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# Introduction

Nitrogen oxides  $(NO_x)$  are among the major air pollutants emitted from power plants and diesel vehicles. Selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> has been demonstrated to be effective for power plant exhaust gas, while  $NO_x$  storage reduction (NSR) technology is a promising method to eliminate  $NO_x$  from diesel vehicles.<sup>1-3</sup> In a common NSR catalyst, Pt/BaO/Al<sub>2</sub>O<sub>3</sub>, NO is oxidized to NO<sub>2</sub> on Pt and subsequently adsorbed on BaO as a nitrate species in the lean-burn period.<sup>4,5</sup> During the short fuel-rich period, hydrocarbons are supplied to reduce  $NO_x$  to  $N_2$ . Recently, Sr-doped perovskite oxides (ABO<sub>3</sub>) were discovered to be efficient platinum substitutes in diesel oxidation and NSR reactions.<sup>6</sup> A-sites of perovskites, such as La or Sr, are good sites for NO<sub>x</sub> adsorption and B-sites (Mn or Co) are highly active for NO oxidation.<sup>7,8</sup> The oxidation activity depends on the reducibility, oxygen mobility within the lattice, and the surface defects.9-11

There are two problems that need to be resolved for the application of these catalysts. Catalysts synthesized by traditional methods have low surface areas and large particle sizes, thereby preventing adequate contact between gaseous



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The idea of rational design of perovskite catalysts for NO<sub>x</sub> storage and reduction (NSR) starts from DFT studies on Sr-doped LaMnO<sub>3</sub> (001) plane models: a Mn-terminated plane (Mn-ter) has a higher activity than La- or Sr-ter planes; the number of A-site defects increases when Sr is doped on the surface; O-vacancy formation energies for both La- and Mn-ter gradually decrease with increased Sr loading, and the values for La-ter are always larger than for Mn-ter with the same Sr loading, indicating that the O-vacancy formation is facile on Mn-ter with Sr-doping. This model yields the highest reactivity for oxidation and the lowest energy barrier for O-vacancy formation. A surface tuning method for La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> is introduced. With the exception of the promotion of surface area and pore volume, the ratio of Sr/La and the number of surface-active oxygen atoms and Mn<sup>4+</sup> cations exposed on the outermost layers are improved with an increased contact time between the raw materials and dilute HNO<sub>3</sub>. However, overtreatment leads to a less stable phase of MnO<sub>2</sub> with a high reducibility but significantly restrained NO<sub>x</sub> adsorption. NSR performances under lean-burn/fuel-rich cycles are measured, and the results correspond well with the NO adsorption or oxidation behaviors and DFT calculations.

 $NO_x$  and the active sites. One of the solutions is to use polymeric materials as soft templates for the preparation of porous perovskites.<sup>12-14</sup> Though this method increases the surface area up to 60 m<sup>2</sup> g<sup>-1</sup>, the templates are too expensive for large scale production in industry. Developing economical methods for perovskite synthesis remains a challenge. Another problem is determining how to modify the catalyst surface to expose most of the active sites for efficient NO<sub>x</sub> adsorption and reduction. The facile strategy is doping alkali or rare-earth metals to the A-sites and transitional or precious metals to the B-sites, which improves the reducibility of the B-sites and provides surface-active oxygen.<sup>15,16</sup> However, the optimized redox sites cannot be easily observed due to the nonstoichiometric nature of perovskites. This property limits the control over the particle size and distribution, as well as the surface anchorage.<sup>11</sup> Therefore, it is necessary to design reasonable models to predict these critical properties of perovskites for a given reaction.

Density functional theory (DFT) is a powerful tool to elucidate the electronic structures of catalytic surfaces and their reactivity.<sup>17,18</sup> Researchers are also interested in the structure of perovskite models. The (001) plane of LaMnO<sub>3</sub> plays an important role in oxygen-related processes. MnO<sub>2</sub> (001) is found to be the most stable termination for a solid oxide fuel cell, and the interaction of O with a surface O-vacancy is the rate-determining step for an oxidation reaction.<sup>19–23</sup> Recently, it has been reported that Sr could increase the oxidation ability and diminish the inhibition of NO<sub>2</sub> for La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>.

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In addition, the formation of vacancy sites is more facile on CoO<sub>2</sub>-terminated surfaces.<sup>19</sup> However, a systematic DFT study on LaMnO<sub>3</sub> perovskite, especially the relationship between electronic structures and reducibility, remains incomplete.

In this work, we employed DFT calculations to study the basic properties for a NSR reaction on Sr-doped LaMnO<sub>3</sub> (001) planes and subsequently introduced a surface tuning method to modulate the La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> catalysts. After characterization by temperature programmed reduction (H<sub>2</sub>-TPR) and X-ray photoelectron spectroscopy (XPS) spectra, the actual NSR performance under alternating lean-burn/fuel-rich cycles was also studied.

## Experimental

#### Models selection and DFT details

For the theoretical calculations, we employed the *ab initio* DFT plane wave based Materials Studio 5.5. The generalized gradient approximation plus Hubbard model (GGA+U), according to Perdew, Burke, and Ernzerhof, was used,<sup>24–26</sup> where the value of U was set to be 5.0 for Mn.<sup>27</sup> The typical plane wave cut-off energy was  $E_{cut} = 450$  eV and the spin polarizations were also applied. The Monkhorst–Pack division scheme was selected to generate a set of *k*-points within the Brillouin zone.

Models were cut from the (001) plane of LaMnO<sub>3</sub> bulk with a lattice constant of a = 3.88 Å and a space group of Pm3m. We selected the seven-layer slab for the geometry optimization, where the periodically repeated slabs were separated by a vacuum gap of 15 Å. The slabs were terminated by different planes: La-O and Mn-O were denoted as La-ter and Mn-ter, respectively. A Sr-doped plane was constructed by replacing the La atoms in the outermost layer and sub-outermost layer with Sr atoms in the La-ter and Mn-ter models. The models were denoted as Sr-ter and Sr-Mn-ter (Fig. 1). To study the electronic structures of the A-site defects, we deleted one surface La and Sr atom on the La-ter and Sr-ter models. In addition, 1 to 4 surface La cations were substituted for Sr atoms to study the O-vacancies and their formation energy  $(E_v)$ . The  $E_v$  value is calculated as:



**Fig. 1** The optimized structures of (a) La-ter, (b) Mn-ter and the corresponding Sr-doped (c) Sr-ter and (d) Sr-Mn-ter perovskite (001) planes. Cyan balls are La, purple balls are Mn, green balls are Sr and red balls are oxygen.

$$E_{\rm v} = E({\rm LSM}_{\rm v}) + \frac{1}{2}E({\rm O}_2) - E({\rm LSM}),$$
 (1)

where  $E(\text{LSM}_v)$  is the energy of the reduced slab by removing a surface oxygen atom,  $E(O_2)$  is the energy of oxygen, and E(LSM) is the energy of the slab. It is important to note that a small value of  $E_v$  indicates the ease of forming O-vacancies.

#### **Catalyst preparation**

The perovskite was synthesized by a hydrothermal method.  $La(NO_3)_3$ ,  $Sr(NO_3)_2$ ,  $KMnO_4$ , and  $MnCl_2$  were mixed with a 20 g KOH solution with stirring. The solution was transferred to a stainless steel lined Teflon vessel for hydrothermal treatment at 260 °C for 24 h, and then the precipitate was washed and dried at 60 °C. The precipitate was crushed and sieved through meshes >60 times. A catalyst surface modification method was then used to dissolve the sample with 3 M HNO<sub>3</sub> for different lengths of time. The samples were first dried and then calcined at 400 °C for 2 h. The raw catalyst was denoted as LSM1, and the samples treated with dilute HNO<sub>3</sub> for 10 min, 1 h, and 10 h were denoted as LSM2, LSM3, and LSM4, respectively.

#### Catalyst characterization

The BET surface area of the samples was investigated with a Micromeritics ASAP 2020 apparatus. The crystal structure was determined using XRD measurements (Rigaku, D/max-2200/PC) between 20° and 80° at a step rate of 10° min<sup>-1</sup>, operating at 40 kV and 30 mA, using Cu Ka radiation. A SEM image was obtained with a Helios NanoLab 600i Dual Beam System, FEI Company. XPS was performed with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Ka radiation. The binding energy was referenced to the C 1s line at 284.8 eV. The bulk element atomic compositions were characterized by ICP-AES with an IRIS Intrepid II XSP apparatus (Thermo Fisher Scientific Inc.). H2-TPR was performed on a ChemiSorb 2720 TPx chemisorption analyzer under 10%  $H_2/Ar$  gas flow (50 mL min<sup>-1</sup>), at a rate of 10 °C min<sup>-1</sup>, up to 1000 °C. The H<sub>2</sub> consumption of each catalyst preparation was calculated by comparison with that of a standard CuO sample.

#### NSR tests

NO oxidation measurements were performed in a fixed-bed quartz reactor using 100 mg of the catalyst. The feed gas mixture contained 500 ppm NO, 3% O<sub>2</sub>, and the balance was N<sub>2</sub>. Temperature programed desorption (NO-TPD) was performed in a fixed-bed quartz reactor. Samples were purged under 1000 ppm NO at room temperature after being pretreated in N<sub>2</sub> at 350 °C for 1 h. After isothermal removal of physically adsorbed NO, the temperature was increased to 600 °C at a rate of 10 °C min<sup>-1</sup>. The lean/rich cycles were evaluated at 250 °C in alternative leanburn (500 ppm NO, 5% O<sub>2</sub>) and fuel-rich (500 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub>) atmospheres. The total flow rate was 200 mL min<sup>-1</sup>.

The concentrations of the gases (NO, NO<sub>2</sub>, and  $C_3H_6$ ) were continually monitored by an FTIR spectrometer (MultiGas TM 2030 FTIR). To better evaluate the catalytic activity, kinetic parameters were calculated according to the following equation, applied with the NO conversion:

$$k = -\frac{V}{W} \times (1 - x), \tag{2}$$

where *k* is the reaction rate constant (mL g<sup>-1</sup> s<sup>-1</sup>), *V* is the total gas flow rate (mL s<sup>-1</sup>), *W* is the mass of catalyst in the reactor, and *x* is the NO conversion. The apparent activation energy was calculated using the Arrhenius equation, which is given by:

$$k = k_0 \mathrm{e}^{-E_{\mathrm{a}}/RT},\tag{3}$$

where  $E_a$  is the energy barrier, and it can be obtained from the slope of the  $\ln(k)$  versus 1/T in formula 3.

## **Results and discussion**

#### Influence of exposed surfaces, dopants, and A-site defects

As can be observed in Fig. 2, the projected density of state (PDOS) of Mn 3d contains a valence band (VB) at -7.5 eV < E < 0 and a conduction band (CB) up to 3.0 eV without a strict band gap. The PDOS graphs for the spin-up and spin-down states are considerably different for Mn 3d on both sides of the Fermi energy (E = 0), while O 2p shows a lower state at these regions. One can conclude from the contribution of Mn and O states to the PDOS that the ionic bond, rather than the covalent component of the Mn–O bond, grows from the lowest surface band to the top of the VB, even though the Mn–O bond is not exposed on the outermost layer (La-ter). The large polarization of the Mn 3d states from the small hopping

integrals between ions and neighboring site electrons led to a strong ionic interaction through the bridged oxygen between Mn atoms.<sup>28</sup> Compared to the top of the VBs of Mn 3d for La-ter and Mn-ter, a slight movement to higher energy was observed from -1.74 eV to -1.65 eV, indicating that the Mn 3d states of Mn-ter exhibit stronger binding to the surface than those of La-ter.

A new impurity level of Sr–Mn-ter occurred across the Fermi energy, and the blue-shift of the VB became more apparent than for Mn-ter. The results imply that Mn in the perovskite lattice might have a higher reactivity when it is exposed on the outermost layer and the reactivity could be further improved by Sr. That is, to enhance the activity of the perovskite during the oxidation process, more Mn–O needs to be exposed, and dopants such as Sr are necessary to modify the proportions of the A-sites.

Fig. 3 demonstrates the PDOS graphs of the La-ter and Srter planes and their corresponding A-site defect (Ad) models, where a surface La or Sr cation was removed (dashed circle on the right side of the figure). The Mn 3d states of La-ter were nearly unchanged by eliminating La. Only the end of the CB shifted 0.5 eV to a higher energy. Mn cations on the sub-outermost layer of La-ter with Ad moved towards the defect site to some extent (indicated by the arrow). In comparison to Mn 3d states of Sr-ter, the top of the VB and the impurity level of the Ad model shifted to the Fermi energy, and the bottom of the CB only presented slight changes. The Ad of Sr-ter also showed differences from the Ad of La-ter model. In addition to the movement of the Mn cations towards the defect site, La on the third layer also moved up to the defect site. The results indicate that Mn on the suboutermost layer can be activated by the formation of A-site defects and can be further improved by the dopant Sr.



Fig. 2 Projected density of state (PDOS) graphs of Mn 3d and O 2p orbitals in the La-ter, Mn-ter and Sr-Mn-ter models.



**Fig. 3** The PDOS of the Mn 3d orbitals in the La-ter, Sr-ter and A-site defect models, and the front views of the defect models.



#### O-vacancy formation energy

To directly obtain the relationship between the oxidation activity and the influence factors discussed above, we calculated the O-vacancy formation energy  $(E_v)$  for both the Later and Mn-ter models with different Sr coverages (Fig. 4). The  $E_v$ values of the La-ter models were greater than those of the Mn-ter models for all Sr-doping models, suggesting that O-vacancies preferred to form on the Mn-ter surface, rather than the La-ter surface, *i.e.* Mn-ter surfaces have a higher oxygen storage/release capacity, thereby increasing the oxidation activity during the reaction process. The results are in agreement with the discussion of the electronic structures in Fig. 2. With increased Sr loading, the  $E_v$  values of both the La-ter and Mn-ter models decreased. The lowest value was less than 2.0 eV for Sr-Mn-ter (the sub-outermost layers were "totally" covered by Sr). It is important to note that we could not prepare La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>3</sub> materials with all of the Sr cations exposed on the outermost layer because high levels of SrCO<sub>3</sub> block the perovskite surface when excess Sr(NO<sub>3</sub>)<sub>2</sub> precursors are introduced during the preparation.<sup>29,30</sup> Therefore, the results above are only applicable for the DFT modeling. However, other researchers have also tried to synthesize La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>3</sub> with high Sr loading, and they found that a value of Sr between 0.3 and 0.5 seemed better for the oxidation reaction.<sup>7,31,32</sup> Overall, the effect of Sr is to promote the oxidation activity and O-vacancy formation in the LaMnO<sub>3</sub> (001) planes. The absolute value of  $E_v$  for the La-ter and Mnter models increased with increased Sr loading, revealing that the improvement caused by Sr is greater in the Mn-ter model than in the La-ter model. Consequently, the surface exposed Mn-O bonds have a higher oxidation activity than the exposed La-O or Sr-O bonds.

In summary, in addition to controlling the catalyst surface areas or pore volumes, Sr improves the number of adsorption sites, modifies the surfaces with A-site defects, and enhances the reactivity of Mn cations. Moreover, the surface with terminated Mn atoms has a higher activity than those with terminated La or Sr atoms, and the surface oxygen has a higher mobility (low  $E_v$ ) with more Sr-doped on the terminated Mn surface. However, one must note that in the NSR reaction, sufficient amounts of alkali metals are necessary for NO adsorption directly from the gas phase or NO<sub>2</sub> adsorption from oxidation sites. The following work is based on the results that improved the properties of the NSR reaction.<sup>33</sup>

#### Physicochemical properties of the perovskite

Fig. 5 presents the XRD patterns and SEM images of the LSM1 to LSM4 catalysts. The SEM images showed that some layer clusters grew up from the bulk materials (LSM2). They became considerable on LSM3, and a large amount of clusters were observed on LSM4. Combined with the XRD patterns, these clusters might be  $MnO_2$  oxides. The main peaks for LSM1 to LSM3 are attributed to the standard perovskite phase (a = 3.88 Å with space group Pm3m), which exhibits good agreement with the bulk model used in DFT. LSM4 displayed low crystallization properties compared to the other three samples, and  $MnO_2$  diffraction peaks appeared. Except for  $MnO_2$ , both  $La_2O_3$  and SrO are soluble in dilute  $HNO_3$ . With increased contact time, more A-site cations escape from the perovskite structures and only  $MnO_2$  is left on the surfaces of the materials.

Table 1 lists the surface area, pore volume and Sr/La element ratios for both the bulk and surfaces, which were all improved with increased contact time between the raw materials and dilute HNO<sub>3</sub>. The surface areas was ranged from 0.36 m<sup>2</sup> g<sup>-1</sup> for LSM1 to 67.15 m<sup>2</sup> g<sup>-1</sup> for LSM4. The pore volumes of the catalysts presented the same trend. We also prepared another sample with a 72 h treatment, which had a surface area of 178.95 m<sup>2</sup> g<sup>-1</sup>, and a crystal phase which was mainly  $\beta$ -MnO<sub>2</sub> after calcined at 400 °C, indicating this modulate method is effective for enlarging the surface area and pores in a material.

The ratios of the surface-active oxygen and the  $Mn^{4+}$  cations were calculated from the XPS spectra (Fig. 6) and are summarized in Table 1. The O 1s peaks can be separated into two peaks, referred to as the lattice oxygen at 529.3–530.3 eV



Fig. 5 SEM images and XRD patterns of the catalysts.

Table 1 Surface area (SA), pore volume (PV), element atomic ratio of Sr and La, proportion of surface adsorbed oxygen, Mn<sup>4+</sup> determined by XPS for the four perovskite materials

Sample	$SA\left(m^2 \ g^{-1}\right)$	$PV (cm^3 g^{-1})$	Sr/La <sup>a</sup>	$Sr/La^b$	$O_{ad}/O_{latt}^{b}$ (%)	${\rm Mn}^{4+}/{\rm Mn}^{3+b}$ (%)
LSM1	0.36	0.02	0.90	0.80	13.7	42.0
LSM2	5.90	0.03	0.92	0.94	27.9	62.8
LSM3	22.22	0.09	0.93	0.99	32.1	63.7
LSM4	67.15	0.20	1.01	1.10	33.9	65.8

<sup>a</sup> Calculated from the ICP results of the catalyst powder. <sup>b</sup> Calculated from the XPS spectra.



 $(O_{latt})$  and the chemisorbed surface oxygen at 530.9–531.9 eV  $(O_{ad})$ .  $O_{ad}$  is highly active in oxidation reactions due to its higher mobility compared to the lattice oxygen  $(O_{latt})$ .<sup>33</sup> The spectra of Mn 2p can also be separated into two peaks, attributed to Mn<sup>3+</sup> (641.1 and 652.8 eV) and Mn<sup>4+</sup> (643.0 and 654.3 eV).<sup>29</sup> They were both enhanced by elevating the contact time: LSM1 only had 13.7%  $O_{ad}/O_{latt}$  and 42.0% Mn<sup>4+</sup>/Mn<sup>3+</sup>, while LSM4 yielded 33.9%  $O_{ad}/O_{latt}$  and 65.8% Mn<sup>4+</sup>/Mn<sup>3+</sup>. Combined with the DFT results, this tuning method increases both the number of surface-active oxygen atoms and the concentration of Mn<sup>4+</sup> cations, leading to more O-vacancy formation.<sup>34</sup>

Fig. 7 illustrates the H<sub>2</sub>-TPR profiles of the catalysts. Two broad bands centered at 505 °C and 755 °C for LSM1 can be attributed to the reduction of Mn4+ to Mn3+ for charge compensation from Sr incorporation, and the reduction of Mn<sup>3+</sup> to Mn<sup>2+</sup>, respectively.<sup>34-36</sup> With an increased contact time, the peak at 505 °C for LSM1 shifted to a lower temperature, at 397 °C for LSM4. Another new peak centered at 293 °C appeared for LSM3 and grew considerably for LSM4. Combined with the structural characterization information, this reduction peak can be attributed to being mainly from the contribution of MnO<sub>2</sub> (Mn<sup>4+</sup> to Mn<sup>3+</sup>). Previous work on a comparative study on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> and  $\beta$ -MnO<sub>2</sub> obtained similar TPR peaks at approximately 300 °C on pure β-MnO<sub>2</sub> material.<sup>37</sup> By calculating the ratio of H<sub>2</sub> consumption, this peak was attributed to the reduction of MnO<sub>2</sub> to Mn<sub>3</sub>O<sub>4</sub>, *i.e.* partial reduction of  $\beta$ -MnO<sub>2</sub>. Therefore, this peak can be specifically



Fig. 7  $\,$  H\_2-TPR profiles of the perovskite materials in the temperature range of 30–1000  $^{\circ}\text{C}.$ 

attributed to the reduction of  $Mn^{4+}$  to  $Mn^{3+}$  on  $MnO_2$  surfaces, and the peaks in the range of 397 °C to 505 °C for the samples were due to the reduction of  $Mn^{4+}$  on the perovskite surfaces. The H<sub>2</sub> consumption peaks for the catalysts are listed in Table 2 and the peaks were enhanced with increased contact time. That is, the method improved both the quantity (peak area) and reducibility (peak position) of the  $Mn^{4+}$  cations on the perovskite structures.

#### NSR performance

Fig. 8(a) displays the Arrhenius plots of NO oxidation over the samples. The apparent energy barrier for LSM1 was relatively high (72.7 kJ mol<sup>-1</sup>), however the energy barriers for the other samples were within 44–50 kJ mol<sup>-1</sup>, and only a slight decrease appeared between LSM3 and LSM4. The results demonstrated that with increased Mn<sup>4+</sup> cations and surface-active oxygen atoms, NO oxidation activity is significantly improved. Moreover, apart from the oxidation ability, NO<sub>x</sub> adsorption is another important property for NSR technology.

Fig. 8(b) presents the NO-TPD profiles of the four samples in the temperature range of 50–600 °C, and the total NO desorption values normalized by surface area are listed in Table 3. The total NO<sub>x</sub> desorption significantly decreased

Table 2 H<sub>2</sub> consumption calculated from the H<sub>2</sub>-TPR profiles

	H <sub>2</sub> consumption (a.u.)				
Sample	<300 °C	<600 °C	<800 °C		
LSM1	0	10.0	4.5		
LSM2	0	11.1	5.7		
LSM3	5.0	11.4	4.0		
LSM4	20.6	13.8	1.0		



Fig. 8 (a) Arrhenius plot of NO oxidation and (b) NO-TPD profiles of the perovskite materials.

with an increased contact time, suggesting the adsorption sites for  $NO_x$  are not improved by surface tuning. Considering the decrease of La and Sr element proportions, it can be concluded that the major adsorption sites for  $NO_x$  are La or Sr cations, rather than Mn cations or  $MnO_2$ . Moreover, the Sr loading from ICP and XPS exhibited the same values for LSM3 and LSM4. This might result from the fact that only some of the Sr atoms are successfully doped in the perovskite lattice and the remnant form SrCO<sub>3</sub> during the preparation process. With increased contact time, most of the SrCO<sub>3</sub> is dissolved in HNO<sub>3</sub> and the remaining Sr cations are enriched on the surface of the materials. Two NO peaks and a  $NO_2$ peak can be observed on the NO-TPD profiles for the catalysts. The low temperature NO peak (below 300 °C) can be attributed to the weakly adsorbed NO or nitrite species, the

Table 3Element atomic compositions of Sr, La and Mn, and total  $NO_x$ desorption calculated by NO-TPD over the four perovskite materials

	Sr loading (%)		La loa (%)	La loading (%)		Mn loading (%)	
Sample	ICP	XPS	ICP	XPS	ICP	XPS	$m^{-2}$ )
LSM1	13.0	27.1	14.4	33.9	23.0	39.0	2.19
LSM2	12.9	25.8	14.0	27.4	23.4	46.8	0.19
LSM3	10.6	10.0	11.4	10.1	24.5	67.5	0.14
LSM4	4.0	4.1	4.0	3.7	29.2	83.2	0.06

<sup>a</sup> Calculated from NO-TPD normalized by SA.

high temperature NO peak can be attributed to the nitrite or nitrate species with strong bonding, and the NO<sub>2</sub> desorption peak can be attributed to the nitrate species.<sup>38,39</sup> In comparison to the peaks for LSM4 and LSM3, the intensity of the low temperature NO peak increased significantly. However, the intensity of the high temperature NO peak decreased, even when it was normalized by the surface area. Based on the crystal structures of the two samples, the low temperature peak is tentatively assigned to NO adsorption on  $MnO_2$ , which is easily desorbed at 200 °C, and it seems ineffective for the NSR process (stable adsorption above 250 °C). The concentration of NO<sub>2</sub> is enhanced for LSM4, which shows a good agreement with the NO oxidation.

The NO adsorption/desorption behaviors of the samples were determined in the periodically alternating lean-burn/ fuel-rich atmospheres, as shown in Fig. 9. After the samples reached steady states, LSM1 only provided limited NO capture: seventy percent of NO escapes out of the reactor directly, and NO<sub>2</sub> reaches equilibrium within 1 min. For LSM2 and LSM3, the escaped NO concentrations are nearly 100 ppm. The equilibrium time of NO<sub>2</sub> in a lean-burn period is reduced; approximately 2 min for LSM2 and 1.5 min for LSM3. The results indicate that increased contact time with the catalysts could improve the NO storage process. Only a small amount of NO is obtained for LSM4 and NO<sub>2</sub> does not achieve a steady concentration within 3 min, implying that the LSM4 catalyst exhibits the best NO oxidation activity among the samples. The improvement in this NSR performance originates from the synergistic effect of positive factors: an increase in surface area, surface-active oxygen atoms and Mn<sup>4+</sup> cations, as well as negative factors, such as a decrease in the number of adsorption sites. Under the fuelrich conditions, the trapped  $NO_x$  is released and reduced by C<sub>3</sub>H<sub>6</sub> and no N<sub>2</sub>O is detected during the entire period. The NO<sub>x</sub> maximums of the samples were improved with increased



Fig. 9 Lean/rich cycles of the perovskite materials operated at 300 °C. Lean-burn period: 3 min, gas composition: 500 ppm NO/5%  $O_2$ ; fuel-rich period: 2 min, gas composition: 500 ppm NO/1000 ppm  $C_3H_6$ .

contact time, suggesting the NO oxidation ability was enhanced.

The outlet  $C_3H_6$  peaks significantly decreased: nearly 800 ppm for LSM1 and 150 ppm for LSM4, indicating that more  $C_3H_6$  can react with the trapped  $NO_x$  to fulfil the NSR process. The NO concentrations of the samples increased under the fuel-rich period, which shows the same trend as the NO-TPD results. Moreover, the NO peak widened for LSM4 compared with LSM2 and LSM3, indicating that perovskite with excess  $MnO_2$  decreases the NSR performance. This can be attributed to the lack of effective adsorption sites such as alkali metals on  $MnO_2$ , and the fact that the adsorption process of NO is weak and NO is easily desorbed from the surface of  $MnO_2$  under NSR working temperatures (250–300 °C). The NO-TPD profiles of LSM4 also showed similar results.

## Conclusions

Combining DFT calculations with experimental results, three aspects of  $La_xSr_{1-x}MnO_3$  catalysts have been modulated and evaluated for NSR technology:

(1) The surface area and pore volume of the catalysts are increased by the modification process because of the corrosion effect of dilute HNO<sub>3</sub> to  $La_2O_3$  and SrO rather than MnO<sub>2</sub>, which provides more effective surfaces for NO<sub>x</sub> adsorption or oxidation;

(2) La or Sr cations in the outermost layer of the perovskite are removed by the modification process, promoting the number of O-vacancies and the reactivity of the  $Mn^{4+}$  cations in the perovskite lattice. From the calculated models, a Mn-terminated surface with Sr-doped in the A-sites of the LaMnO<sub>3</sub> (001) plane yields the highest activity for oxidation and the lowest energy barrier for O-vacancy formation. This exhibits good agreement with the apparent energies barriers for NO oxidation;

(3) The crystallized  $MnO_2$  oxides might form on the outermost layer of the perovskite if the contact time with  $HNO_3$ becomes too long. Although the reducibility of the material is further enhanced, the number of NO adsorption sites dramatically decreases even when normalized by the surface area. The adsorbed  $NO_x$  is unstable and can easily desorb from the catalyst surface, leading to a NO adsorption blockage in the NSR process.

Therefore, we tentatively propose the goal of rationally designing perovskite catalysts for NSR technology: to improve the surface area or pore volume, to expose more transitional metals in the outermost layer of the catalyst which can provide adequate adsorption sites, and to increase the doping amount to the catalyst. This improvement could result in  $SrCO_3$  crystallization on the surface to cover the oxidation sites.

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