Effect of Ce on NO direct decomposition in the absence/presence of O_2 over $La_{1-x}Ce_xSrNiO_4$ ($0 \leq x \leq 0.3$)

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Abstract

Effect of cerium ions on the activity of $La_{1-x}Ce_xSrNiO_4$ ($0 \leq x \leq 0.3$) for NO decomposition was investigated both in the absence and presence of oxygen. The amount of Ce in the frame reached 30 at.% ($x = 0.3$) in the present case without destroying the matrix structure. The Ce-substituted samples showed high activity for NO decomposition not only in the absence of O_2 but also in the presence of O_2, and the specific activity reached 1.59 $\mu mol\, s^{-1}\, m^{-2}$ even 6.0% O_2 was fed to the reactant gas ($La_{0.7}Ce_{0.3}SrNiO_4$, $T = 1123$ K), indicating that the Ce addition can enhance the oxygen forbearance of catalyst. In addition, a new highly active site, which facilitates oxygen mobilization and desorption, might be formed in the sample due to the Ce addition, which thus resulted in the high activity for NO decomposition.
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Keywords: Nitrogen oxide; Direct decomposition; Ce; Active site; Oxygen forbearance

1. Introduction

Nitrogen oxides (NO_x), one of the serious pollutants in the earth's atmosphere, have been received much attention even a century ago because of the harm to environment and human body. Their removal from all sources remains great challenge, in spite of all progress made over the years [1–3]. Catalytic NO decomposition is the most desirable way of removing NO_x from exhaust gas streams since it does not involve the addition of a supplemental reductant and the products of the reaction (N_2 and O_2) are nontoxic [4]. However, it is known that in the process of NO decomposition, the oxygen produced from NO dissociation is often strongly bonded to the catalyst surface, poisoning NO dissociation site and preventing NO dissociation further [5]. Hence, to promote the oxygen desorbing from the active site is one of the effective ways to improve the activity of NO decomposition.

Among the catalysts for NO decomposition, Cu-ZSM-5 is the most excellent one and exhibits high activity even at

low temperatures ($\sim$773 K) [6,7]. But the shortcomings of Cu-ZSM-5 are the narrow temperature range with high activity and the unstable structure at high temperatures. When O_2 and/or H_2O, especially SO_2 coexisted in the reactant, the activity of NO decomposition decreased abruptly. Another sort of interesting catalysts for NO decomposition are perovskite(-like) mixed oxides with ABO_3 or A_2BO_4 structure [2], in which the valence of B-site transition metal, as well as the number of oxygen vacancies are controllable by partial substitution of A- and/or B-sites ions, without destroying the matrix structure. Here, the active site is thought to be F-center, described as: $[\ ]M^{n+} \Leftrightarrow [e^-]M^{n+1}$ [8].

Recently, cerium received much attention in designing catalyst for NO decomposition because of its excellent performance for oxygen storing/scavenging. Delmon and co-workers [9] found that the activity of $LaCoO_3$ was significantly improved when CeO_2 doping in $LaCoO_3$. Pomonis and co-workers [10,11] found that the NO decomposition rate accelerated with the increase of CeO_2 content in La–Sr–Ce–Fe–O system. Misono and co-workers [12,13] investigated the property of Sr-, Ce- and Th-substituted $LaMO_3$ (M = Mn, Fe, Co) in detail and found that only

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the Ce-substituted samples showed improving property for oxygen mobility. All these results showed that catalytic performance of catalyst could be improved by cerium addition.

In this paper, based on our previous works [14–16] we investigated the transformation of active site as well as the effect of Ce content on the catalytic performance of $La_{1-x}Ce_xSrNiO_4$. The high activity of $La_{1-x}Ce_xSrNiO_4$ ($x \leq 0.3$) for NO decomposition suggests that a new highly active site, which facilitates oxygen mobilization and desorption, is formed due to the Ce addition.

2. Experiment

2.1. Preparation

$La_{1-x}Ce_xSrNiO_4$ with x from 0 to 0.7 was prepared by the conventional citrate method [17]. Briefly, to an aqueous solution of La^{3+}, Ce^{3+}, Sr^{2+} and Ni^{2+} nitrates (all are in A.R. pure grade) with appropriate stoichiometry, a solution of citric acid 50% in excess of stoichiometry was added. The resulting solution was evaporated to dryness, and then the precursors obtained were decomposed in air at 573 K, calcined at 873 K for 1 h and finally pelletized and calcined at 1173 K in air for 6 h, the synthesized pellets were pulverized to 40–80-mesh size to be used.

2.2. Characterization

Powder X-ray diffraction (XRD) data were obtained from an X-ray diffractometer (type D/MAX B, Rigaku) operated at 40 kV and 10 mA at room temperature, using Cu Kα radiation combined with nickel filter. The diffraction angle 2θ falls between 20° and 80°.

Specific surface areas (SSA) of catalyst were measured by N_2 adsorption at 77 K with a Micromeritics ASAP2010 instrument.

Infrared spectra (IR) in the range 1800–400 cm^{-1} were recorded on a Nicolet-5DX FT-IR spectrometer with a TGS detector. Samples were produced in the form of KBr pellets.

Temperature programmed desorption of oxygen (O_2-TPD) was carried out on conventional apparatus equipped with a thermal conductivity detector (TCD). The samples (0.2 g) were first treated in O_2 at 1073 K for 1 h and cooled to room temperature in the same atmosphere, then swept with helium at a rate of 11.8 mL/min until the base line on the recorder remained unchanged. Finally, the sample was heated at a rate of 20 K/min in helium to record the TPD profile.

2.3. Catalytic activity measurement

Steady-state activities of catalysts were evaluated using a single-pass flow micro-reactor made of quartz, with an internal diameter of 6 mm. The reactant gas was passed through 0.5 g catalysts (1%NO/He) at a rate of 25 mL/min or 0.8 g catalysts (1%NO + 1–6%O_2/He) at a rate of 40 mL/min (to keep W/F = 1.2 g s mL^{-1}). The gas composition was analyzed before and after the reaction by an online gas chromatography, using molecular sieve 5 A column for separating NO, N_2 and O_2. N_2O was not analyzed here because it was difficult to form between 773 and 1123 K [18]. Before the data were obtained, reactions were maintained for a period of ~2 h at each temperature to ensure the steady-state conditions. The activity of NO decomposition was evaluated by the following equation:

$$N_2 \text{ yield (specific activity)} = \frac{1}{A_S} \frac{2[N_2]_{out}}{[NO]_{in}} \times 100$$

where A_S represented the specific surface areas of catalyst; $[NO]_{in}$ and $[N_2]_{out}$ were the concentration of NO and N_2 measured before and after the reaction, respectively.

3. Results and discussion

3.1. Study of powder X-ray diffraction

Fig. 1(a) shows the XRD patterns of $La_{1-x}Ce_xSrNiO_4$ with x from 0 to 0.7 (also see Table 1). All the samples have the perovskite-like structure with A_2BO_4 type. The peak at $2\theta = \sim28°$ (characteristic diffraction peak of CeO_2 phase) increased with the increase of Ce content, which might imply the appearance of CeO_2 phase, but this peak was also the reflection peak of $La_{1-x}Ce_xSrNiO_4$ (see XRD patterns of sample $x = 0$). Hence, in order to clarify whether this peak contains the contribution of CeO_2, the intensity ratio of CeO_2 ($2\theta = \sim28°$) to $La_{1-x}Ce_xSrNiO_4$ ($2\theta = \sim31.8°$) was plotted [9]. The results in Fig. 1(b) shows that this ratio (curve I) was almost unvaried at the beginning ($0 \leq x \leq 0.3$), then increased abruptly after $x > 0.3$, suggesting that the peak ($2\theta = \sim28°$) appeared in the sample $x \leq 0.3$ does not include the contribution of CeO_2. Namely, Ce occupied the La-site of $La_{1-x}Ce_xSrNiO_4$ completely at $x \leq 0.3$ without destroying the matrix structure. After $x > 0.3$, the abrupt increase of the ratio indicated that Ce cannot occupy the La-site of $LaSrNiO_4$ completely and CeO_2 phase appeared. Besides, a minor evidence obtained from XRD patterns also supported the result that Ce can occupy the La-site of $La_{1-x}Ce_xSrNiO_4$ completely at $x = 0.3$ (here, "minor" means that the peak analyzed is not the first strongest peak of CeO_2, but the fourth one). From Fig. 1(c), which

Table 1
Crystal structure and specific surface area (SSA) of the used catalysts

Catalysts	Crystal structure	BET surface area (m^2/g)
LaSrNiO$_4$	P-l	6.5
La$_{0.9}$Ce$_{0.1}$SrNiO$_4$	P-l	7.0
La$_{0.7}$Ce$_{0.3}$SrNiO$_4$	P-l	5.0
La$_{0.5}$Ce$_{0.5}$SrNiO$_4$	P-l + CeO$_2$	4.8
La$_{0.3}$Ce$_{0.7}$SrNiO$_4$	P-l + CeO$_2$ + P′	4.5

P-l: perovskite-like structure ($La_{1-x}Ce_xSrNiO_4$); P′: other perovskite phase(s).
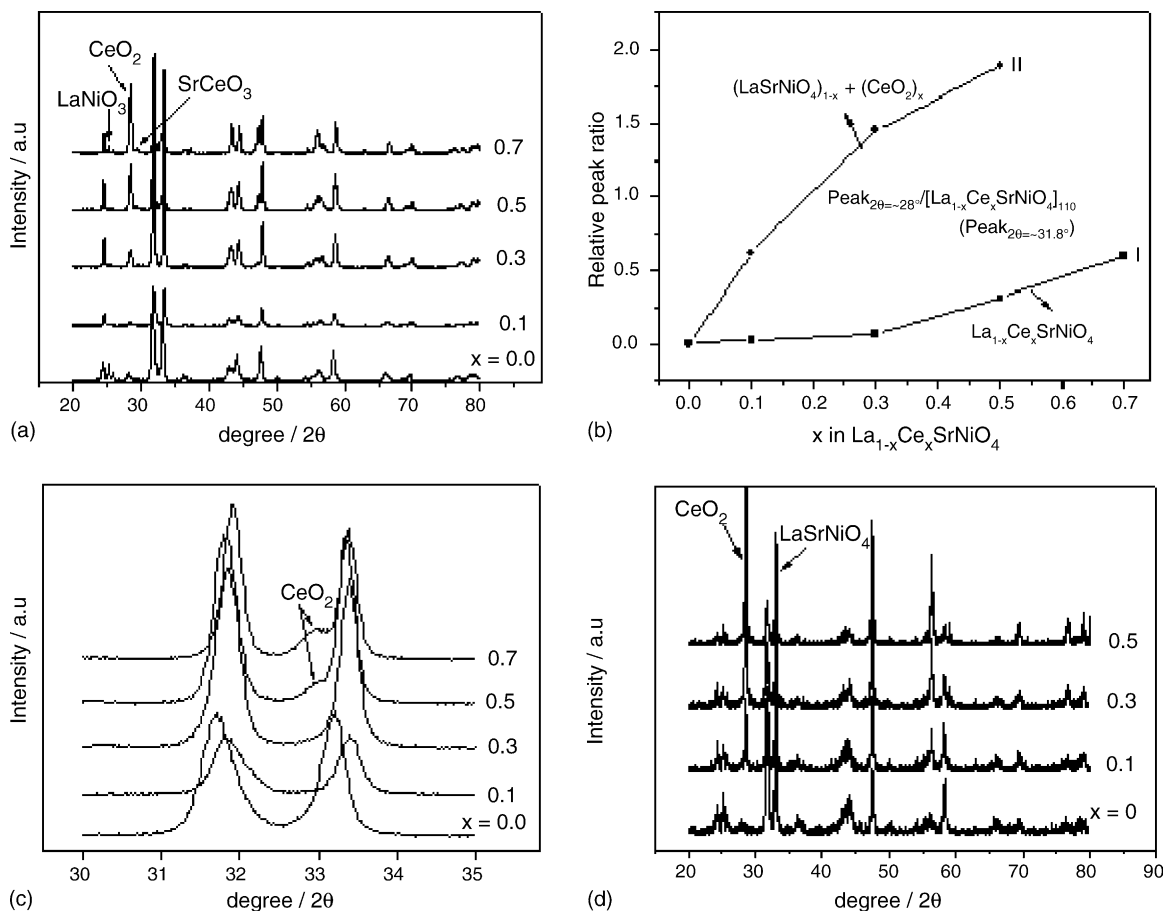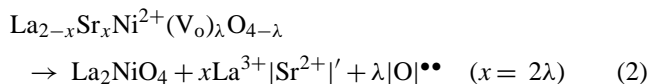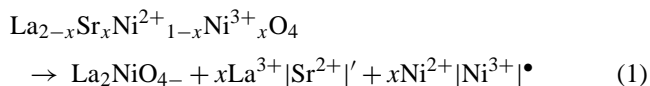
Fig. 1. (a) XRD patterns of $La_{1-x}Ce_xSrNiO_4$ ($0 \leq x \leq 0.7$); (b) the intensity ratio of the peak ($2\theta = \sim 28°$) to that of $La_{1-x}Ce_xSrNiO_{4(110)}$ at peak $2\theta = \sim 31.8°$, 'I' obtained from $La_{1-x}Ce_xSrNiO_4$; 'II' obtained from $(LaSrNiO_4)_{1-x} + (CeO_2)_x$; (c) fine XRD spectra of $La_{1-x}Ce_xSrNiO_4$ ($30° \leq 2\theta \leq 35°$); (d) XRD patterns of the mechanical mixture of "$(LaSrNiO_4)_{1-x} + (CeO_2)_x$" ($0 \leq x \leq 0.5$).

reflected the fine XRD patterns of $La_{1-x}Ce_xSrNiO_4$ at the range $30° \leq 2\theta \leq 35°$, it is seen that a small shoulder peak at $2\theta = \sim 33.08°$, which only belongs to CeO_2 phase, appeared at $x \geq 0.5$ and its intensity increased with the increase of Ce content, indicating that CeO_2 phase appeared only at $x \geq 0.5$. Namely, Ce can occupy the La-site of $La_{1-x}Ce_xSrNiO_4$ completely at $x = 0.3$. Finally, the XRD patterns of mechanical mixture, $(LaSrNiO_4)_{1-x} + (CeO_2)_x$, was also measured and the results were shown in Fig. 1(d). By comparing with Fig. 1(a) and (d), one can find that the peak intensity of "$(LaSrNiO_4)_{1-x} + (CeO_2)_x$" at $2\theta = \sim 28°$ was far stronger than that of "$La_{1-x}Ce_xSrNiO_4$" especially at $x \leq 0.3$, suggesting that the peak of $La_{1-x}Ce_xSrNiO_4$ ($x \leq 0.3$) at $2\theta = \sim 28°$ is ascribed not to CeO_2, but to $La_{1-x}Ce_xSrNiO_4$ ($x \leq 0.3$) itself. In addition, from the intensity ratio of CeO_2 ($2\theta = \sim 28°$) to $La_{1-x}Ce_xSrNiO_4$ ($2\theta = \sim 31.8°$) in the mechanical mixture (see Fig. 1(b), curve II), it is seen that this ratio increases continuously with the increase of CeO_2 content and is far higher than that measured in $La_{1-x}Ce_xSrNiO_4$, indicating that the peak of $La_{1-x}Ce_xSrNiO_4$ ($x \leq 0.3$) at $2\theta = \sim 28°$ is indeed not ascribed to CeO_2. In all, all the evidences supported that Ce can occupy the La-site of $La_{1-x}Ce_xSrNiO_4$ completely at $x = 0.3$ without destroying the matrix structure.

As reported earlier about $LaSrNiO_4$ [14,17] the presence of oxygen vacancy and the mixed oxidative state of Ni in $LaSrNiO_4$ could be explained by the following equations (V_o, $'$ and $•$ represent the oxygen vacancies, cation holes and anion electrons, respectively):

$$La_{2-x}Sr_xNi^{2+}_{1-x}Ni^{3+}_xO_4$$
$$\rightarrow La_2NiO_{4-} + xLa^{3+}|Sr^{2+}|' + xNi^{2+}|Ni^{3+}|^• \qquad (1)$$

$$La_{2-x}Sr_xNi^{2+}(V_o)_\lambda O_{4-\lambda}$$
$$\rightarrow La_2NiO_4 + xLa^{3+}|Sr^{2+}|' + \lambda|O|^{••} \quad (x = 2\lambda) \qquad (2)$$

When a low valence cation (Sr^{2+}) occupied the frame at La^{3+}-site, the oxidative state of nickel, as well as the number of oxygen vacancy would increase in order to satisfy the electroneutrality. In this experiment, we cannot measure the average oxidative state of Ni by means of iodometry because the valence of Ce is alterable (3+ and 4+). However, it might be deduced that the number of oxygen vacancy, as well as the average oxidative state of B-site ion would decrease when a high valence cation (Ce^{4+}) occupied the frame at La^{3+}-site. This is true as certified by the following data.

3.2. Study of IR spectra

Results obtained from IR spectra supported the results analyzed from XRD patterns. In Fig. 2, all the samples show a vibration absorption band at $500\,cm^{-1}$, which is the stretching vibration of A–O–B (La–O–Ni) in A_2BO_4 belonging to A_{2u} vibration mode and is the characteristic absorption band of K_2NiF_4-type (A_2BO_4) mixed oxides [19]. This indicated that all the samples have the perovskite-like structure with A_2BO_4 type. The absorption band at $500\,cm^{-1}$ was slightly split into two when Ce was added, which might be caused by the small radius and high valence of Ce^{4+} (compared with that of La^{3+}). This result suggested that some of Ce ions do occupy the La-site $LaSrNiO_4$.

The absorption bands at 858 and $1460\,cm^{-1}$ were ascribed to the contribution of $SrCO_3$ [20]. Because of the large amount of Sr elements in the precursor and the samples were prepared by citrate method, which will introduce carbon to the catalyst, it is possible for $SrCO_3$ phase being formed, since the decomposition temperature of $SrCO_3$ is higher than 1173 K. However, as the $SrCO_3$ phase was not detected in XRD patterns, it must be highly dispersed on the catalyst surface [21]. In addition, as the sensitivity of $CO_3{}^{2-}$ in IR spectra is far stronger than that of other compound oxides, therefore, the absorption band of $SrCO_3$ was detected.

The reason that Ce can enter the frame of $La_{1-x}Ce_xSrNiO_4$ even at $x = 0.3$ might be partly ascribed to that, the system chosen here is in perovskite-like with A_2BO_4 type, the structure of which is more stable than that of perovskite with ABO_3 type (in perovskite oxides La(Ce, Sr)MO_3, the maximum content of Ce in the La-site is 10 at.%, i.e., $x = 0.1$ [9–13]). In addition, in the present structure there existed a large amount of low valence cations (Sr^{2+}), which facilitated the Ce^{4+} ions to the frame from the electroneurality.
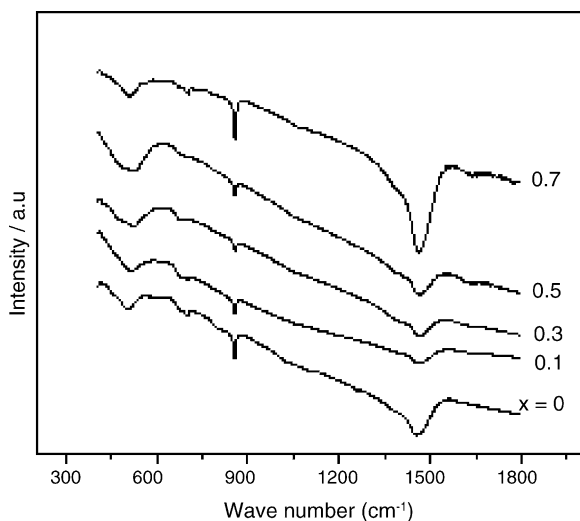

Fig. 2. IR spectra of the series of catalysts, $La_{1-x}Ce_xSrNiO_4$ ($0 \leq x \leq 0.7$).

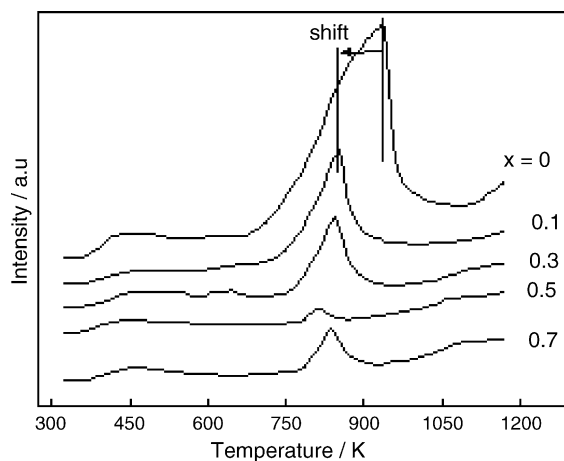Fig. 3. O_2-TPD profiles measured from $La_{1-x}Ce_xSrNiO_4$ ($0 \leq x \leq 0.7$).

3.3. O_2-TPD spectra

Fig. 3 shows the O_2-TPD profiles of $La_{1-x}Ce_xSrNiO_4$ at the range of 323–1173 K. Three kinds of oxygen desorption peaks were observed in the profile. The peak appeared at $350 < T < 670\,K$ is weak and is ascribed to the oxygen chemically adsorbed on the surface (denoted as: α oxygen); the peak appeared at $670 < T < 1050\,K$ is ascribed to the oxygen chemically adsorbed on the oxygen vacancy (denoted as: β oxygen); the peak appeared at $T > 1050\,K$ then is ascribed to the oxygen escaped from the lattice (denoted as: γ oxygen) [22].

Among the three oxygen desorption peaks, the β oxygen desorption peak is interesting. The desorption area of β oxygen decreased with the increase of Ce content at $0 \leq x \leq 0.5$, suggesting the decrease of the number of oxygen vacancies. It also suggested that the existence of Ce in the frame is not in Ce^{3+} form, but in Ce^{4+} form, otherwise the desorption area will not decrease due to the same oxidative state of La^{3+} and Ce^{3+}. But it should be noted that the desorption area of β oxygen in sample $x = 0.7$ was larger than that in sample $x = 0.5$, due to the appearance of the new perovskite phase (for example, $LaNiO_3$) in sample $x = 0.7$ (see Fig. 1(a)). Certainly, the oxidative state of Ni will decrease also, as discussed below.

The temperature of the β oxygen desorption peak shifted to lower temperature with the addition of Ce, suggesting that the oxygen desorption from the Ce-substituted samples is easier than that from $LaSrNiO_4$. It might be that a new highly active site, which facilitates oxygen mobilization and desorption, was formed in these samples, due to the Ce addition (see Section 3.6).

3.4. Oxidative state of Ni

As mentioned above, the average valence of Ni cannot be measured by means of iodometry in the present case due to the addition of Ce, the valence of which is alterable. Hence, the oxidation state of Ni discussed here is the calculated results
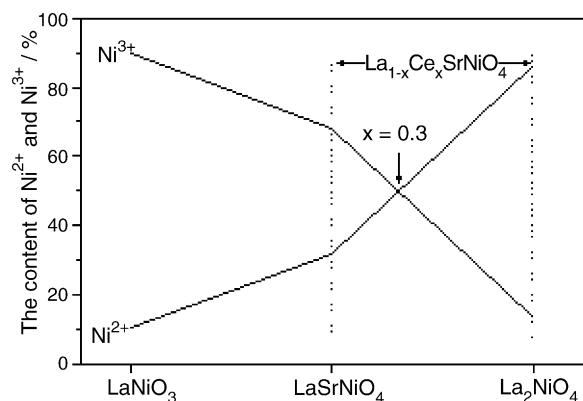
Fig. 4. The Ni^{2+} and Ni^{3+} content calculated from the four catalysts ($LaNiO_3$, $LaSrNiO_4$, $La_{1-x}Ce_xSrNiO_4$ and La_2NiO_4).

based on the reference of $LaNiO_3$, $LaSrNiO_4$ and La_2NiO_4. From the data of our previous works [14], we summarized the change of Ni^{2+} and Ni^{3+} content in the above three catalysts, as shown in Fig. 4. Obviously, in the two curves there appeared an intersection, at which the content of Ni^{2+} and Ni^{3+} are equal (50% for each). On the other, from the molecular formula of $LaSrNiO_4$, $La_{1-x}Ce_xSrNiO_4$ and La_2NiO_4, it is known that the average valence of Ni in $La_{1-x}Ce_xSrNiO_4$ should be in between that in $LaSrNiO_4$ and La_2NiO_4, according to the valence of Sr^{2+} and Ce^{4+} (see Fig. 4). Hence, the average valence of Ni will decrease when increasing the Ce^{4+} content in $La_{1-x}Ce_xSrNiO_4$, and it is possible for the Ni^{2+} and Ni^{3+} content to get equal by changing the Ce^{4+} content. According to the literature [23], when the Ni^{2+} and Ni^{3+} content is equal, the catalyst possesses more percentage of "Ni^{2+}-[ ]-Ni^{3+}" pairs (active site), which favors the surface reaction to occur and thus results in the high activity. In Fig. 4, it could be calculated that the intersection is at $x = 0.3$ of $La_{1-x}Ce_xSrNiO_4$, which implies that $La_{0.7}Ce_{0.3}SrNiO_4$ is the most suitable catalyst for NO decomposition since the amount of active sites is in the largest. This is in compliance with the result shown in Fig. 5.

3.5. Catalytic activity of NO decomposition

Activities of NO decomposition over the series of catalysts were measured and shown in Fig. 5. The activity increased monotonously with the increase of reaction temperature, since the thermal desorption of oxygen [24,25] and/or the decomposition of NO_2^*/NO_3^* species [26,27] is facilitated at high temperatures. As a result, the desorption of oxygen, or the regeneration of active site, could be carried out easily and quickly in NO decomposition process, which thus resulted in the high activity.

The activity measured in the presence of 1%O_2 could compare to that measured in the absence of oxygen, and the difference in them was small, especially for those with Ce-substituted (see curves d and e in Fig. 5), indicating that the Ce-substituted samples possess strong forbearance to oxygen and can accommodate 1%O_2 in the feed gas with minor
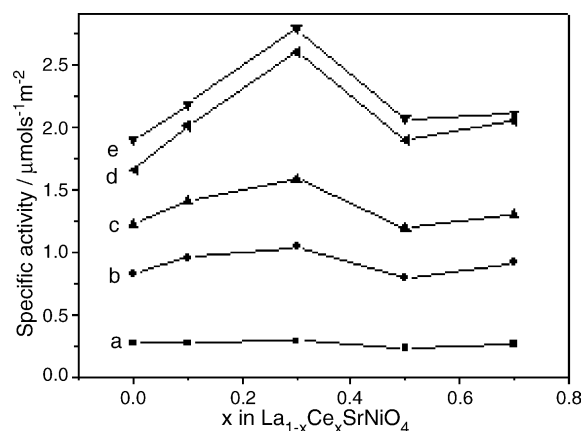

Fig. 5. Specific activity of $La_{1-x}Ce_xSrNiO_4$ ($0 \leq x \leq 0.7$) for NO decomposition at different temperature and oxygen content, $W/F = 1.2 \, g \, s \, mL^{-1}$. Curves a–c were measured in the presence of 6.0%O_2 at $T = 973$, 1023, 1123 K, respectively; curve d was measured in the presence of 1.0%O_2 at $T = 1123$ K; curve e was measured in the absence of oxygen at $T = 1123$ K.

effect on the activity. It is probably ascribed to the new highly active site formed in these samples due to the Ce addition. As a result, the removal of oxygen or the regeneration of active site could be carried out in time and the activity measured in the presence of 1%O_2 could be compared to that measured in the absence of oxygen. Besides, it should be noted that the activity increased with the increase of Ce content at the beginning ($x \leq 0.3$), then decreased with further increasing the Ce content ($x > 0.3$). The increase of activity ($x \leq 0.3$) suggested that the NO decomposition rate depends largely on the Ce content and the optimum value is 30 at.% ($x = 0.3$), at which Ce occupied the La-site of $La_{1-x}Ce_xSrNiO_4$ completely and the amount of active sites is in the largest (see Section 3.4). However, when Ce was further increased ($x \geq 0.5$), Ce cannot occupy the La-site of $La_{1-x}Ce_xSrNiO_4$ completely and CeO_2 phase appeared. Also, the number of oxygen vacancies, which is the active site of NO adsorption, was further decreased and was almost zero at $x = 0.5$ (see O_2-TPD), which thus resulted in the decrease of activity. The higher activity of $La_{0.3}Ce_{0.7}SrNiO_4$ (compared with that of $La_{0.5}Ce_{0.5}SrNiO_4$) might be ascribed to the synergistic effect of the various perovskite (-like) oxides (see XRD patterns). In all, a certain amount of Ce in the frame of $La_{1-x}Ce_xSrNiO_4$ (here, $x = 0.3$) is necessary for improving the activity of NO decomposition. Many authors [9–13] have reported the similar results, except that the Ce content in their catalyst system was low (10 at.%, $x = 0.1$) and the catalyst system they investigated is perovskite oxides with ABO_3 structure.

The activity measured at high O_2 partial pressure (6%O_2) was lower than that measured at low O_2 partial pressure (1%O_2), but it could keep in high value still (the specific activity at 1123 K reached 1.59 μmol s^{-1} m^{-2} for $La_{0.7}Ce_{0.3}SrNiO_4$), suggesting that the present Ce-substituted samples are excellent catalyst for NO decomposition even in the presence of excess oxygen (6%O_2). The specific activity of $La_{0.7}Ce_{0.3}SrNiO_4$ was always in the highest
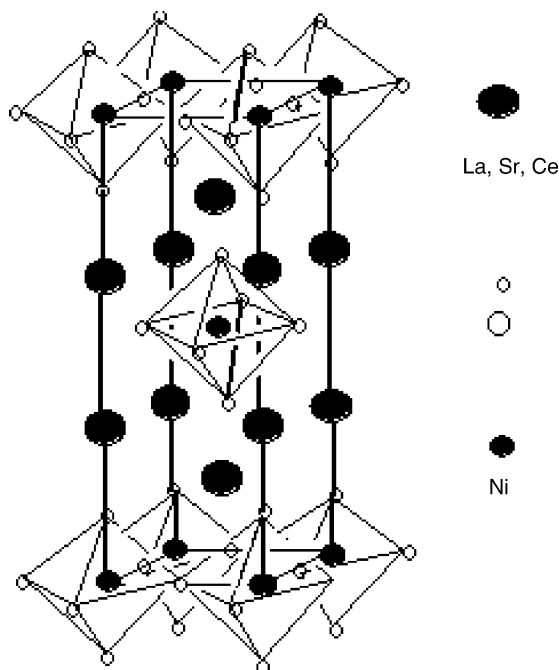
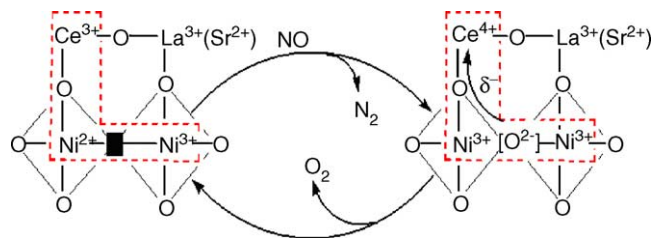Scheme 1. Ideal structure of $La_{1-x}Ce_xSrNiO_4$.

at the temperature range of $923 \leq T \leq 1123$ K, indicating that at high oxygen concentration ($6\%O_2$), the new highly active site is the main factor corresponding for the activity. Namely, the formation of a new highly active site that facilitates oxygen mobilization and desorption is very important for NO decomposition, especially in the presence of excess oxygen.
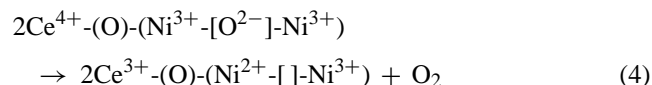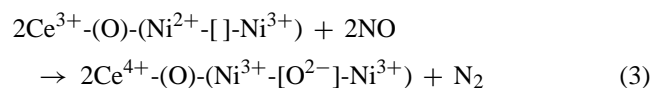
Ishihara et al. [27] reported recently that $La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O_3$ was active for NO decomposition at elevated temperature and that the N_2 yield at 1073 K reached ca. 15% when W/F was set at $3\,g\,s\,mL^{-1}$ (in the presence of $6\%O_2$, feed gas: $1\%NO/He$). Although the present experimental conditions were serious than their conditions, the present Ce-substituted catalysts showed higher activity for NO decomposition (the N_2 yield reached 32% for $La_{0.7}Ce_{0.3}SrNiO_4$, W/F $= 1.2\,g\,s\,mL^{-1}$; in the presence of $6\%O_2$; feed gas: $1\%NO$; $T = 1073$ K), suggesting that the present Ce-substituted samples are suitable catalysts for NO decomposition at elevated temperature, especially in the presence of excess oxygen.

3.6. Structure and active site

Scheme 1 shows the structure of perovskite-like oxides with ideal K_2NiF_4-type. This structure can be described as containing alternate layering of perovskite (ABO_3) and rock-salt (AO) units. In general, the active sites of perovskite (-like) oxides for NO decomposition are composed of B-site cation with low oxidative state and oxygen vacancy, described as: Ni^{2+}-[ ]-Ni^{3+}. But in the present case ($La_{1-x}Ce_xSrNiO_4$, $0 < x \leq 0.3$), a new complex active site, Ce^{3+}-(O)-(Ni^{2+}-[ ]-Ni^{3+}), might also appear in the sample (see Fig. 6) due to the addition of Ce, of which the valence is alterable

Fig. 6. Active site structure of $La_{1-x}Ce_xSrNiO_4$ for NO decomposition (■: oxygen vacancy).

($Ce^{4+} \Leftrightarrow Ce^{3+}$), to the La-site of $LaSrNiO_4$. Namely, the Ce in La-site would take part in the reaction and is one part of the active sites. The participation of Ce in the reaction might be written as follows:

$$2Ce^{3+}\text{-}(O)\text{-}(Ni^{2+}\text{-}[\ ]\text{-}Ni^{3+}) + 2NO$$
$$\rightarrow 2Ce^{4+}\text{-}(O)\text{-}(Ni^{3+}\text{-}[O^{2-}]\text{-}Ni^{3+}) + N_2 \qquad (3)$$

$$2Ce^{4+}\text{-}(O)\text{-}(Ni^{3+}\text{-}[O^{2-}]\text{-}Ni^{3+})$$
$$\rightarrow 2Ce^{3+}\text{-}(O)\text{-}(Ni^{2+}\text{-}[\ ]\text{-}Ni^{3+}) + O_2 \qquad (4)$$

In conclusion, the substitution of Ce for La in $LaSrNiO_4$ resulted two actions: one is to decrease the number of oxygen vacancies; the other is to improve the catalytic activity for NO decomposition. This seems self-contradiction, but it is true. The reason is that Ce^{4+} with higher Pauling electronegativity (more than La^{3+}) possessed stronger force to draw the electron from Ni^{3+}-O-Ni^{3+}, resulting in the easier removal of oxygen in Ni^{3+}-O-Ni^{3+} to form Ni^{3+}-[ ]-Ni^{2+} or the regeneration of active site (see Fig. 6). The optimum value of Ce content in $La_{1-x}Ce_xSrNiO_4$ is at $x = 0.3$ (i.e., $La_{0.7}Ce_{0.3}SrNiO_4$), which showed the highest activity for NO decomposition. However, with further increasing the Ce content ($x \geq 0.5$), the number of oxygen vacancies reduced and other phase(s) appeared and the perovskite-like structure were destroyed. As a result, the activity of NO decomposition decreased. As seen above (XRD and O_2-TPD), $La_{0.5}Ce_{0.5}SrNiO_4$ almost loss all the oxygen vacancy and CeO_2 phase appeared.

Based on the above discussion, it can be concluded that both the existence of oxygen vacancy and the formation of the new highly active site are necessary for improving the activity of NO decomposition, and the synergistic effect of them reached the maximum at $x = 0.3$ of $La_{1-x}Ce_xSrNiO_4$.

4. Conclusion

Pure $La_{1-x}Ce_xSrNiO_4$ phase with x from 0 to 0.3 was prepared and showed high activity for NO decomposition not only in the absence but also in the presence of gaseous oxygen. A new highly active site Ce^{3+}-(O)-(Ni^{2+}-[ ]-Ni^{3+}) that facilitates oxygen mobilization and desorption might be formed in the sample due to the addition of Ce, of which the valence is alterable. As a result, the catalysts exhibited

strong forbearance to O_2 and showed high activity for NO decomposition even in the presence of excess oxygen. It might be a suitable amount of Ce in $La_{0.7}Ce_{0.3}SrNiO_4$, which showed the highest activity for NO decomposition. Compared with that reported elsewhere, the present Ce-substituted catalysts showed higher activity for NO decomposition even in the presence of excess oxygen, and hence suggested that they are potential catalysts for NO removal at elevated temperature.

Acknowledgements

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