Kinetics investigation of NO + CO reaction on La–Sr–Mn–O perovskite-type mixed oxides

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Abstract

Substituted perovskite-type mixed oxides of the general formula La 1−x Sr x (Mn III/Mn IV)O 3 prepared by the nitrate method were examined by X-ray diffractionometry (XRD) and the diffraction data were analyzed using the Rietveld refinement method. The amount of desorbed oxygen from the samples when heating in a He atmosphere was estimated with thermogravimetric techniques. The substitution of La III by Sr II leads to a gradual increase of Mn IV in the solids and to the transition from an oxygen excess state to an oxygen deficient one. The samples were checked controlling them. This methodology of simulation provides easily kinetic (activation energies) as well as thermodynamic (heats of adsorption) parameters which otherwise would necessitate differentiated experimental set-ups. The reaction rate profiles were simulated using a relationship of the form H ads 1 = E app 1 + R T low and high temperatures R app 1 . From the fitting data the true activation energies E 1 and E 2 were estimated for R app 1 and R app 2 as well as the heats of adsorption ΔH ads NO and ΔH ads CO for the NO and CO species. Finally, the values of R app 1 estimated from typical Arrhenius plots in R 1 = f(T) at the low temperature region are in reasonable agreement with the difference E 1 = ΔH ads NO , a fact validating the results of simulation/fitting and indicating its usefulness for describing the reaction rates and estimating the kinetic and thermodynamic parameters controlling them. This methodology of simulation provides easily kinetic (activation energies) as well as thermodynamic (heats of adsorption) parameters which otherwise would necessitate differentiated experimental set-ups.

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1. Introduction

Perovskite-type oxides of the general formula ABO 3 predominate among the mixed metal oxides, which are used in various physicochemical applications like sensors, conductors and superconductors, photocatalysts and catalysts. The unique electrical and catalytic properties of perovskites with a lanthanide in A-position and a transition metal in B-position have rendered these solids effective for various industrial applications [1]. A great deal of interest has been devoted to manganese–lanthanum perovskites due to their unusual transport and magneto-transport properties [2]. It has also been shown that LaMnO 3 perovskite exhibited an abrupt change in conductivity as well as in magnetic susceptibility as a function of temperature close to 720 K [3]. Conductivity can be enhanced considerably by partial substitution of the lanthanide by a divalent ion. For the system La 1−x Sr x MnO 3 the Mn ions are Mn II for x ≤ 0 whether an increase in x results in the creation of Mn IV ions, thereby increasing conductivity. Additionally, La 1−x Sr x MnO 3 type perovskites have been extensively used as cathode materials in ZrO 2 based solid oxide fuel cells [4]. These materials have also been considered of great interest concerning their utilization as catalysts for exhaust gas de-pollution processes and their catalytic performance has been compared with that of noble metals [5,6]. Their catalytic activity has been studied for various oxidation and reduction processes. The catalysts LaMnO 3, La 1−x Sr x MnO 3 (M = Fe, Co, Mn, Cr) and LaMn 0.6 Fe 0.4 O 3 prepared via various methods have shown a noticeable activity for the catalytic reduction of NO by CO [7–9] despite their low specific surface area.

LaMnO 3 is a non-stoichiometric compound [10] in which, in order to reduce the static Jahn–Teller distortion of...
Mn$^{III}$, cationic vacancies are created, accompanied by the formation of Mn$^{IV}$ ions and an oxygen excess [11–14]. The substitution of the trivalent metal ion in A-position (La) with a divalent cation (Sr) is accompanied by the modification of the oxidation state of metal cation in B-position, thus leading to the formation of structural defects and oxygen excess is denoted. As a result by increasing the degree of substitution $x$ the amount of released oxygen decreases due to a decrease of cation vacancies concentration [15–17]. It can be concluded that the substitution of a divalent cation for La$^{3+}$ is accompanied by oxidation of the B cation (Mn). The system LaMnO$_{3-x}$ is one of the few perovskite systems that display apparent oxygen excess. This sample, prepared by calcination of the corresponding oxides in air at 1473 K, proved to have a composition of LaMnO$_{3-x}$ [10] while similar $\delta$ values for lanthanum manganates were also reported elsewhere [11,18–20]. Neutron diffraction studies revealed that oxygen excess in LaMnO$_{3-x}$ is accommodated by vacancies at the A- and B-sites with partial elimination of La (as La$_2$O$_3$), the composition of the perovskite being La$_{1-x}$Sr$_x$MnO$_{3-x/2}$, where V is a cation vacancy. The non-stoichiometry in LaMnO$_{3-x}$ can also be modified by partial substitution of A and B cations [21–23]. For Sr$_{1/2}$La$_{1/2}$MnO$_{3-\delta}$ perovskites ($x = 0.0–0.5$) it has been found [23] oxygen non-stoichiometry in the temperature range from 873 to 1273 K.

In the present work, eight perovskite-type mixed oxides of general formula La$_{1-x}$Sr$_x$MnO$_{3-x/2}$ ($x = 0.0, 0.15, 0.3, 0.4, 0.6, 0.7, 0.8, 0.9$) were prepared according to the nitrate method as follows: calculated amounts of La(NO$_3$)$_3$·6H$_2$O (Fluka), Sr(NO$_3$)$_2$ (Ferak) and Mn(NO$_3$)$_2$·4H$_2$O (Riedel-de Haën) were mixed and heated up to 400 °C at a rate of 3 °C/min. After no NO$_2$ fumes were visible, the samples were further heated for 4 h at 900 °C at atmospheric conditions. At the end of this step, the mixtures were cooled and after grinding in an agate mortar they were heated again for another 4 h at 1000 °C. The solids were then slowly cooled to room temperature and stored for further use. The obtained materials with some of their properties are shown in Table 1.

### 2. Characterization of the solids

#### 2.1. XRD data and Rietveld analysis

The specific surface area of the prepared materials was checked by N$_2$ adsorption (BET) at 77 K using a single point Carlo-Erba Sorpty 1750 apparatus. All samples before

**Table 1.** Prepared solids, detected crystal phases (XRD), amount of oxygen desorbed (thermogravimetric O$_2$/TPD) in $\mu$mol/g and specific surface area (BET) in m$^2$/g.

<table>
<thead>
<tr>
<th>Solid composition</th>
<th>Crystal phases</th>
<th>Oxygen desorbed ((\mu)mol of sample)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO$_{3-x}$</td>
<td>La$_2$MnO$_3$, La$_2$O(lm)</td>
<td>109.6</td>
<td>2.3</td>
</tr>
<tr>
<td>La$<em>{0.675}$Sr$</em>{0.325}$MnO$_{3-x}$</td>
<td>La$_2$MnO$_3$, La$_2$O(lm)</td>
<td>62.5</td>
<td>2.1</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_{3-x}$</td>
<td>La$_2$MnO$_3$, La$_2$O(lm)</td>
<td>35.0</td>
<td>2.1</td>
</tr>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$MnO$_{3-x}$</td>
<td>La$_2$MnO$_3$, La$_2$O(lm)</td>
<td>33.0</td>
<td>2.0</td>
</tr>
<tr>
<td>La$<em>{0.3}$Sr$</em>{0.7}$MnO$_{3-x}$</td>
<td>La$_2$MnO$_3$, La$_2$O(lm)</td>
<td>50.2</td>
<td>2.2</td>
</tr>
<tr>
<td>La$<em>{0.2}$Sr$</em>{0.8}$MnO$_{3-x}$</td>
<td>La$_2$MnO$_3$, La$_2$O(lm)</td>
<td>47.0</td>
<td>2.0</td>
</tr>
<tr>
<td>La$<em>{0.1}$Sr$</em>{0.9}$MnO$_{3-x}$</td>
<td>Mixture of SrMnO$<em>3$, and LaMnO$</em>{3-x}$</td>
<td>70.1</td>
<td>2.1</td>
</tr>
<tr>
<td>La$<em>{0.0}$Sr$</em>{1.0}$MnO$_{3-x}$</td>
<td>Mixture of SrMnO$<em>3$, and LaMnO$</em>{3-x}$</td>
<td>234.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Main crystal phase.
The percentage of the observed crystal phases as calculated by Rietveld analysis and the unit cell parameters of the perovskite phase are shown in Table 2.

<table>
<thead>
<tr>
<th>Solid (nominal composition)</th>
<th>Observed phases</th>
<th>Unit cell parameters of perovskite (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO₃ ± δ</td>
<td>Not present</td>
<td>87% La₀.₉₅ MnO₃ ± x R⁻³ c</td>
</tr>
<tr>
<td>La₂Sr₂MnO₄</td>
<td>Not present</td>
<td>89% La₀.₇₉ Sr₀.₂₁ MnO₃ ± δ</td>
</tr>
<tr>
<td>La₃Sr₃MnO₄</td>
<td>10% Not present</td>
<td>85% La₀.₇₀ Sr₀.₃₀ MnO₃ ± δ</td>
</tr>
<tr>
<td>La₀.₇Sr₀.₃MnO₃ ± δ</td>
<td>15% Present</td>
<td>Mixture of SrMnO₃ ± δ and LaMnO₃</td>
</tr>
<tr>
<td>La₀.₆Sr₀.₄MnO₃ ± δ</td>
<td>13% Present</td>
<td>Mixture of SrMnO₃ ± δ and LaMnO₃</td>
</tr>
<tr>
<td>La₀.₅Sr₀.₅MnO₃ ± δ</td>
<td>10% Present</td>
<td>Mixture of SrMnO₃ ± δ and LaMnO₃</td>
</tr>
<tr>
<td>La₀.₄Sr₀.₆MnO₃ ± δ</td>
<td>5% Not present</td>
<td>Present Mixture of SrMnO₃ ± δ and LaMnO₃ ± δ</td>
</tr>
</tbody>
</table>

* Due to low crystallinity of these samples Rietveld analysis was unable to be performed.

Measurement were degassed at 250°C for 4 h at P = 4 mbar. The obtained results are included in Table 1.

2.2.3. Thermogravimetric O₂/TPD analysis

Temperature-programmed desorption (TPD) experiments for the prepared solids were conducted using a NETZSCH STA 449C thermobalance. The detailed description of the experimental procedure has been published previously [22]. Briefly, each sample (~70 mg) was placed in an alumina crucible and Al₂O₃, which undergoes no thermal change in the temperature range of the experiment, was placed in an identical crucible as a reference sample. The temperature of the samples was measured by thermocouples of platinum and of platinum plus 10% rhodium. The sample was first pretreated in He stream (20 ml/min) from ambient temperature up to 700°C. Following this, it was cooled to 550°C in the same atmosphere and then it was kept under O₂ flow (20 ml/min) for 1 h. After cooling at 70°C, a gas flow of He (10 ml/min) was passed through the sample subjected to...
heating until 900°C. A weight loss is observed during the last calcination step of the procedure which corresponds to oxygen desorption. The results are summarized in Fig. 3.

2.2.4. Iodometric determination of Mn\(^{III}\) and Mn\(^{IV}\) state

An adaption of the iodometry method described by Vogel [24] was used for the determination of the amount of Mn\(^{III}\) and Mn\(^{IV}\). As originally suggested, Mn\(^{III}\) and Mn\(^{IV}\) are reduced with excess hydrochloric acid to the divalent state as follows: Into a 500 ml flask, 30 ml of 0.5 N HCl and 25 ml of 0.16 M KI solution, excess in both cases, were added. The flask was warmed to about 50°C and a weighed amount of the sample (∼0.2 g) was added. Chlorine is produced by the reactions:

\[
2\text{Mn}^{\text{III}} + 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{Mn}^{\text{II}} \quad (1)
\]

The produced chlorine reacts with the surplus of potassium iodide solution and iodine is formed. After the sample dissolved completely, the flask was cooled in a dark place and its content was titrated with standard thiosulfate solution 0.02 N using starch as indicator. The results are given in Table 3 as equivalent Mn ox per 100 g of sample. The same results are shown in Fig. 4 as a function of substitution \(x\) of La by Sr in La\(_{1-x}\)Sr\(_x\)MnO\(_3\pm\delta\).

2.2.5. Catalytic activity

The catalytic activity of the perovskite series La\(_{1-x}\)Sr\(_x\)MnO\(_3\pm\delta\) was studied for the reduction of nitric oxide by carbon monoxide using a bench scale plug–flow reactor.

Table 3
Isomery results, calculated coefficients of manganese and oxygen in the formula La\(_{1-x}\)Sr\(_x\)Mn\(_y\)(III)Mn\(_{1-y}\)(IV)O\(_3\)±δ and the absolute values |\(\delta\)|

| \(x\) | \(\text{Mn}^{\text{III}}\) (mol/100 g) | \(\text{Mn}^{\text{IV}}\) (equivalent/100 g) | Coefficients for elements in formula | |\(\delta\)| |
|---|---|---|---|---|---|
| 0 | 0.4135 | 0.4818 | 0.83 | 0.17 | 3.083 | 0.083 |
| 0.15 | 0.4271 | 0.5107 | 0.80 | 0.20 | 3.023 | 0.023 |
| 0.3 | 0.4416 | 0.5499 | 0.75 | 0.25 | 2.972 | 0.028 |
| 0.4 | 0.4518 | 0.5896 | 0.68 | 0.32 | 2.962 | 0.038 |
| 0.6 | 0.4718 | 0.6587 | 0.61 | 0.30 | 2.895 | 0.105 |
| 0.7 | 0.4856 | 0.7131 | 0.53 | 0.47 | 2.884 | 0.116 |
| 0.8 | 0.4980 | 0.7668 | 0.52 | 0.48 | 2.840 | 0.160 |
| 0.9 | 0.5110 | 0.7412 | 0.55 | 0.45 | 2.775 | 0.225 |

Fig. 3. A typical TG curve with the temperature program of: (a) the TPD \(\text{O}_2\) experiments and (b) the temperature profiles of all samples during the last step of the procedure.

Fig. 4. The percentage values of: (a) Mn\(^{III}\) and Mn\(^{IV}\), (b) \(\delta\) values found by isomeric analysis of La\(_{1-x}\)Sr\(_x\)Mn\(_y\)(III)Mn\(_{1-y}\)(IV)O\(_3\)±δ samples and (c) both values of |\(\delta\)| and of the desorbed \(\text{O}_2\) from TPD experiments as a function of the degree of substitution \(x\).
PFR, under atmospheric pressure. The reactor was connected to a gas chromatograph (GC) for analysis of reactants and products equipped with a TCD with He as a carrier gas and connected to a PC for data acquisition. Briefly a gas mixture of NO (2%), CO (2%) and He (96%) was fed at a flow rate of 100 ml/min through the catalyst bed containing a constant amount of the catalyst ($w = 200 \text{ mg}$). Flow rates were adjusted using MKS Type 247 mass flow controllers. The system was heated externally via a tubular furnace, regulated by a SUR BERLIN controller, using a thermocouple placed in the centre of the catalyst bed, within ±2°C. A 10-port valve enables sampling of 1 cm³ of reactants and products for analysis using two columns, one Porapac Q for N₂O and CO₂ and one molecular sieve 13x for N₂, NO and CO. The procedure of the analysis was similar to that described in [33]. The catalysts were tested in the temperature region of 220–560°C and from the data obtained the degrees of conversion and the reaction rates were calculated. The temperature profiles for the percentage conversion of NO and CO, the selectivity towards N₂ as well as the production of N₂O in arbitrary units are shown in Fig. 5.

3. Results

3.1. Catalysts characterization

3.1.1. XRD data and Rietveld analysis

The XRD patterns of the catalysts summarized in Fig. 1, were compared to the relevant data in the Data Bank available in the diffractometer. The results reveal that a pure perovskite structure has not been formed. The formation of such a pure phase for materials prepared via ceramic method necessitates a calcination at higher temperatures than 1000°C employed in the present case. Furthermore, it is well known that a single phase perovskite cannot be formed for the tested system $La_{1-x}Sr_xMnO_3$ with the conventional solid state method for $x > 0.6$ [17,25,26]. In the case of the first samples of the series ($x \leq 0.4$) apart from the perovskite-type
structure, La(OH)3 was also detected. The exact composition of the perovskite phase for each sample is shown in Table 1. With further substitution of La by Sr (x ≥ 0.4), in addition to the major perovskite phase, a second phase of Sr2MnO4 was observed. For higher degrees of substitution, La(OH)3 is not detected anymore. In the present study for x ≥ 0.7 a mixture of LaMnO3±c and SrMnO3±c is detected and the phase Sr2MnO4 is also present. In Fig. 1, the peak positions of the phases La(OH)3 and Sr2MnO4 are denoted in the top by vertical bars while the rest of the peaks correspond to the major perovskite phase.

A Rietveld refinement of the obtained XRD data was made using a relevant computer program [27] for quantitative phase analysis of the multicomponent systems. Typical results for two of the tested samples are shown in Fig. 2 where the experimental and calculated XRD patterns are marked with (+) symbols and by solid lines, respectively. The satisfactory matching of the experimental with the calculated values of XRD data can be evaluated from the curve presented at the bottom of each figure which corresponds to the difference between these two quantities. The corresponding percentages of the crystal phases are included in Table 2 together with the unit cell parameters for the main phase. The content of Sr in the samples in accordance with other data reported in the literature for similar samples [28] is only pointed in the graph because the rhombohedral lanthanum-deficient phase La63Sr37MnO3±c cannot be connected and therefore compared with the rest hexagonal perovskite phases.

### 3.1.3. Thermogravimetric O2/TPD analysis

The applied temperature program and a typical TG curve are presented in Fig. 3a while the TPD profiles of all the samples during the last step where the desorption of oxygen takes place are shown in Fig. 3b. During the first calcination step, from room temperature to 700 °C in He atmosphere (flow of 20 cm3/min), a weight loss of 0.4 observed corresponding to the desorption of oxygen and probably other absorbed molecules like water and carbon dioxide. In the second step, the temperature is kept to 700 °C, always under He flow, and the TG curve remains constant. In the third step, the temperature is lowered to 550 °C and the He flow is switched to O2 (20 cm3/min). At this stage a sharp increase of the weight is observed due to O2 adsorption. In the fourth step, the temperature is lowered to 70 °C, under O2 atmosphere, and kept there for 20 min. Further increase of the weight is observed during this step as expected due to further O2 adsorption.

Finally, at the fifth and last calcination step from 70 to 900 °C under helium flow, a weight loss is observed (Fig. 2b) which corresponds to oxygen desorption. The amount of desorbed oxygen, during this last calcination step is reported in Table 1 as micromoles of oxygen desorbed per gram of solid. We observe that for low degrees of substitution of La by Sr the amount of desorbed oxygen decreases as the Sr content of the sample increases while for higher degrees of substitution (x > 0.7) the desorbed oxygen increases noticeably reaching the maximum value for x = 0.9. As shown in Fig. 3b, the amount of desorbing oxygen for the catalyst La0.7Sr0.3MnO3±c is more than double of the corresponding amount for the catalyst LaMnO3±c containing no Sr at all.

### 3.1.3.1. Iodometric analysis

The content of MnIII and MnIV can be calculated [29] from the titration results (Mnox) knowing the total manganese content (Mn) from the preparation data of the solids from Eqs. (3) and (4):

\[ \text{Mn}_n = n_1 \text{Mn}^{\text{III}} + n_2 \text{Mn}^{\text{IV}} \]  
\[ \text{Mn}_\text{ox} = n_1 \text{Mn}^{\text{III}} + 2n_2 \text{Mn}^{\text{IV}} \]

It can be derived that

\[ \text{Mn}^{\text{III}} = 2\text{Mn}_n - \text{Mn}_\text{ox} \]  
\[ \text{Mn}^{\text{IV}} = \text{Mn}_\text{ox} - \text{Mn}_n \]

The resulting coefficients for the manganese in the formula La1−xSrMn1−xIII+xIVO3±c are reported in Table 3. We observe that the percentage of Mn(IV) increases as La is substituted by Sr reaching the value of about 50% in high degrees of substitution. Fig. 4a presents the calculated percentage values of MnIII and MnIV in the solids versus the degree of substitution of La for Sr. The amount of MnIII declines as x increases while MnIV increases with x until the value of about 50%. Oxygen content was evaluated from the cation composition based on the charge neutrality condition. In Fig. 4b, δ values found by the above-described analysis are plotted against the degree of strontium substitution x. The transition from an oxygen excess state to an oxygen deficiency one is apparent as shown by the decrease of δ values as a function of Sr substitution. The positive
values of δ for the first two samples (x < 0.2) are replaced by negative ones for the rest six samples of the examined series (0.2 < x < 0.9). This behavior is also reported in Table 3 in the form of the oxygen coefficient in the formula La$_{1-x}$Sr$_x$Mn$_{1+y}$Mn$_{30-x}$O$_{32+y}$.

3.2. Catalytic studies

The solids La$_{1-x}$Sr$_x$MnO$_{3+δ}$ were active for the interconversion of NO and CO between 220 and 560 °C showing a significant activity in this temperature range. In Fig. 5, apart from the temperature profiles for the percentage conversion of NO (XNO) and CO (XCO), the N$_2$ formation and the N$_2$O production in arbitrary units are also shown versus temperature. At temperatures higher than about 480-500 °C the N$_2$ selectivity is always 95–100%. It is noted that the production of N$_2$O starts at low temperatures and reaches a maximum at 340–380 °C depending on the composition of the sample and at higher temperatures its production decreases. We observe that the production of N$_2$O decreases as the degree of substitution of Sr for La increases while the peak is shifted to higher reaction temperatures.

The integral reaction rates of NO consumption (μmol/(g s)) at T = 300, 360, 420 and 500 °C as well as the corresponding rates of CO consumption, both as a function of the catalyst composition, are shown in Fig. 7a and b, respectively. It is obvious that LaMnO$_3$ is the most active catalyst and the activity declines as Sr content increases. In the third part of Fig. 7, the values of N$_2$O production in arbitrary units, read out from Fig. 5, are also plotted against x. It can be seen that the catalysts with higher Sr content produce less N$_2$O. Combining this with the above described iodometric results, we can say that the lower activity and lower selectivity towards N$_2$O, correspond to lower values of the ratio Mn$^{II}$/Mn$^{IV}$ as well as lower values of δ, which express the oxygen excess (+δ) or deficiency (−δ) in the samples (see Fig. 4). In Fig. 7c, we notice that for low temperatures (300 and 360 °C) the curves showing the N$_2$O production are characterized by a continuous decline while at higher temperatures (420 and 500 °C), where about the maximum production of N$_2$O is observed for all samples, the curves show a different trend as mentioned previously (see Fig. 5).

In Fig. 8, the variation of the ratio of the products CO$_2$/(N$_2$ + N$_2$O) is shown as a function of reaction temperature. It is observed that this ratio takes values of about unity at low temperatures and increases towards values of two as the temperature increases. We emphasize that this transition is more obvious for the last four samples of the series tested where the amount of Sr and Mn$^{IV}$ is higher. In these catalysts, the production of nitrous oxide is less compared to the first four samples with less Sr and Mn$^{IV}$.

In the same Fig. 8 we have drawn Arrhenius-type plots of the form ln R$_{NO} = f(1000/T)$ as well as ln R$_{CO} = f(1000/T)$, where R is the observed rate of conversion in μmol/(g s). As observed from the Arrhenius-type plots, at low temperatures there is a straight-line part and from its slope the apparent activation energies in this low-temperature region (E$_{app}$,low T) can be estimated. These values are tabulated in Table 5. At this low-temperature region the ratio CO$_2$/(N$_2$ + N$_2$O) reaches values around the value of 2. Then as the temperature increases we reach the medium reaction range which is shaded in Fig. 8. In this medium shaded region the Arrhenius lines return to a steeper slope. It is in this region that the transition of the ratio CO$_2$/(N$_2$ + N$_2$O) takes place from 1 towards 2. Then at higher temperatures the Arrhenius lines return to a steeper slope. In this temperature range the ratio CO$_2$/(N$_2$ + N$_2$O) reaches values around 2. These results will be discussed extensively next.

4. Discussion

As shown by the determination of the reaction rates, the substitution of lanthanum by strontium decreases the catalytic activity. Additionally, iodometric analysis showed that the increase of Sr content leads to a transition from an oxygen excess state to an oxygen deficient one. There is an obvious similarity between the graphs depicting the reaction rates for the NO and CO elimination versus the degree of substitution (Fig. 7a and b) on one hand and the graph of the parameter δ decreasing linearly with x (Fig. 4b) on the other. By increasing x the oxygen vacancies in the samples increase and the catalytic activity declines accordingly. In
other words, samples deficient in oxygen (low $\delta$ values) show lower activity in catalytic experiments compared to the ones with oxygen excess (high $\delta$ values). This should be due to the fact that the oxygen deficient samples retain a part of the oxygen produced by the decomposition of NO ($\text{NO}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{O}_{\text{ads}}$) thus inhibiting all the reaction steps requiring mobile oxygen in order to take place. These reactions are described next. So, the smaller the value of $\delta$ is, the lower the interconversion of NO and CO proves to be.

In Fig. 4c, two parameters related to the presence of oxygen in the samples and determined by different methods are shown as a function of the substitution $x$: first, the absolute value of $\delta$ ($|\delta|$) as derived by the results taken from iodometric analysis and second the amount of desorbed oxygen as determined by O$_2$/TPD experiments. Obviously, these two curves show close similarity. For low values of $x$, the samples with oxygen excess probably desorb a part of this excess during the O$_2$/TPD experiments except for the suprafacial adsorbed oxygen, while for high degrees of $x$, the increased values
of desorbed oxygen are due to both suprafacial and oxygen desorbed from the bulk of the solid which had occupied the inner anion vacancies created by substitution of Sr for La. The catalytic reduction of nitric oxide by carbon monoxide on perovskites [30–32] has been described to proceed according to the following elementary surface processes:

\[
\begin{align*}
\text{NO}_\text{gas} & \rightarrow \text{NO}_{\text{ads}} \quad (a) \\
\text{NO}_{\text{ads}} & \rightarrow \text{N}_{\text{ads}} + \text{O}_{\text{ads}} \quad (b) \\
\text{CO}_{\text{gas}} & \rightarrow \text{CO}_{\text{ads}} \quad (c) \\
\text{CO}_{\text{ads}} + \text{O}_{\text{ads}} & \rightarrow \text{CO}_2 \quad (d) \\
2\text{N}_{\text{ads}} + \text{NO}_{\text{ads}} & \rightarrow \text{N}_2\text{O}_{\text{ads}} \quad (e) \\
\text{N}_2\text{O}_{\text{ads}} & \rightarrow \text{N}_2 + \text{O}_{\text{ads}} \quad (f) \\
2\text{O}_{\text{ads}} & \rightarrow \text{O}_2 \quad (h)
\end{align*}
\]

These reactions can be expressed by the following three main routes [31–33]:

1. **Route (A):**
   - \(2\text{NO} \rightarrow \text{CO}_2 + \text{N}_2\) (A)

2. **Route (B):**
   - \(2\text{NO} \rightarrow \text{CO} + \text{N}_2\) (B)

3. **Route (C):**
   - \(2\text{NO} \rightarrow \text{CO}_2 + \text{N}_2\) (C)

The last route (C) includes only nitric oxide transformation and can take place on top of any one of the previous routes. Which route is actually followed can be verified by checking the ratio of the products. As it has been reported previously for similar materials [33], for low reaction temperatures (\(\Theta \leq 350^\circ\text{C}\)) and low degrees of NO and CO conversion (<5%), the ratio of \(\text{CO}_2/(\text{N}_2 + \text{N}_2\text{O})\) takes values around and above unity (Fig. 8), which means that route (B) predominates, but also route (C) takes place. Then at higher reaction temperatures (above \(\sim 350^\circ\text{C}\)) a gradual change from values \(\text{CO}_2/(\text{N}_2 + \text{N}_2\text{O}) \approx 1\) to \(\approx 2\) is observed. This transition from route (B) to route (A) indicated/covers the shaded area in Fig. 7 has been completed at \(\Theta \gtrsim 450^\circ\text{C}\). From this point onwards, only route (A) takes place. The same behavior was observed in other works too [34,31] where it was suggested that the catalytic transformation following route (B) at low temperatures is controlled by oxygen generated from the decomposition of NO described by reaction (b) while at high temperatures where it follows route (A) is controlled by reaction (d). The higher amount of \(\text{N}_2\) in the middle transition rate (Fig. 5) shows that route (C) does not occur extensively while at higher temperatures the decomposition of \(\text{N}_2\text{O}\) takes place according to reaction \(\text{N}_2\text{O} \rightarrow \text{N}_2 + 1/2\text{O}_2\) producing \(\text{N}_2\).

The two reaction rate components, the first at low temperature (\(R_{\text{low},\Theta}\)) and the second at higher temperature (\(R_{\text{high},\Theta}\)), can be expressed by the following equations:

\[
\begin{align*}
R_{\text{low},\Theta} &= k_1\Theta_{\text{NO}} \\
R_{\text{high},\Theta} &= k_2\Theta_{\text{CO}}\Theta_{\text{O}}
\end{align*}
\]

where \(\Theta\) is the corresponding surface coverage.

The total reaction rate is then expressed by the sum:

\[
R_{\text{total}} = w_1R_{\text{low},\Theta} + w_2R_{\text{high},\Theta}
\]

where \(w_1, w_2\) are the weighing coefficients for routes (B) and (A), respectively, that can be estimated precisely from the ratio \(\text{CO}_2/(\text{N}_2 + \text{N}_2\text{O})\) (see Fig. 7). The \(w_1, w_2\) values are listed in Table 4 for all tested samples in the whole range of reaction temperature.

Then the reaction rates can be described by the relationships

\[
\begin{align*}
R_{\text{low},\Theta} &= k_1\Theta_{\text{NO}} = k_1 \frac{K_{\text{NO}}P_{\text{NO}}}{1 + K_{\text{NO}}P_{\text{NO}}} \\
R_{\text{high},\Theta} &= k_2\Theta_{\text{CO}}\Theta_{\text{O}} = k_2 \frac{K_{\text{CO}}P_{\text{CO}}K_{\text{O}}P_{\text{O}}}{1 + K_{\text{CO}}P_{\text{CO}}K_{\text{O}}P_{\text{O}}}
\end{align*}
\]

### Table 4

The values of the weighing coefficient \(w_1\) estimated from the ratio \(\text{CO}_2/(\text{N}_2 + \text{N}_2\text{O})\) in the whole range of temperature reaction for the eight catalysts

<table>
<thead>
<tr>
<th>(\Theta (^\circ\text{C}))</th>
<th>(x)</th>
<th>0.0</th>
<th>0.15</th>
<th>0.3</th>
<th>0.4</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
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<tbody>
<tr>
<td>260</td>
<td>0.9999</td>
<td>0.9997</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.8582</td>
<td>0.9854</td>
<td>1.0000</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>0.7157</td>
<td>0.9136</td>
<td>0.9487</td>
<td>0.4797</td>
<td>0.9999</td>
<td>0.8262</td>
<td>0.9767</td>
<td>1.0000</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.7022</td>
<td>0.6252</td>
<td>0.9123</td>
<td>0.4760</td>
<td>0.8715</td>
<td>0.9999</td>
<td>0.9568</td>
<td>0.9076</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.6864</td>
<td>0.6687</td>
<td>0.7406</td>
<td>0.4923</td>
<td>0.9308</td>
<td>0.7169</td>
<td>0.9999</td>
<td>0.9856</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>0.5947</td>
<td>0.6742</td>
<td>0.6616</td>
<td>0.4491</td>
<td>0.9154</td>
<td>0.6581</td>
<td>0.9042</td>
<td>0.5286</td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>0.5005</td>
<td>0.4045</td>
<td>0.6388</td>
<td>0.3712</td>
<td>0.7574</td>
<td>0.6091</td>
<td>0.9564</td>
<td>0.6139</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>0.2635</td>
<td>0.3325</td>
<td>0.4741</td>
<td>0.2885</td>
<td>0.5566</td>
<td>0.3934</td>
<td>0.7441</td>
<td>0.7926</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.2236</td>
<td>0.2327</td>
<td>0.3319</td>
<td>0.1808</td>
<td>0.4107</td>
<td>0.2231</td>
<td>0.6704</td>
<td>0.7555</td>
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</tr>
<tr>
<td>420</td>
<td>0.0740</td>
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<td>0.2277</td>
<td>0.1417</td>
<td>0.3077</td>
<td>0.1121</td>
<td>0.4082</td>
<td>0.5514</td>
<td></td>
</tr>
<tr>
<td>440</td>
<td>0.0318</td>
<td>0.0258</td>
<td>0.1641</td>
<td>0.0827</td>
<td>0.1992</td>
<td>0.1134</td>
<td>0.0927</td>
<td>0.4007</td>
<td></td>
</tr>
<tr>
<td>460</td>
<td>0.0113</td>
<td>0.0383</td>
<td>0.0754</td>
<td>0.0235</td>
<td>0.0609</td>
<td>0.0621</td>
<td>0.0865</td>
<td>0.2674</td>
<td></td>
</tr>
<tr>
<td>480</td>
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<td>0.0392</td>
<td>0.0570</td>
<td>0.0368</td>
<td>0.0223</td>
<td>0.0443</td>
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</tr>
<tr>
<td>500</td>
<td>0.0025</td>
<td>0.0022</td>
<td>0.0825</td>
<td>0.0416</td>
<td>0.0371</td>
<td>0.0899</td>
<td>0.2062</td>
<td>0.2059</td>
<td></td>
</tr>
<tr>
<td>530</td>
<td>0.0078</td>
<td>0.0187</td>
<td>0.0175</td>
<td>0.0105</td>
<td>0.1209</td>
<td>0.0749</td>
<td>0.1203</td>
<td>0.2152</td>
<td></td>
</tr>
<tr>
<td>560</td>
<td>0.0122</td>
<td>0.0121</td>
<td>0.0176</td>
<td>0.0756</td>
<td>0.0387</td>
<td>0.0782</td>
<td>0.0272</td>
<td>0.2376</td>
<td></td>
</tr>
</tbody>
</table>
In the high temperature region (260–460 \degree R K)

reduced to:

the term \( P_0 \) is not accessible and in order to express it via other terms that can be calculated, we follow the oncoming procedure. At high temperatures, where the second term of Eq. (9) refers to, the ratio \( \frac{d}{dt} \) equals zero and therefore the rates \( R_{\text{low}} \) and \( R_{\text{high}} \) are equal. This leads to the expression:

\[
R_{\text{low}} \Rightarrow k_2 \theta_{\text{NO}} \theta_0 = k_2 \frac{K_{\text{CO}} P_{\text{CO}}}{1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{NO}} P_{\text{NO}}} \tag{12}
\]

Relationship (11) is then reduced to the following expression

\[
R_{\text{high}} = k_2 \frac{(K_{\text{NO}} P_{\text{NO}}/k_2 K_{\text{CO}} P_{\text{CO}})}{(1 + K_{\text{CO}} P_{\text{CO}} + (k_1 K_{\text{NO}} P_{\text{NO}}/k_2 K_{\text{CO}} P_{\text{CO}}))^2} \tag{13}
\]

Finally, the total reaction rate is expressed by Eq. (15):

\[
R_{\text{total}} = w_1 R_{\text{low}} + w_2 R_{\text{high}} \Rightarrow w_1 (k_2 K_{\text{NO}} P_{\text{NO}})
\]

||
\[
+ w_2 \left( K_{\text{CO}} P_{\text{CO}} (1 + K_{\text{NO}} P_{\text{NO}}/k_2 K_{\text{CO}} P_{\text{CO}})^2) \right) \tag{15}
\]

where \( w_1, w_2 \) the normalized coefficients referred to the two routes as mentioned, \( k_1, k_2 \) the rate constants; \( K_{\text{NO}}, K_{\text{CO}} \) the adsorption equilibrium constants of NO and CO; \( P_{\text{NO}}, P_{\text{CO}} \) the partial pressures of NO and CO.

Using the above equation we simulated the experimental results in the range of reaction temperature between 260 and 460 \degree C. The simulation took place using a suitable computer program written in ForTran 90/95 and based on the well-known “Simplex” method and the least-squared method of Levenberg-Marquardt [35–37]. The program was executed in Linux.

For the simulation of data the corresponding parameters \( k_1, k_2, K_{\text{NO}} \) and \( K_{\text{CO}} \) are expressed as follows:

\[
k_1 = A_1 \exp \left( \frac{-E_1}{R T} \right) \tag{16}
\]

\[
k_2 = A_2 \exp \left( \frac{-E_2}{R T} \right) \tag{17}
\]

\[
K_{\text{NO}} = A_{\text{NO}} \exp \left( \frac{\Delta H_{\text{ads(NO)}}}{R T} \right) \tag{18}
\]

\[
K_{\text{CO}} = A_{\text{CO}} \exp \left( \frac{\Delta H_{\text{ads(CO)}}}{R T} \right) \tag{19}
\]

The results of simulation for the eight examined catalysts in the high temperature region (260–460 \degree C) are shown in Fig. 9. In this figure the points correspond to the experimental data and the solid lines correspond to the simulation by Eq. (15). The fitting of the data with the simulation was quite satisfactory as shown by the correlation coefficients \( R^2 \) included in Table 5.

The determined parameters \( E_1, E_2, \Delta H_{\text{ads(NO)}} \) and \( \Delta H_{\text{ads(CO)}} \) are shown as a function of degree of substitution \( \delta \) in Fig. 10. A comparison graph between the variations of the \( R_{\text{app}} \) values, calculated by the Arrhenius plots, and the values of the term \( E_1 - \Delta H_{\text{ads(NO)}} \), obtained by the simulation technique, is depicted in Fig. 11.

From Fig. 9 we observe that the simulation of experimental points with Eq. (15), into which the relationships (16), (17), (18) and (19) have been substituted, is quite satisfactory. Some systematic discrepancies are observed for the samples with high content of Sr, namely \( \text{La}_0.7 \text{Sr}_0.3 \text{MnO}_3 \), \( \text{La}_0.5 \text{Sr}_0.5 \text{MnO}_3 \) and perhaps \( \text{La}_0.3 \text{Sr}_0.7 \text{MnO}_3 \). In those samples the “knee” apparent in the experimental data is not so well fitted. So we shall keep some reservations for the simulation parameters describing the catalytic performance of those samples.

The variation of activation energies \( E_1 \) and \( E_2 \) as a function of Sr content is shown in Fig. 10. In the majority of the cases, \( E_1 \) is larger than \( E_2 \). This might well reflect the fact that \( E_1 \) corresponds to the NO decomposition (see
The values of $E_1$ and $E_2$ do not show appreciable changes with $x$ and, with the exception of the last two samples ($x = 0.8$ and 0.9) for which the fitting is not so successful, remain in the range (kJ/mol) $110 < E_1 < 130$ and $105 < E_2 < 115$.

For the samples with $x = 0.8$ and 0.9 both $E_2$ and $E_3$ values decrease systematically ($E_1 = 93 \pm 63$ kJ/mol and $E_2 = 89 \pm 42$ kJ/mol respectively). Those values should be compared with values of activation energies estimated via similar simulation catalytic kinetic studies on three-way catalysts Pt-Rh/Al$_2$O$_3$-CeO$_2$ [38,39]. As far as we know there are no similar simulation studies in the literature concerning ceramic mixed valence state catalysts like the present ones. These previously estimated values can be summarized as follows: Mattheus et al. [38] found that the apparent activation energy for the reaction $2\text{NO} + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{N}_2$ was $E_{\text{app}} \approx 86.6$ kJ/mol while for the reaction $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ the corresponding value was $E_{\text{app}} \approx 112–119$ kJ/mol whereas for the above mentioned reactions Kotsiakis et al. [39] found $E_{\text{app}} \approx 70.0$ and $\approx 95$ kJ/mol, respectively. Those values are compared satisfactorily with the $E_1$ and $E_2$ values estimated in the present study.

The variation of the heats of adsorption for NO ($\Delta H_{\text{ads(NO)}}$) and CO ($\Delta H_{\text{ads(CO)}}$) are also shown in Fig. 10. The $\Delta H_{\text{ads(CO)}}$ values are in the range of $50–60$ kJ/mol while the $\Delta H_{\text{ads(NO)}}$ values appear lower in the range of $30–40$ kJ/mol. Those values indicate weaker adsorption of CO on the La–Sr–Mn–O catalysts compared to NO as expected. A comparison should be made between these values and similar ones reported for the heat of adsorption of NO which on LaF$_3$O$_5$ is $38$ kJ/mol at surface coverage $\Theta = 0.65$ [40], on Mn$_3$O$_4$ is $117$ kJ/mol [41], on La$_2$O$_3$ is $117$ kJ/mol [42] and on Fe$_3$O$_4$ is $69.3$ kJ/mol [43]. Nevertheless, a direct comparison is not feasible because of the different conditions.

**Table 5**

The values for the parameters $A_1$, $A_2$, $E_1$, $E_2$, $A_{\text{NO}}$, $A_{\text{CO}}$, $\Delta H_{\text{ads(NO)}}$ and $\Delta H_{\text{ads(CO)}}$ estimated according to the fitting of catalytic data by Eq. (15) in the region of 260–460°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$A_{\text{NO}}$</th>
<th>$A_{\text{CO}}$</th>
<th>$\Delta H_{\text{ads(NO)}}$</th>
<th>$\Delta H_{\text{ads(CO)}}$</th>
<th>$R^2$</th>
<th>$E_{\text{app}}$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO$_3$</td>
<td>1.54E4</td>
<td>1.14E9</td>
<td>131</td>
<td>114</td>
<td>3.74E-3</td>
<td>1.70E-6</td>
<td>66</td>
<td>28</td>
<td>0.9951</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>La$_2$Sn$_2$MnO$_4$</td>
<td>1.00E4</td>
<td>2.03E8</td>
<td>129</td>
<td>106</td>
<td>2.29E-5</td>
<td>3.01E-7</td>
<td>67</td>
<td>34</td>
<td>0.9991</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>La$_2$Sr$_2$MnO$_4$</td>
<td>1.12E4</td>
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<td>104</td>
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<td>3.07E-7</td>
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<td>0.9980</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>La$_2$Sr$_2$MnO$_4$</td>
<td>8.12E3</td>
<td>4.54E8</td>
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<td>109</td>
<td>1.72E-3</td>
<td>3.74E-7</td>
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<td>29</td>
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<td>52</td>
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<td>La$_2$Sr$_2$MnO$_4$</td>
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<td>112</td>
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<td>1.32E-6</td>
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<td>89</td>
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<td>50</td>
<td>0.9996</td>
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<td>La$_2$Sr$_2$MnO$_4$</td>
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<td>28</td>
<td>49</td>
<td>0.9864</td>
<td>51</td>
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</tr>
</tbody>
</table>

The fitting criterion $R^2$ is also shown. The $E_{\text{app}}(\Theta)$ values estimated from plots $\ln R_{\text{app}} = f(1000/T)$ at the low temperature region are shown in the right end column.

Eqs. (7) and (10), while $E_2$ corresponds to CO oxidation (see Eqs. (8) and (11)). The first of these reactions exhibits higher activation energies compared to the second. But in general the values of $E_1$ and $E_2$ do not show appreciable changes with $x$ and, with the exception of the last two samples ($x = 0.8$ and 0.9) for which the fitting is not so successful, remain in the range (kJ/mol) $110 < E_1 < 130$ and $105 < E_2 < 115$.

For the samples with $x = 0.8$ and 0.9 both $E_2$ and $E_3$ values decrease systematically ($E_1 = 93 \pm 63$ kJ/mol and $E_2 = 89 \pm 42$ kJ/mol respectively). Those values should be compared with values of activation energies estimated via similar simulation catalytic kinetic studies on three-way catalysts Pt-Rh/Al$_2$O$_3$-CeO$_2$ [38,39]. As far as we know there are no similar simulation studies in the literature concerning ceramic mixed valence state catalysts like the present ones. These previously estimated values can be summarized as follows: Mattheus et al. [38] found that the apparent activation energy for the reaction $2\text{NO} + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{N}_2$ was $E_{\text{app}} \approx 86.6$ kJ/mol while for the reaction $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ the corresponding value was $E_{\text{app}} \approx 112–119$ kJ/mol whereas for the above mentioned reactions Kotsiakis et al. [39] found $E_{\text{app}} \approx 70.0$ and $\approx 95$ kJ/mol, respectively. Those values are compared satisfactorily with the $E_1$ and $E_2$ values estimated in the present study.

The variation of the heats of adsorption for NO ($\Delta H_{\text{ads(NO)}}$) and CO ($\Delta H_{\text{ads(CO)}}$) are also shown in Fig. 10.

The $\Delta H_{\text{ads(CO)}}$ values are in the range of $50–60$ kJ/mol while the $\Delta H_{\text{ads(NO)}}$ values appear lower in the range of $30–40$ kJ/mol. Those values indicate weaker adsorption of CO on the La–Sr–Mn–O catalysts compared to NO as expected. A comparison should be made between these values and similar ones reported for the heat of adsorption of NO which on LaF$_3$O$_5$ is $38$ kJ/mol at surface coverage $\Theta = 0.65$ [40], on Mn$_3$O$_4$ is $117$ kJ/mol [41], on La$_2$O$_3$ is $117$ kJ/mol [42] and on Fe$_3$O$_4$ is $69.3$ kJ/mol [43]. Nevertheless, a direct comparison is not feasible because of the different conditions.

Fig. 10. The parameters $E_1$, $E_2$, $A_2$, $\Delta H_{\text{ads(NO)}}$, $\Delta H_{\text{ads(CO)}}$ calculated from the simulation method as a function of the degree of substitution $x$. In the inset, the percentage of perovskite phase vs. $x$.

Fig. 11. The apparent activation energy $E_{\text{app}}(\Theta, T)$ calculated from the Arrhenius plots (Table 5) and the difference $E_1 - \Delta H_{\text{ads(NO)}}$ obtained from the simulation technique as a function of Sr substitution. In the inset, $E_{\text{app}}(\Theta, T)$ vs. the difference $E_1 - \Delta H_{\text{ads(NO)}}$ is shown.
experimental differences and the difficulty in the estimation of surface coverage $θ_{NO}$ in each case, which affects the values of the heat of adsorption $ΔH_{ads(NO)}$.

It is apparent that the trend characterizing the determined kinetic parameters which express the catalytic activity ($E_1$ and $E_2$), shown in Fig. 10a, corresponds to a similar trend characterizing the percent of the perovskite phase determined from Rietveld analysis, shown in the inset of Fig. 10a. Such correlation cannot be made for the rest three samples of the tested series where the Rietveld analysis could not be performed.

Finally the values $E_1$ and the difference $E_1 - ΔH_{ads(NO)}$, as shown in Fig. 11, differ in a percentage fluctuating from 8 to 31%. This reasonable agreement leads us to the conclusion that simulation/fitting can be used to describe the reaction rate satisfactorily and allows us to determine the $E_i$ ($i = 1, 2$) and $ΔH_{ads}$ ($j = NO, CO$) parameters quite easily since otherwise a large number of complicated measurements would be demanded.

5. Conclusions

Substituted perovskite-type mixed oxides La$_{1-x}$Sr$_x$(Mn$^{IV}$/Mn$^{III}$)$_{2}$O$_{3-δ}$ show catalytic activity for the reaction NO + CO in the range of 220–560 °C, which decreases linearly with the substitution of La by Sr and the gradual increase of the ratio Mn$^{IV}$/Mn$^{III}$. At low temperatures, the reaction proceeds via equimolecular conversion of NO and CO and the reaction rate is described by $R_{NO,COD} = k_{θ}θ_{NO}θ_{CO}$ while at higher temperatures (>350 °C) the conversion ratio for NO/CO equals 2:1 and the reaction rate was assumed to be described by $R_{NO,COD} = k_{θ}θ_{NO}θ_{CO}$, where $θ_{NO}$ the corresponding surface coverage of $i = NO, CO$. The rate $R$ of conversion can be simulated satisfactorily using the expression $R = w_{1}R_{NO} + w_{2}R_{CO}$, where $w_{1}$, $w_{2}$ the weighing coefficients of reactions $R_{NO}$ and $R_{CO}$. The obtained results provide values for the true activation energies $E_1$ (for low T) and $E_2$ (for high T) as well as the heats of adsorption $ΔH_{ads(NO)}$ for NO and $ΔH_{ads(CO)}$ for CO. The values of $E_1$, $E_2$ and $ΔH_{ads(NO)}$ suffer a gradual drop with the addition of Sr while $ΔH_{ads(CO)}$ increases. These values are reasonably compared to previously reported data. Perhaps more important is the fact that the described method of simulation provides, using only one kind of experiment, kinetic ($E_1$, $E_2$) and thermodynamic ($ΔH_{ads(NO)}$, $ΔH_{ads(CO)}$) parameters which otherwise would necessitate a large number of experimental set-ups.

Acknowledgements

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