, Saarbrücken, Germany) equipped with an Al K α X-ray radiation source, we were able to precisely determine the chemical composition and oxidation states of surface elements in catalysts. To calibrate the binding energy measurements, we utilized the C1s peak (BE = 284.6 eV) as a reference standard.

2.3. Catalytic Activity Measurements

2.3.1. NO Oxidation Experiments

The investigation into the oxidation process of NO was conducted using the temperature-programmed oxidation (NO-TPO) technique. Prior to the experimentation, the catalysts underwent a pretreatment process involving exposure to N₂ at a temperature of 500 °C for a duration of one hour, followed by natural cooling to room temperature. Subsequently, the gas mixture was converted to contain 1000 ppm NO/N₂ and 5% O₂/N₂, and left to stabilize for a certain period. Finally, once the NO_x concentration at the outlet remained constant, the temperature was increased to 700 °C at a rate of 5 °C per minute. The concentration of NO_x was measured using a chemiluminescence NO_x analyzer.

2.3.2. NO_x Adsorption–Desorption Measurements

The catalysts (50 mg, 40–80 mesh) were examined for their NO_x adsorption and storage capacity (NAC/NSC) using a custom-built catalyst sample evaluation system equipped with a chemiluminescence NO_x analyzer (Thermo 42i–HL) (Thermo Fisher Scientific, Waltham, MA, USA). Initially, the feed gas was composed of 1000 ppm of NO and 5% O₂ for NO_x adsorption, while N₂ was utilized as the balance gas. After adsorbing NO_x for 1 h, the system was purged by introducing N₂ into the reaction chamber. Subsequently, the temperature was ramped up to 700 °C at a heating rate of 10 °C/min. The total flow rate was maintained at 100 mL/min. The LS5 catalyst after hydrothermal aging and sulfur poisoning was re-tested under the same conditions as those used for the fresh catalyst. The NAC/NSC was determined by calculating the NO_x adsorption–desorption curves using Equations (1) and (2).

$$\text{NAC} = \left(\int_0^t (\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}) \times V \right) / (22.4 \times m_c) \quad (1)$$

$$\text{NSC} = \left(\int_0^t (\text{NO}_{x,\text{out}}) \times V \right) / (22.4 \times R \times m_c) \quad (2)$$

where NO_{x,in} is the NO_x concentration at the inlet, NO_{x,out} is the NO_x concentration at the outlet, t is time, V is the flow rate, m_c is the catalyst quantity, and R is the heating rate.

2.3.3. NO_x Storage and Reduction Measurements

To assess the efficiency of catalysts in reducing NO_x emissions, a comprehensive array of NO_x storage and reduction experiments was executed, spanning diverse temperature ranges. The experimental design entailed 15 cycles, wherein each lean phase persisted for 2 min, incorporating a gas mixture comprising 500 ppm of NO/N₂ and 7.5 vol.% of O₂/N₂. Conversely, the rich phase spanned 1 min, during which a gas composition of 500 ppm of NO/N₂ and 1200 ppm of C₃H₈/He was employed. The overall volumetric flow rate was consistently maintained at 50 mL/min (GHSV: 60,000 h^{−1}). The chemiluminescence NO_x analyzer was used to measure the NO_x concentration at the outlet, and subsequently, the NO_x removal efficiency of the catalysts was determined using Equation (3).

$$\text{NO}_x \text{ conversion (\%)} = \frac{\int_0^t (\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}) dt}{\int_0^t (\text{NO}_{x,\text{in}}) dt} \cdot 100\% \quad (3)$$

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of LSX perovskite catalysts are illustrated in Figure 1a. Pure perovskite diffraction patterns were obtained with Sr doping amounts lower than 30%, indicating the absence of impurities. However, after Sr doping reached 50%, trace amounts of impurities in the form of SrCO₃ and SrCoO_x were detected on the LS5 catalyst. In addition, the impurity phase SrCoO_x was distinctly observed on the LS7 sample. Therefore, it can be concluded that the LS5 catalyst allows for higher Sr accommodation in the lattice compared to the LS7 catalyst. The cobalt in perovskite serves as the active oxidation site [23], while the hybrid SrCoO_x species may occupy the LS7 catalyst surface and cover the active component, thereby influencing the catalyst activity.

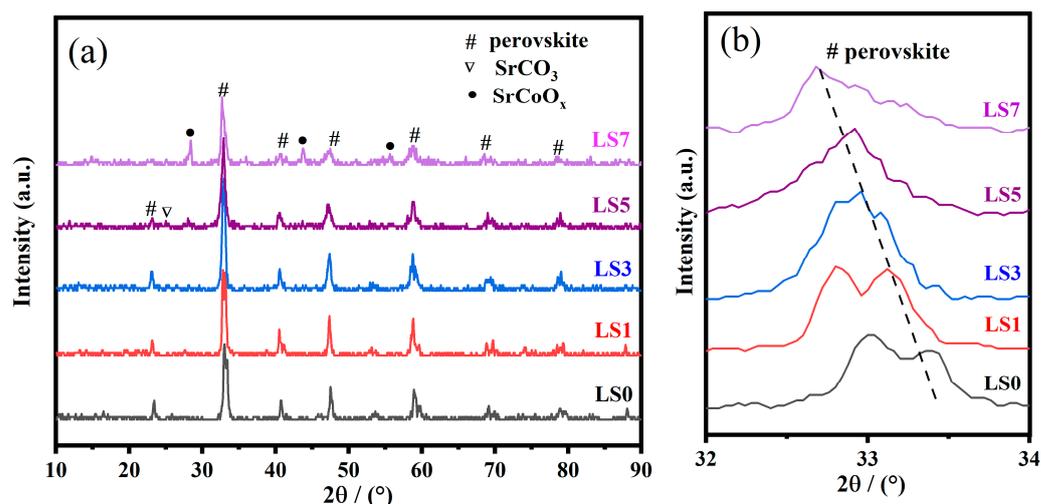


Figure 1. (a) XRD and (b) the peak of crystal plane (110) of LSX catalysts.

An enlarged version of the peak from the crystal plane (110) of LSX perovskite catalysts is presented in Figure 1b. The peak of the crystal plane (110) shifts to a lower 2θ angle as the Sr doping content increases. This shift is caused by lattice expansion resulting from the isomorphous substitution of Sr^{2+} cations with larger ionic radii replacing La^{3+} ions. Furthermore, the LSX catalysts exhibit a rhomboid bimodal structure in the absence of, or with low, strontium doping ($X \leq 1$) [24]. As the Sr doping content increases, this typical rhomboid bimodal structure weakens and gradually transforms into a cubic symmetric singlet structure [25].

3.2. SEM and EDS Mapping Analysis

The scanning electron microscope (SEM) images of LS0 and LS5 catalysts are presented in Figure 2a,b. Both catalysts exhibit similar loose and porous spongy morphological structures, both before and after Sr doping. The formation of abundant pores can be attributed to the release of CO_2 , N_2 , and H_2O during the combustion of the precursor materials [26,27]. This porous structure enhances the dispersion, absorption, and desorption of gas reactants. However, there are differences in grain size and dispersion between the two catalysts, which can be attributed to the variation in Sr doping. The LS5 catalyst has smaller particle diameters and appears to be in a looser state. A smaller grain size provides more catalytic active sites, leading to higher catalytic activity.

The energy-dispersive X-ray spectroscopy (EDS) mapping of LS0 and LS5 catalysts is shown in Figure 2c,e, revealing the uniform distribution of La, Sr, Co, and O atoms across their respective surfaces. Furthermore, the distribution diagram depicted in Figure 2d,f facilitates the determination of the $(\text{La} + \text{Sr})/\text{Co}$ ratio on the catalyst surfaces, which aligns with the theoretical outcomes as illustrated in Table 1.

Table 1. Textural parameters for S_{BET} , V_p , and D_p of the LSX catalysts.

Catalyst	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)	Mesopore Fraction	$(\text{La} + \text{Sr})/\text{Co}$
LS0	5.58	0.05	41	0.36	1.20
LS1	12.38	0.08	32	0.66	-
LS3	13.44	0.13	29	0.76	-
LS5	17.71	0.11	22	0.75	1.09
LS7	15.96	0.09	23	0.70	-

(La + Sr)/Co: EDS results; Mesopore Fraction: Percentage of mesopore to total pore; D_p : Average Pore diameter.

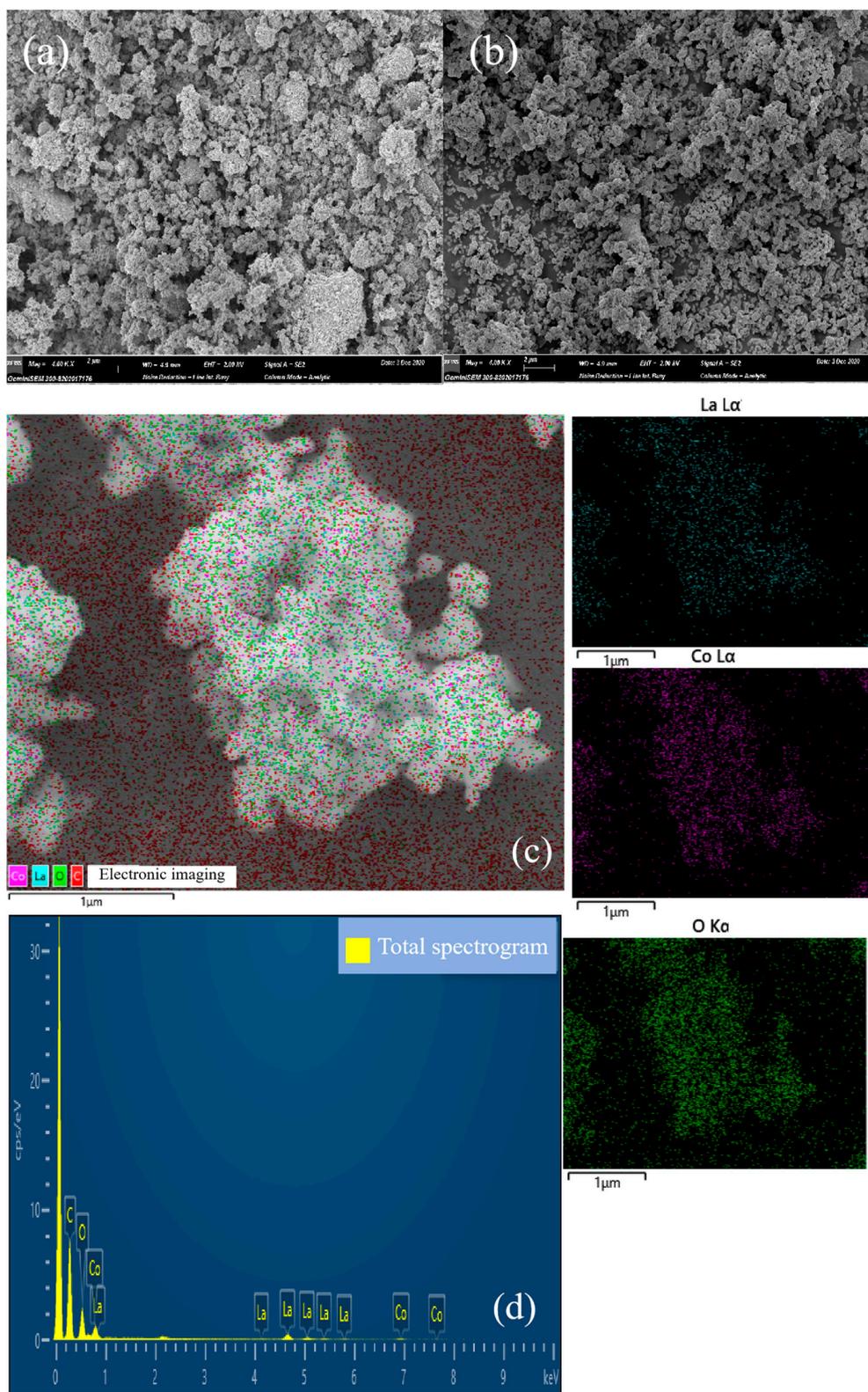


Figure 2. Cont.

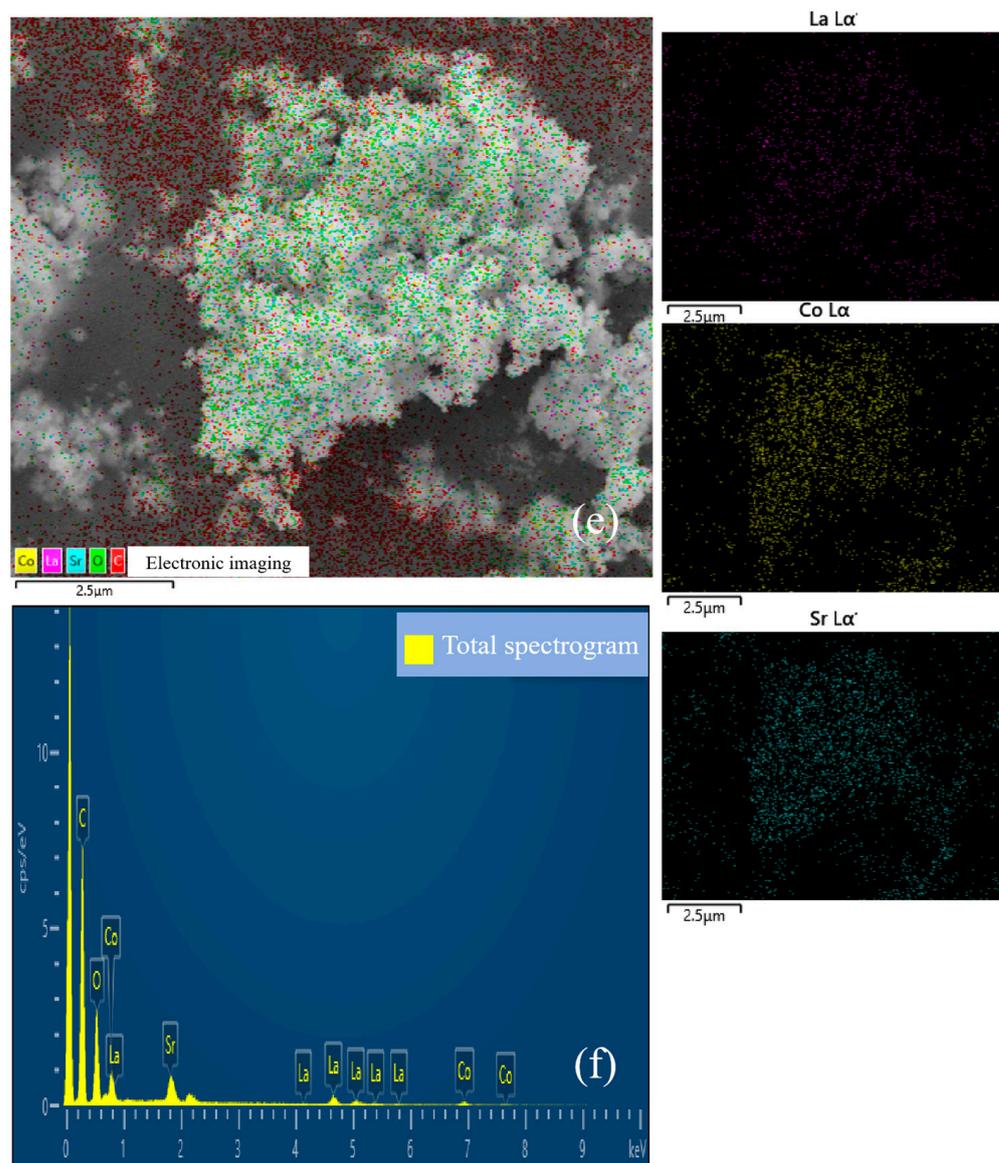


Figure 2. SEM and EDS mapping images of (a,c,d) LS0 and (b,e,f) LS5 catalysts.

3.3. N_2 Adsorption–Desorption Analysis

The N_2 adsorption–desorption curves of the samples are depicted in Figure 3a. All catalysts exhibit IUPAC type II isotherms, and a H3 type hysteresis loop is observed in the range of $p/p_0 = 0.8–1.0$, indicating the presence of macroporous materials [28]. The pore size distribution curve in Figure 3b combined with SEM images reveals that all catalysts possess a multistage pore structure consisting of both mesopores and macropores.

In Table 1, the LSX catalysts are characterized by their BET surface areas (S_{BET}), pore volume (V_p), and average pore size (D_p). Among them, the LS0 sample possesses the smallest surface area of $5.58 \text{ m}^2/\text{g}$ and a corresponding pore volume of $0.05 \text{ cm}^3/\text{g}$. Through Sr doping, the LSX catalysts exhibit an increasing trend in both surface area and pore volume with the escalating Sr doping amount, while the pore size demonstrates the opposite relationship. The LS5 sample demonstrates the largest surface area of $17.71 \text{ m}^2/\text{g}$, coupled with a pore volume of $0.11 \text{ cm}^3/\text{g}$. However, as the Sr doping content further rises ($X = 7$), LS7 experiences a slight reduction in both surface area and pore volume. This may be due to impurities, such as SrCoO_x and SrCO_3 , which block the catalyst's pores and affect its textural parameters. Previous studies [29,30] have proposed that optimizing the pore structure by reducing its size can significantly improve gas transport properties and

boost catalytic activity. Furthermore, Table 1 reveals that Sr doping significantly increases the mesoporous rate of the catalysts, leading to a larger surface area in the corresponding samples. This larger surface area exposes more active sites, facilitating contact between the catalyst and gas, and thus improving reaction efficiency [31].

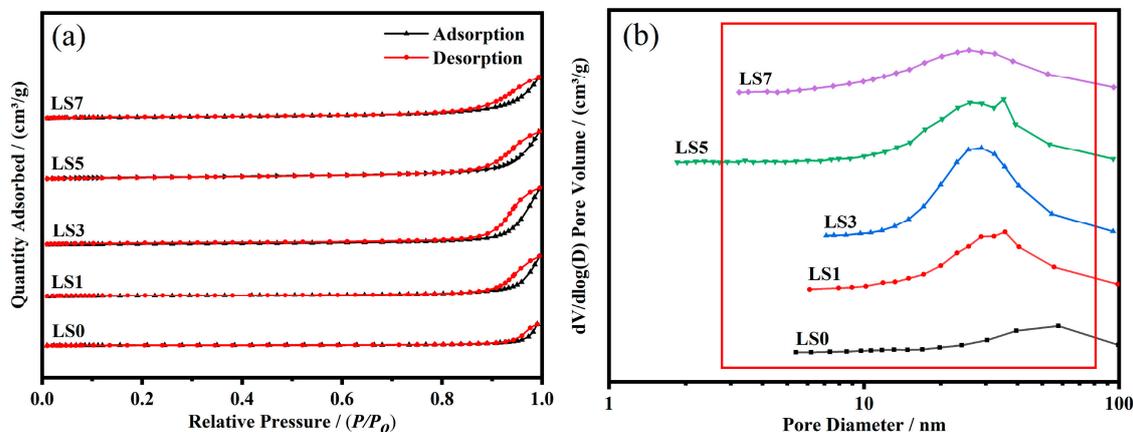


Figure 3. (a) N₂ adsorption–desorption curves and (b) pore size distributions of LSX catalysts.

3.4. FTIR and H₂-TPR Analysis

The FTIR spectra of the LSX catalysts are presented in Figure 4a. Among the catalysts with varying amounts of Sr doping, it is observed that the bending vibration of Co-O bonds in the octahedral structure of perovskite BO₆ is assigned to approximately 580 cm⁻¹ [32]. This suggests the successful preparation of the perovskite structure. Additionally, the peaks at 858 and 1451 cm⁻¹ are attributed to surface carbonate [33,34]. When considering the XRD results, it is further confirmed that SrCoO₃ exists in the samples. Comparing the catalysts before and after Sr doping, it is evident that the characteristic peak of perovskite is significantly weakened upon the introduction of Sr, indicating that Sr has a certain impact on the integrity of the perovskite crystal.

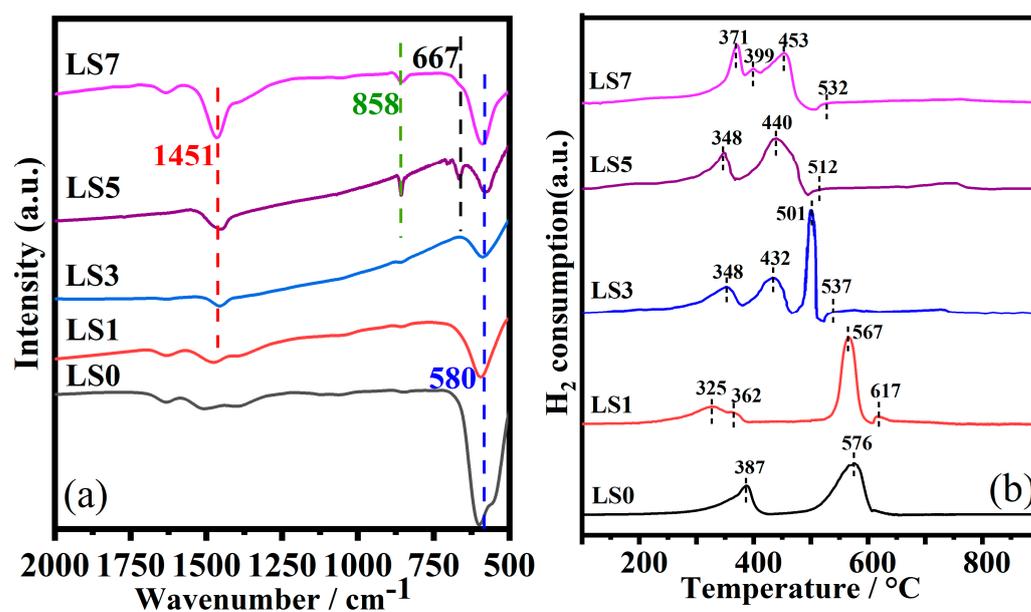


Figure 4. (a) FTIR spectra and (b) H₂-TPR profiles of the LSX catalysts.

The reducibility of the LSX samples was assessed via H₂-TPR, as depicted in Figure 4b. The peaks observed in the temperature range of 100 °C to 800 °C can all be attributed solely to the reduction of Co³⁺. This finding is consistent with the notion that La³⁺ and Sr²⁺ are impervious to reduction under the specific experimental conditions employed [24]. In all catalysts, the reduction peaks witnessed in the 300–430 °C range correspond to the reduction of Co³⁺, whereas those observed within the 440–620 °C range align with the reduction of Co²⁺ [35,36]. Specifically, between 300 and 430 °C, there are two reduction peaks for Co³⁺ with $x > 1$. The peak at the lower temperature is related to surface/highly reactive Co³⁺, which is in accordance with the stepwise reduction behavior of fine Co₃O₄ particles [37]. Notably, the reduction temperature of Co species on the doped catalysts exhibits a noticeable decrease compared to that of the undoped catalyst when the Sr doping level is maintained below 50%. This noteworthy trend alludes to the beneficial influence of Sr doping, which serves to enhance the reduction performance of the catalysts and facilitate the reduction of surface oxygen [24]. However, when $X \geq 5$, the intensity of the reduction peak in the range of 500–540 °C decreased significantly. Combined with the XRD results, it is speculated that the reason for this occurrence may be the inhibitory effect of the presence of SrCoO_x and SrCO₃ impurities on the reduction of Co²⁺. Furthermore, exceeding a certain threshold of Sr doping leads to a slight elevation in the reduction temperature of Co species, signifying that excessive Sr doping does not favor the reduction process of the catalysts.

The H₂ consumption of all samples is listed in Table 2. It can be concluded that Sr doping increases the H₂ consumption of the catalysts. Noticeably, the LS3 catalyst possesses the highest H₂ consumption (8.1 mmol/g), followed by the LS5 catalyst (7.5 mmol/g). The result shows that LS3 and LS5 catalysts have better reducibility.

Table 2. H₂-TPR and O₂-TPD results.

Catalyst	H ₂ Consumption (mmol/g)	Peak Area	
		α -Peak	β -Peak
LS0	5.7	100	-
LS1	6.2	177	39
LS3	8.1	194	369
LS5	7.5	219	578
LS7	6.9	172	668

3.5. O₂-TPD

O₂ temperature-programmed desorption tests were conducted on the LSX catalysts and the results are presented in Figure 5. The integral areas of the α and β peaks were determined from the O₂-TPD spectra, as shown in Table 2. Except for LS0, all LSX catalysts exhibited a α -oxygen desorption peak below 300 °C and a β -oxygen desorption peak above 600 °C. The α -peak in the graph represents the desorption of surface-adsorbed oxygen (O²⁻) species, whereas the β -peak corresponds to the liberation of lattice oxygen (O²⁻) ions [38]. The graph displays an upsurge in the intensity of the α -peak during Sr doping, indicating that Sr doping facilitates the desorption of surface oxygen species. Typically, an increase in the concentration of oxygen species associated with the α -peak enhances catalytic activity [12]. Among the catalysts, LS5 demonstrated the lowest α -peak temperature of 118 °C and the largest peak area, indicating a higher concentration of surface oxygen species and stronger oxidation properties. Furthermore, the intensity of the β -oxygen desorption peak increased with Sr doping, with the maximum observed for the LS7 catalyst.

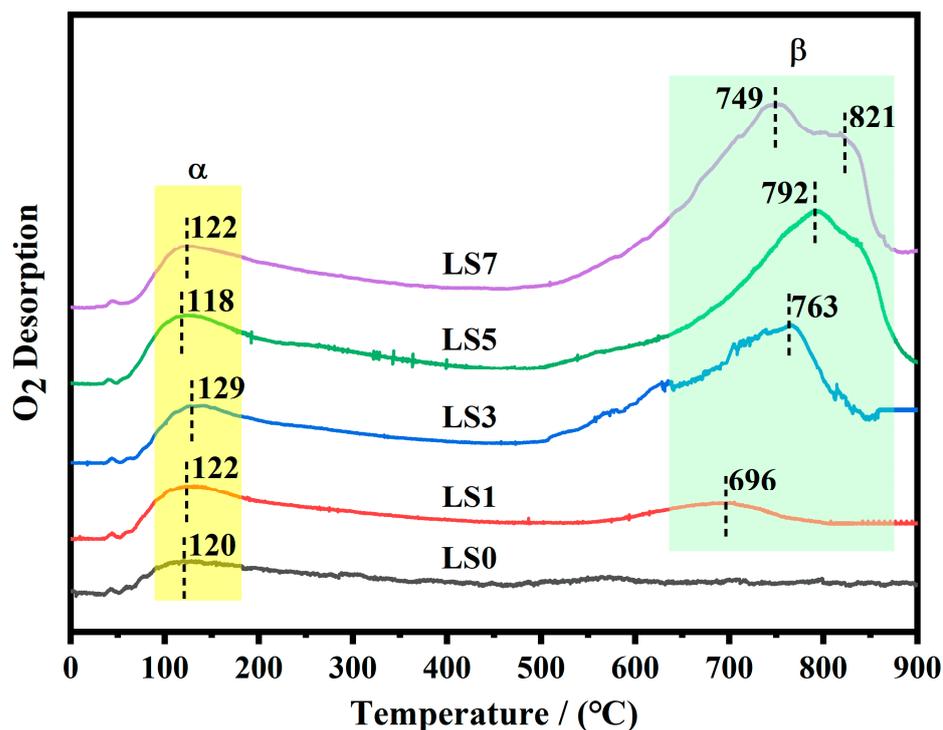


Figure 5. O₂-TPD spectra of the LSX catalysts.

3.6. XPS

The surface properties of the synthesized LSX catalysts were confirmed using X-ray photoelectron spectroscopy (XPS), as illustrated in Figure 6. The Sr 3d XPS peak exhibited two distinct sets of doublets, specifically Sr 3d_{5/2} and 3d_{3/2}. The peaks observed at binding energies of 131.7 and 134.1 eV can be assigned to Sr_{latt}, while the peaks detected at 133.1 and 135.2 eV can be attributed to Sr_{surf} [11,39]. The ratios of Sr_{surf}/Sr_{latt} are summarized in Table 1. The proportion of Sr_{surf} increases with an increase in Sr doping. It is likely that Sr_{surf} species are present in the form of SrCO₃, as suggested by XRD and FTIR results. An increase in the amount of Sr_{surf} signifies an increase in the content of SrCO₃. This is significant because SrCO₃ is an important storage phase for NO_x adsorption, suggesting that the LS5 catalyst may possess a strong capacity for NO_x adsorption and storage.

The Co 2p XPS peak was fitted with two sets of Co 2p_{3/2} and 2p_{1/2} doublets. The peaks at 779.7 and 794.9 eV were assigned to Co³⁺, while the peaks at 781 and 796.5 eV were attributed to Co²⁺. The peaks at 790 and 804 eV were considered satellite peaks [40,41]. The bands of the fitted O1s spectra at 528.8–529.1 eV, 530.3–531.5 eV, and 533.0–533.8 eV could be assigned to lattice oxygen (O_I), surface reactive oxygen (O_{II}), and chemisorbed water (O_{III}), respectively [42]. Table 3 presents the (La + Sr)/Co, Co²⁺/Co³⁺, and O_{II}/(O_I + O_{II} + O_{III}) ratios. The (La + Sr)/Co ratio increases with the decrease in the Sr doping amount, indicating that Sr doping results in the partial bulk Co ion segregation on the LSX surface. The high value of the (La + Sr)/Co ratio can be attributed to various reasons, one of which is the significant variation in this molar ratio from one site to another. This variation is caused by the swift application of high power densities, which leads to a highly heterogeneous structure [43]. As a result, there are abrupt changes in the (La + Sr)/Co values, both chemically and morphologically [44]. Therefore, this change is denoted by “1 – λ” in La_{1–x}Sr_xCo_{1–λ}O_{3–δ}. The quantities of both Co²⁺ cations and O_{II} species also increase with the Sr doping content. Notably, the LS3 catalyst exhibits the highest number of reactive oxygen species on its surface. This suggests that the content of reactive oxygen does not completely determine the activity of the catalysts. It has been shown that the oxygen vacancy is formed on the site of oxygen, coupled with cobalt [45]. Therefore, variations in O_{II} fractions may be due to differences in oxygen vacancies or defects on the sample

surface, or differences in oxygen-deficient regions in the cobalt-containing structures [46]. Changes in the concentration of oxygen vacancies or defects in the sample may favor the chemisorption process. The LS5 catalyst contains a higher amount of surface Co^{2+} , which leads to the formation of oxygen vacancies and improves the NO oxidation capacity of the catalyst, thereby enhancing the NO_x storage performance.

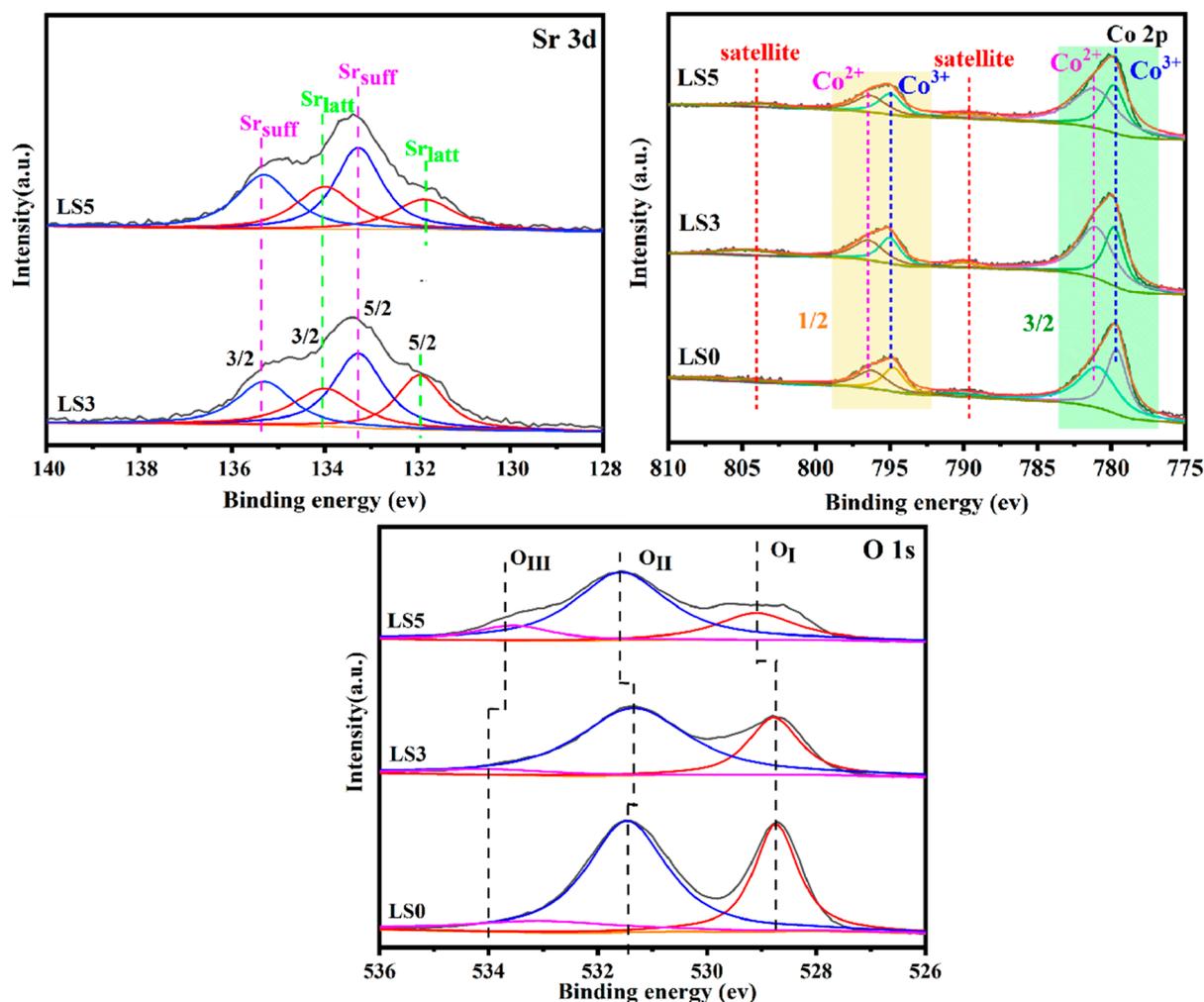


Figure 6. Sr 3d, Co 2p, O 1s XPS spectra of the LSX catalysts.

Table 3. XPS results.

Catalyst	$\text{O}_{\text{II}}/(\text{O}_{\text{I}} + \text{O}_{\text{II}} + \text{O}_{\text{III}})$ (%)	$\text{Co}^{2+}/\text{Co}^{3+}$	(La + Sr)/Co	$\text{Sr}_{\text{surf}}/\text{Sr}_{\text{latt}}$
LS0	57.6	1.13	2.33	-
LS3	68.6	1.41	1.28	1.23
LS5	65.8	1.43	1.05	1.6

O_{I} : lattice oxygen; O_{II} : surface-active oxygen; O_{III} : Chemical adsorption of oxygen in water; Sr_{latt} : Sr lattice components; Sr_{surf} : Sr surface components.

3.7. NO Oxidation

The NO_x storage capacity of non-noble metal catalysts is subject to the influence of their NO oxidation capability [47]. The temperature-programmed oxidation of NO was conducted on LSX catalysts and the corresponding results are illustrated in Figure 7. The presence of the catalysts facilitates the conversion of NO to NO_2 through oxidation reactions. Remarkably, even at temperatures as low as 100–150 °C, a considerable fraction of NO,

amounting to approximately 15%, can be converted into NO_2 . The LSX catalysts reach their peak NO conversions within the temperature range of 300–365 °C. As the temperature continues to rise, the decline in NO conversion can be attributed to the thermodynamic equilibrium associated with NO oxidation. Notably, LaCoO_3 exhibits remarkable catalytic activity towards NO oxidation, resulting in a peak conversion rate of 49.5% at 365 °C. The achievement of a higher conversion rate at a lower peak temperature indicates an enhanced capability for NO oxidation. Based on the data presented in Figure 7, it can be deduced that Sr doping enhances the NO oxidation capability of the catalysts, leading to a conversion rate surpassing 50%. Among the catalysts examined, LS3 demonstrates the optimal NO oxidation ability, achieving a maximum conversion rate of 76.8% at 305 °C. This observation can be attributed to an elevated presence of surface oxygen species and Co^{2+} in LS3. The generation of a substantial amount of NO_2 during NO_x adsorption proves advantageous for adsorption via the “nitrate” pathway [48].

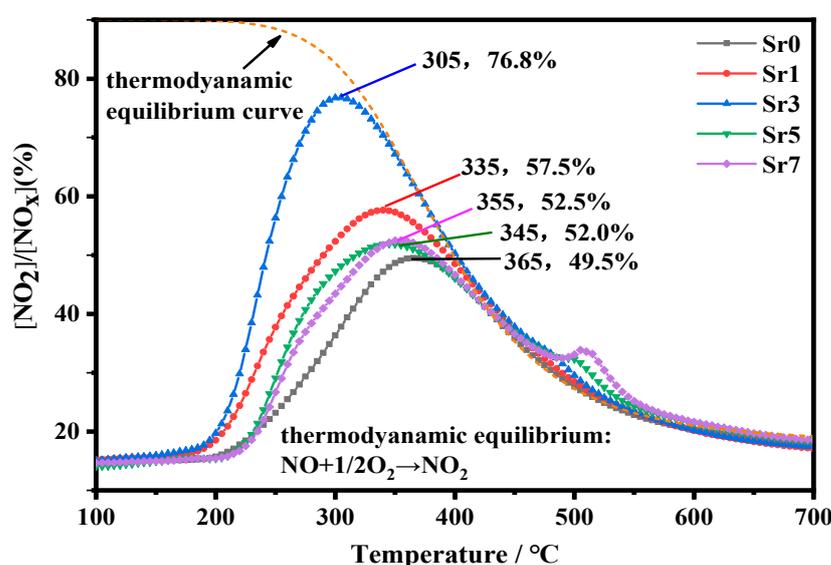


Figure 7. Oxidation curves of NO on the LSX catalysts.

3.8. NO_x Adsorption/Storage Capacity

To assess the impact of Sr doping on the efficiency of NO_x storage, experiments were conducted to measure the adsorption and desorption of NO_x at a temperature of 300 °C. The results are presented in Figure 8. The adsorption curve (Figure 8a) clearly demonstrates that at the initial stage of adsorption, NO_x is almost entirely adsorbed. As adsorption progresses, the concentration of NO_x at the outlet gradually increases and stabilizes, suggesting that NO_x adsorption reaches saturation. Throughout this process, NO_2 is detected at the outlet, indicating the oxidation of NO to NO_2 . Previous studies have indicated that NO_2 can be readily stored in the form of nitrate, and the conversion of NO to NO_2 is the rate-determining step for NO_x storage in Pt/BaO/ Al_2O_3 catalysts [49]. Figure 8b illustrates the desorption behavior of the LSX catalysts. All catalysts exhibit a one-step desorption process. With increasing Sr doping content, the desorption peak of the catalysts shifts to higher temperatures, indicating that the addition of more strontium to perovskite leads to greater stability of the nitrate species.

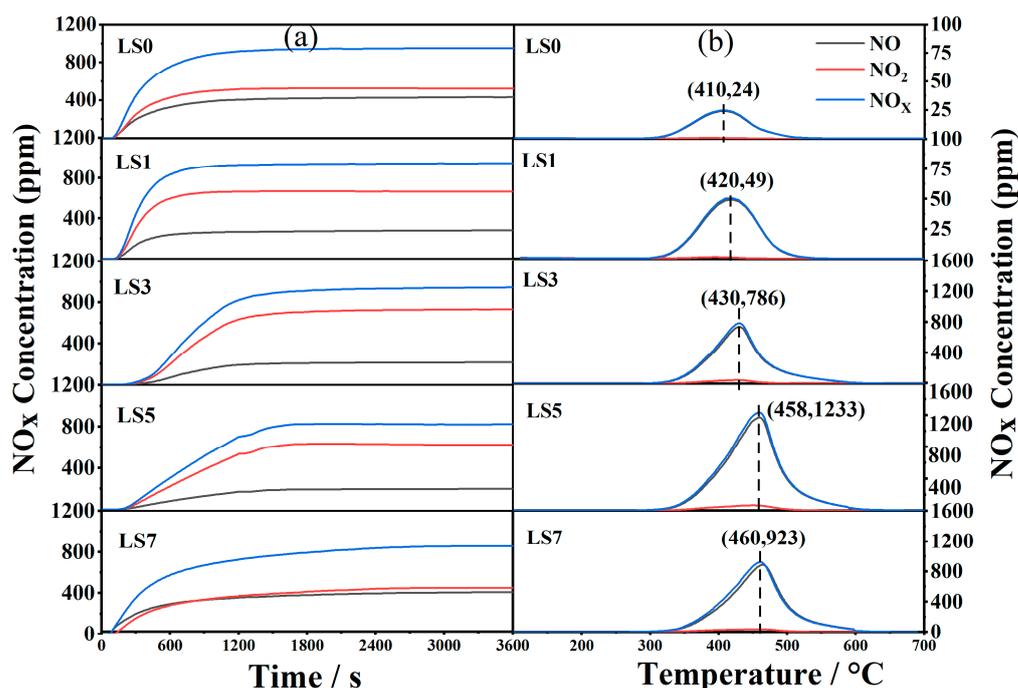


Figure 8. (a) NO_x adsorption curves and (b) desorption curves (at 300 °C) of the LSX catalysts.

Table 4 provides the data for the NO_x adsorption capacity (NAC) and NO_x storage capacity (NSC) of the LSX catalysts, as determined from their NO_x adsorption–desorption profiles. It is important to note that the NAC and NSC show significant increases after Sr doping, suggesting that Sr enhances the storage of NO_x. Additionally, both the NAC and NSC of the catalysts increase with higher levels of Sr doping ($X \leq 5$). Among the catalysts, LS5 exhibits the highest adsorption and storage capacity, with an NAC of 1889 $\mu\text{mol/g}$ and an NSC of 1084 $\mu\text{mol/g}$. This can be attributed to its larger surface area, strong reducibility, excellent NO oxidation activity, and the charge imbalance caused by Sr doping at the A-site, which promotes the generation of more active Co²⁺ cations and surface reactive oxygen species [24]. However, when Sr doping continues to increase, the NAC and NSC of the catalysts decrease. This is likely due to an excessive amount of Sr doping, which results in the formation of large amounts of SrCO₃ and SrCoO_x. These heterogeneous compounds do not disperse well on the surface, and the presence of a significant quantity of SrCoO_x reduces the availability of effective storage sites and active sites, ultimately weakening the storage capacity of the catalysts.

Table 4. NAC and NSC of the LSX catalysts at 300 °C.

Catalysts	NAC ($\mu\text{mol/g}$)	NSC ($\mu\text{mol/g}$)
LS0	831	23
LS1	865	48
LS3	1485	635
LS5	1889	1084
LS7	1556	810

Wang et al. [50] developed LaCo_{0.90}Pt_{0.10}O₃ catalysts based on chalcogenides. These catalysts achieved a maximum NSC of 22.6 $\mu\text{mol/g}$ at 300 °C. Additionally, Wen et al. [51] studied the impact of adding LaCoO₃ chalcogenide to 1 wt% Pt/LaCoO₃/K/Al₂O₃ on NSR performance. Their results showed that a maximum NSC of 44.8 $\mu\text{mol/g}$ could be achieved at 400 °C. Furthermore, Xie et al. [52] tested the catalytic performance of LaCoO₃-Meso with a high surface area in the NSR reaction. LaCoO₃-Meso demonstrated a

maximum NSC of 124 $\mu\text{mol/g}$ at 300 $^{\circ}\text{C}$. Although this is only a rough comparison of the data, it still demonstrates the superiority of the LS5 catalyst in terms of NO_x adsorption/storage capacity.

Based on the above studies, it was observed that the LS5 catalyst demonstrates remarkable performance in NO_x storage. Therefore, an investigation into its NO_x storage capabilities at varying adsorption temperatures (200–400 $^{\circ}\text{C}$) was conducted. The findings are presented in Figure 9. Initially, the LS5 catalyst completely traps NO, resulting in minimal NO_x levels. However, as the reaction time increases, the concentration of NO_x gradually rises until it reaches a certain threshold. Based on the NO_x concentration at the outlet, the conversion rate of NO can be calculated and is shown in Table 5: 300 $^{\circ}\text{C}$ (63%) > 250 $^{\circ}\text{C}$ = 350 $^{\circ}\text{C}$ = 400 $^{\circ}\text{C}$ (42%) > 200 $^{\circ}\text{C}$ (30%). Analysis of the NO_x desorption curve reveals that catalyst desorption follows a one-step process at different temperatures. Moreover, the desorption peak of the catalysts shifts to higher temperatures with increasing temperature. This suggests that elevating the temperature enhances the stability of nitrate.

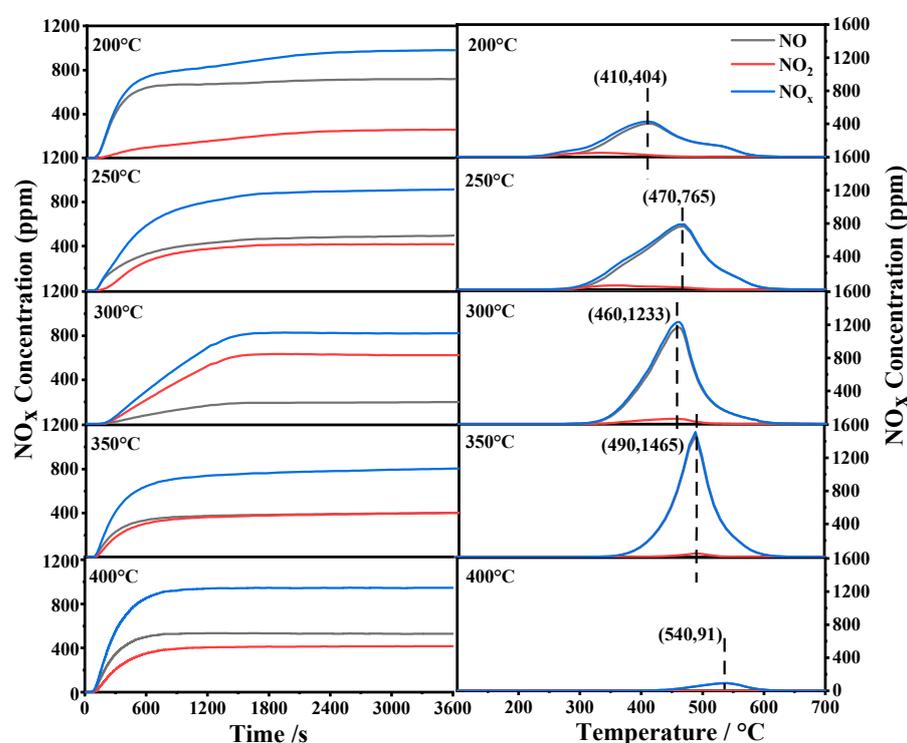


Figure 9. NO_x absorption–desorption curves of the LS5 catalyst at different temperatures (200–400 $^{\circ}\text{C}$).

Table 5. NAC, NSC, and R_{NO_2} at different adsorption temperatures on the LS5 catalyst.

Adsorption Temperature ($^{\circ}\text{C}$)	NAC ($\mu\text{mol/g}$)	NSC ($\mu\text{mol/g}$)	R_{NO_2} (%)
200	937	609	30
250	1297	984	42
300	1889	1084	63
350	1633	1007	42
400	750	80	42

R_{NO_2} : NO to NO_2 conversion after reaching a steady state during the adsorption process.

The NAC and NSC of the LS5 catalysts were presented in Table 5. The catalyst's NAC and NSC reach their maximum values at 300 $^{\circ}\text{C}$. However, as the adsorption temperature increases, the capacity for NO_x adsorption/storage decreases due to the exothermic nature of the process [48].

To investigate the impact of hydrothermal aging and sulfur on the NO_x storage performance of LS0 and LS5 catalysts, experiments were performed to analyze NO_x adsorption and desorption at 300 °C. Tables 6 and 7 summarize the NO_x adsorption capacity and R_{NO2} of LS0 and LS5 catalysts. The results reveal that the presence of water reduces the catalyst's acidity after hydrothermal aging, leading to decreased efficiency in NO to NO₂ conversion and a subsequent loss in NO_x storage performance. However, perovskite promotes Sr dispersion and stability during hydrothermal aging, mitigating negative effects on the catalyst. The presence of impurities SrCoO_x and SrCO₃ also affected the NO_x storage performance of the catalysts. It is hypothesized that hydrothermal aging increases the likelihood of SrCoO_x and SrCO₃ production, which has a reverse effect on catalysis. Moreover, the smaller decrease in NAC of Sr-doped catalysts suggests that Sr doping enhances the hydrothermal resistance of the catalysts. Table 7 depicts the effect of sulfur on the LS0 and LS5 catalysts. The NAC decrease rate of the LS5 sample is lower than that of the LS0 sample. This may be because Sr completely enters the perovskite lattice in the LS0 catalyst. After the introduction of SO₂, SO₂ directly poisons perovskite. However, in the LS5 catalyst, Sr exists in the form of perovskite and SrCO₃, and after the introduction of SO₂, SO₂ easily reacts with SrCO₃. This weakens the toxicity of the perovskite structure, resulting in a small decrease in the NAC of the catalysts. This indicates that Sr doping enhances the sulfur-resistant performance of the LS5 catalyst. Additionally, Sr doping increases the specific surface area, which supports better dispersion of the storage sites. Therefore, the small amount of sulphate species generated by the reaction of SO₂ with SrCO₃ is not sufficient to completely inactivate the NO_x storage sites of the catalyst. This is another reason for the superior NO_x storage performance of the sulfided LS5 chalcogenide catalyst.

Table 6. Comparison of NAC and R_{NO2} after hydrothermal aging of LS0 and LS5 catalysts.

Catalyst	NAC (μmol/g)		R _{NO2}		The Decline Rate of NAC
	Fresh	Hydrothermal Aging	Fresh	Hydrothermal Aging	
LS0	831	461	52	33	44.5
LS5	1889	1262	63	38	33.2

Table 7. Comparison of NAC and R_{NO2} before and after sulfurization of LS0 and LS5 catalysts.

Catalyst	NAC (μmol/g)		R _{NO2}		The Decline Rate of NAC
	Fresh	Sulfur Poisoning	Fresh	Sulfur Poisoning	
LS0	831	554	52	19	33.3
LS5	1889	1434	63	28	24.2

Overall, the LS5 catalyst exhibits a wide operating temperature range (200–400 °C), with higher NAC (750–1899 μmol/g) and NSC (80–1084 μmol/g), which indicates its excellent ability to capture NO_x at low to medium temperatures. In addition, the LS5 catalyst also exhibits excellent stability after hydrothermal and sulfur poisoning. Consequently, LS5 can be considered a promising material for NO_x storage.

3.9. IR Study of NO_x Storage

In order to determine the storage species of the samples, FTIR analysis was conducted on the catalysts after NO_x storage. The results, depicted in Figure 10, reveal that the predominant adsorbed species on the LSX surface are primarily bulk nitrate (736 cm⁻¹, 814 cm⁻¹), nitrate ions (1360 cm⁻¹, 1384 cm⁻¹) [53], and bidentate nitrate (1502 cm⁻¹) (1502 cm⁻¹) [54,55]. Additionally, the characteristic peak at 580 cm⁻¹ corresponds to the perovskite structure, while peaks at 667, 858, and 1451 cm⁻¹ indicate the presence of carbonate species. Lastly, the peak at 1633 cm⁻¹ is attributed to H₂O. Overall, the NO_x

storage on LS0 and LS5 catalysts follows the “nitrate” route, aligning with the findings of the NO_x desorption stage (Figures 8 and 9).

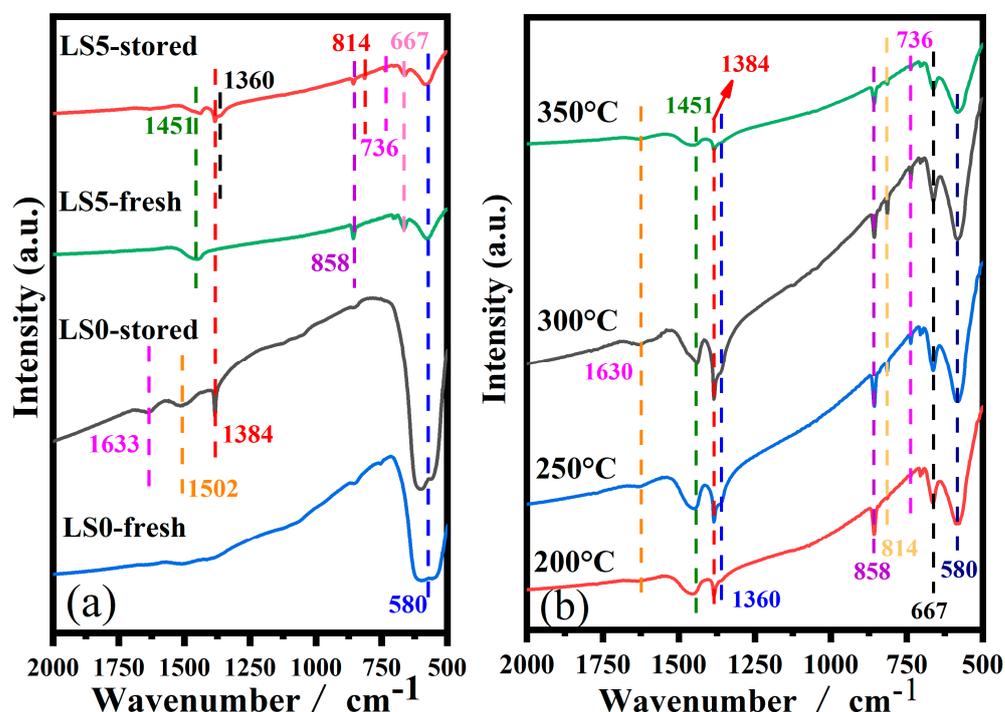


Figure 10. (a) IR spectra of the LSX catalysts before and after NO_x storage at 300 °C; (b) IR spectra of LS5 at different NO_x storage temperatures.

As illustrated in Figure 10a, the LS0 catalyst exhibits nitrate ions and bidentate nitrate species as the stored NO_x , with the storage phase consisting solely of the perovskite phase. On the other hand, the LS5 catalyst displays stored NO_x in the form of nitrate ions and bulk nitrate species. Notably, the peak of carbonate diminishes while, the peak of bulk nitrate species emerges after storage, suggesting a possible conversion from carbonate to bulk nitrate. Moreover, the storage phase consists of perovskite and strontium carbonate following Sr doping [56]. Consequently, it can be inferred that the LS5 catalyst demonstrates favorable NAC and NSC, with the presence of SrCO_3 contributing to this effect.

Based on Figure 10b, LS5 adsorbs NO_x at different storage temperatures and stores it as bulk nitrates and nitrate ions, indicating that the storage phase encompasses both perovskite and strontium carbonate. The intensity of the nitrate species peaks increases as the temperature rises from 200 °C to 300 °C. However, beyond 350 °C, the intensity diminishes, suggesting a decline in the storage phase’s effectiveness at this temperature. Notably, the catalyst exhibits the strongest infrared peak of nitrate at 300 °C, aligning with the LS5’s maximum adsorption–desorption capacity at this temperature.

3.10. NO_x Storage and Reduction Performance

Figure 11 displays the results of lean–rich cycling tests performed on the LS5 sample at different temperatures. During the lean periods, NO undergoes oxidation to NO_2 and is subsequently stored as nitrates. In the rich periods, the stored nitrates decompose and release NO_x [31]. The released NO_x is reduced by C_3H_8 . At different reaction temperatures, there is minimal release of NO_x in the first cycle, indicating complete reduction of NO_x by C_3H_8 . However, as the number of cycles increases, the concentration of NO_x gradually rises while the conversion of NO_x decreases. This can be attributed to the stable storage of NO_x , which occupies the storage sites, and the partial deactivation of active sites on the catalysts, resulting in lower reduction efficiency.

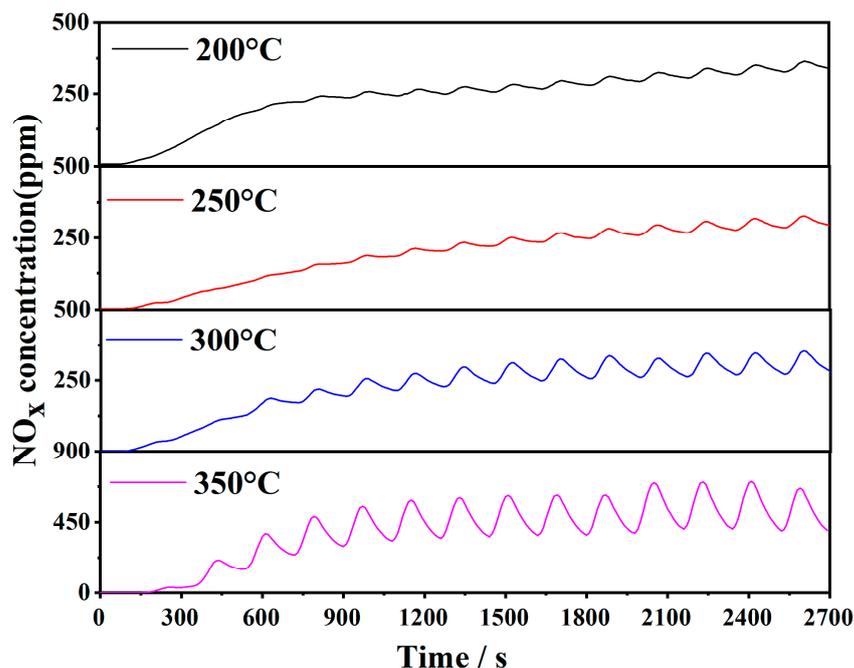


Figure 11. NO_x concentration curves of the LS5 catalyst during the NSR process at different temperatures (200–350 °C).

Figure 12 displays the average NO_x conversion of the LS5 catalyst at different temperatures. As shown, the catalyst achieves an average NO_x removal rate of over 52% within the temperature range of 200–300 °C, with maximum NO_x removal of 61% observed at 250 °C. Subsequently, as the reaction temperature increases, the average NO_x conversion decreases. These findings align with the adsorption and desorption behavior of NO_x. It is likely that the positive correlation between temperature and nitrate stability hampers the decomposition of nitrate and catalyst regeneration, thereby reducing the average NO_x removal rate. In conclusion, when utilizing C₃H₈ as the reducing gas, the LS5 catalyst exhibits a superior average NO_x conversion rate at low temperatures.

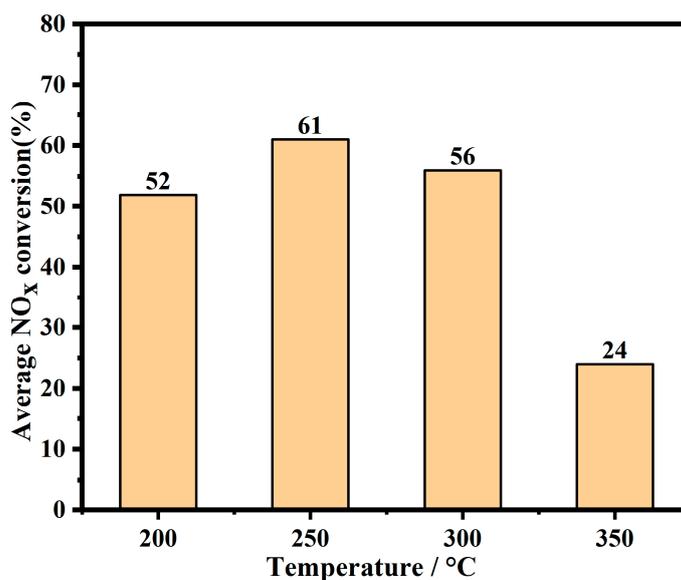


Figure 12. Average NO_x conversion of the LS5 catalyst at different temperatures during lean-rich cycling experiments.

4. Conclusions

In summary, the perovskite $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-\lambda}\text{O}_{3-\delta}$ nanomaterials were successfully synthesized using the solution combustion method. The incorporation of Sr strongly influences the crystalline phase, textural properties, desorption of surface oxygen species, and redox performance of the perovskite catalysts. As a result, it promotes the NO oxidation, NO_x adsorption and storage, and NO_x reduction. In addition, the incorporation of Sr enables the catalysts to exhibit superior resistance to hydrothermal aging and sulfur. The adsorption of NO_x over LSX catalysts at 300 °C occurs predominantly via the “nitrate route”. Substituting 50% of La^{3+} with Sr^{2+} doubled the NO_x adsorption capacity of perovskite LaCoO_3 at 300 °C, which could be attributed to the large surface area, strong reducibility, more surface oxygen species, and elevated surface Co^{2+} concentration. During the lean-rich cycling experiments, the LS5 catalyst achieved an average NO_x conversion rate of over 50% in the temperature range of 200–300 °C, with a maximum NO_x conversion of 61% recorded at 250 °C. Thus, Sr-doped LaCoO_3 perovskite catalysts prepared using the solution combustion method demonstrate outstanding NO_x storage performance at low–medium temperatures, making them a potential material for De- NO_x applications.

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