Structure–activity relationship of an A-site-doped LaNiO₃/SiO₂ catalyst

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Abstract

Improving the anti-carbon deposition and anti-sintering ability under the premise of maintaining high catalytic activity is the core issue of Ni-based catalysts applied in CO methanation reactions. To address this issue, a La₀.₇₅A₀.₂₅NiO₃/SiO₂ (A = Ce, Sr, Sm, and Ca) catalyst is prepared via a citric acid complexation method. XRD results show that the substituted elements (Sr, Sm, and Ca) enter the LaNiO₃ lattice and partially replace the A-site element La. The reduced Ni⁰ is beneficial to improve the medium temperature activity of the catalyst. The substitution of different elements produces different electronic effects that significantly affect the size of the Ni particles and the interaction between Ni and La₂O₃. The catalyst with doped Ca²⁺ as the A-site substituted element demonstrates better adsorption, storage, and migration capabilities for oxygen due to the lattice distortion that easily produces oxygen vacancies. Catalysts doped with Sr, Sm, and Ca as the A-site substituted element produce La₂O₂CO₃ after the reactions, which plays a role in eliminating carbon deposits.

Keywords

A-site substitution, CO methanation, LaNiO₃, Ni-based catalysts, structure–activity relationship

Date received: 16 June 2021; accepted: 6 October 2021
**Introduction**

The coal-to-natural conversion gas is an important method for the clean utilization of coal, with a key step being syngas methanation. The most practical methanation catalyst is Ni as the active component and Al2O3, SiO2, or ZrO2 as the support.1-7 The coal-based CO methanation reaction is a strong exothermic process. Ni-based catalysts are prone to carbon deposition and sintering under high-temperature conditions, causing catalyst deactivation and hindering their industrial application process.8,9 Therefore, starting from the catalyst structure, researchers have made significant progress in improving the anti-sintering and anti-carbon performance of Ni-based catalysts by reducing the size of Ni0 after reduction, increasing the dispersion of Ni0 in the support, and increasing the oxygen vacancies in the material.10-14

The perovskite composite oxide (ABO3) decomposes after reduction, forming elemental metal (B) and the oxide substrate (oxide of A).15-19 For example, LaNiO3 decomposes into Ni metal particles and La2O3 after reduction. Compared with the traditional Ni-based catalyst, a catalyst with LaNiO3 as the precursor can give a smaller Ni metal particle size and high dispersibility after reduction. The above-mentioned specific reducibility of perovskite makes it widely used in the catalytic fields of carbon hydroxide, CO, NO catalytic oxidation, and photocatalytic hydrogen production.20-23 It is reported during the literature that an Ni-based catalyst with LaNiO3 as the precursor shows good stability during the partial oxidation of methane, CO2 reforming of CH4, steam reforming of CH4, steam reforming of ethanol, and the methanation of CO2.16-24

However, perovskite has the inherent defect of a small specific surface area. Taking LaNiO3 as an example, the small specific surface area inevitably causes the reduced Ni to be densely distributed on the La2O3 substrate. However, the reduction temperature of the LaNiO3 increases. For the above two reasons, the catalytic activity of the LaNiO3 catalyst is lower than that of the supported Ni-based catalyst.

The redox characteristics of ABO3 mainly depend on the characteristics of the elements at the A and B sites. A-site elements can be replaced by elements of the same or of different valences to form $A_{x}A_{1-x}^{3+}B^{6+}$ perovskite, usually including La, Sr, K, Rb, Pb, Ba, Ca, and so on.30-33 This substitution causes defects in the crystal lattice, increases the mobility of oxygen, and changes the oxidation state of the B-site ion and the acidity and alkalinity of the catalyst surface.

Based on the above, our work reported herein adopts the citric acid complex method and the equal volume impregnation method to combine the precursors in the perovskite-type composite oxide (PTO), and make the PTO-type LaNiO3 crystal grains highly dispersed on the SiO2 support to prepare the supported LaNiO3/SiO2 catalyst. Different elements (Ce, Ca, Sr, and Sm) are used for A-site substitution to realize the doping of auxiliary ions in LaNiO3, such that the two auxiliary ions and the active component ions are highly dispersed and restricted to the precursor crystal grains. The reduced A, A’, and B are in close contact and are highly dispersed on the SiO2 support. The design of ABO3-type catalysts substituted at the A-sites is used to study the influence of the substitution of different elements on the structure of the catalyst, the reduced state of the active components and the catalytic performance, in order to solve or significantly improve the low activity of the perovskite-type CO methanation catalyst.

**Results and discussion**

**Crystalline structures**

The XRD patterns of the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A=Sr, Ce, Sm, and Ca) catalyst prepared by ion doping with different additives are shown in Figure 1.

As shown in Figure 1(a), the peaks at $2\theta$ = 23.32°, 32.91°, 47.35° and 69.82° (PDF No. 85-0797) are characteristic diffraction peaks of LaNiO3. The peaks at $2\theta$ = 20.85°, 26.55°, 36.59°, 40.29°, 42.46°, 50.18° and 60.07° (PDF No. 85-0797) are attributed to the characteristic diffraction peaks of SiO2, indicating its higher crystallinity. Due to the high diffraction peak of SiO2, the diffraction peaks of the other phases are not obvious. In order to further study the structures of the other phases, the characteristic peaks of SiO2 are removed for analysis and the result is shown in Figure 1(b).

It can be seen from Figure 1(b) that, except for the Ce-doped catalyst, the peaks at $2\theta$ = 32.77°, 47.35°, and 58.7° are the characteristic peaks of the typical rhombohedral perovskite structure (PDF no. 34-1077), indicating that this method can be used to prepare a relatively pure perovskite structure LaNiO3. The doped Sm, Sr, and Ca catalysts have a shift in the position of the characteristic peak of LaNiO3 at 47.35°, which is closely related to the doping of Sm, Sr, and Ca.35,36

The La$_{0.75}$Ce$_{0.25}$NiO$_3$/SiO$_2$ catalyst prepared by Ce doping shows diffraction peaks due to NiO (PDF no. 75-0179) at $2\theta$ = 37.3° and 43.3°, and the diffraction peak of cubic phase La$_2$O$_3$ (PDF no. 04-0856) at $2\theta$ = 27.2°, 31.4°, 45.2°, and 53.5°. However, the diffraction peak of LaNiO3 did not appear, nor was the related diffraction peak of Ce observed. This is consistent with the literature report that a high content of Ce was not easy to incorporate into the perovskite structure.37 Ce easily enters the La$_3$O$_7$ crystal lattice to form a La–Ce–O solid solution, which causes the crystal lattice to shrink and become a cubic phase La$_2$O$_3$.38

The La$_{0.75}$Ca$_{0.25}$NiO$_3$/SiO$_2$ catalyst prepared by calcium doping showed diffraction peaks due to LaNiO3 (PDF no. 10-0341) at $2\theta$ = 23.3° and 47.2°, and hexagonal diffraction peaks of La$_2$O$_3$ (PDF no. 40-1281) at $2\theta$ = 25.8° and 44.6°. The characteristic peak at $2\theta$ = 30.2° is attributed to CaO2 (PDF no. 03-0865), and a diffraction peak due to NiO appears, indicating that Ca did not completely enter the perovskite structure, and separated phase oxides are produced. The A-site substitution will affect the formation of the ABO3 structure of the perovskite. The influencing factors include (1) A-site ion radius and (2) substitution of A-site ions with different valences, resulting in changes in the valence of B and the size of potential ions.39 The ion radius of Ca$^{2+}$ (rCa$^{2+}$ = 99 pm) is smaller than that of La$^{3+}$ (rLa$^{3+}$ = 106 pm), which after doping will cause the average...
Figure 1. XRD patterns of fresh La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Ce, Sm, and Ca) and LaNiO$_3$/SiO$_2$ catalysts. (a) XRD patterns of all the phases and (b) XRD spectrum after SiO$_2$ is removed.

Table 1. PTO lattice parameters of catalysts prepared by doping different elements.

| Sample | Catalysts            | Lattice parameters of PTO (ESD values $\times 10^{-4}$) |
|--------|----------------------|--------------------------------------------------------|
| 1      | LaNiO$_3$/SiO$_2$    | a: 5.457(9), b: 5.457(9), c: 6.572(3)                  |
| 2      | La$_{0.75}$Ce$_{0.25}$NiO$_3$/SiO$_2$ | (No perovskite structure formed)                        |
| 3      | La$_{0.75}$Ca$_{0.25}$NiO$_3$/SiO$_2$ | a: 4.824(12), b: 4.824(12), c: 9.564(19)               |
| 4      | La$_{0.75}$Sr$_{0.25}$NiO$_3$/SiO$_2$ | a: 5.409(10), b: 5.409(10), c: 6.648(9)                |
| 5      | La$_{0.75}$Sm$_{0.25}$NiO$_3$/SiO$_2$ | a: 5.705(19), b: 5.705(19), c: 6.169(12)               |

PTO: perovskite-type composite oxide.

radius of A-site ions to decrease, and cause the allowable factor of the lattice structure to decrease, resulting in lattice distortion. However, the different valence states of Ca$^{2+}$ and La$^{3+}$ will also cause distortion, and the aggravated degree of distortion will produce impurity phases.

The catalyst prepared by doping Sr and Sm showed the characteristic peaks of LaNiO$_3$ (PDF no. 79-2448) (PDF no. 33-0711) at $2\theta$ = 33.24°, 58.16°, 32.9°, and 57.89°, respectively. Compared with the LaNiO$_3$/SiO$_2$ catalyst, the $2\theta$ value is slightly shifted. The peak shift phenomenon after doping can directly prove that Sr$^{2+}$ and Sm$^{3+}$ replaced La$^{3+}$ cations and entered the LaNiO$_3$ lattice, resulting in a change of the lattice parameters (Table 1). At the same time, the characteristic peak of La$_2$NiO$_4$ appeared at $2\theta$ = 24.0° and 31.68°.

Table 1 shows the PTO lattice parameters of the catalyst prepared by doping with different elements. Combined with the XRD results, it can be seen that Ca, Sr, and Sm doping can partially replace La$^{3+}$ and form a perovskite structure, resulting in changes in the crystal parameters of the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ catalyst, which is helpful in distributing the NiO active species. The 0.25% Ce failed to enter the perovskite lattice. However, due to the different radius of the doped ions, the positions of the diffraction peaks are different, which is also reflected in the differences in the lattice parameters of each sample.

The XRD spectra of the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Sm, and Ca) and LaNiO$_3$/SiO$_2$ catalysts after reduction are shown in Figure 2.

As shown in Figure 2(a), all the catalysts showed sharp SiO$_2$ diffraction peaks after reduction, indicating that the SiO$_2$ support remained stable during the reduction process. The XRD spectrum after excluding the SiO$_2$ diffraction peak is shown in Figure 2(b). As can be seen, the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Sm, and Ca) and LaNiO$_3$/SiO$_2$ catalysts showed the characteristic peaks due to the hexagonal phase La$_2$O$_3$ (PDF no. 74-1144) and Ni$^0$ after reduction, but none of the perovskite phase was detected. This indicates that the perovskite structure of the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ catalysts are destroyed during the reduction process, and that La$_2$O$_3$ and Ni are formed. At the same time, there are no related diffraction peaks due to doped elements.

The intensity and sharpness of the diffraction peaks of Ni$^0$ after reduction of the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ catalyst substituted by different elements are obviously different. The characteristic peaks of the Ni(111) crystal plane are calculated from the Scherrer formula to obtain the average particle size of the Ni particles (Table 2). After reduction of the La$_{0.75}$Sm$_{0.25}$NiO$_3$/SiO$_2$ catalyst, the diffraction peak of the Ni particles is too weak to be able to calculate the grain size. As shown in Table 2, compared with reduced LaNiO$_3$/SiO$_2$, the size of the Ni particles of the reduced La$_{0.75}$Sr$_{0.25}$NiO$_3$/SiO$_2$ catalyst is significantly reduced, indicating that the substitution of Sr for the A-site element La is helpful for the dispersion of Ni$^0$ on the surface of the support. The Ni$^0$ particle size of the La$_{0.75}$Ca$_{0.25}$NiO$_3$/SiO$_2$ catalyst prepared by doping with Ca increases after reduction. This is due to the incomplete doping of Ca, combined with XRD, there is reduction of NiO. It is reported in the literature that the size of the reduced Ni$^0$ particles from NiO is larger than that of reduced Ni$^0$ particles from LaNiO$_3$.
Catalytic performances

The catalytic activity tests on the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Sm, and Ca), LaNiO$_3$/SiO$_2$, and commercial MCR-2X catalysts are shown in Figure 3. The activities of all the catalysts showed a similar trend with increasing temperature. The CO conversion rate, CH$_4$ selectivity, and CH$_4$ yield increased first and then decreased with an increase in the temperature. The catalytic performance of the doped catalysts also improved. Compared with the commercial catalyst MCR-2X and LaNiO$_3$, the doped catalysts all show better selectivity and yield of CH$_4$ at medium and high temperatures. The La$_{0.75}$Sr$_{0.25}$NiO$_3$/SiO$_2$ and La$_{0.75}$Ca$_{0.25}$NiO$_3$/SiO$_2$ catalysts prepared by Sr and Ca doping at the A-site have a significantly higher CO conversion rate than the undoped catalyst LaNiO$_3$/SiO$_2$. When the temperature reached 550 °C, the CO conversion rate was above 90%, but when the temperature was higher than 550 °C, the CO conversion rate was lower than LaNiO$_3$/$SiO_2$. Compared with LaNiO$_3$/SiO$_2$, the La$_{0.75}$Sm$_{0.25}$NiO$_3$/SiO$_2$ catalyst improved the CO conversion rate only in the middle temperature region.

The methane selectivity (Figure 3(b)) and yield (Figure 3(c)) of the catalyst are significantly improved after the A-site is doped with different elements. As shown in Figure 3, the highest CH$_4$ selectivity is at about 500 °C. When the temperature is lower than 500 °C, the CH$_4$ selectivity increases on increasing the temperature. The three catalysts doped with Ca, Sr, and Sm elements are beneficial to improve the selectivity of CH$_4$ at medium temperature.

Reduction behavior

The cations at the B position (Ni) of the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ catalyst are reduced to metals, and the cations at the A position (La-A) are converted into the corresponding oxides.\textsuperscript{41} It is reported in the literature that the reduction of LaNiO$_3$ oxide is carried out in two steps. The reduction peak between 300 and 450 °C corresponds to the reduction of Ni$^{3+}$ to Ni$^{2+}$, forming La$_2$NiO$_4$, and the reduction peak above 450 °C corresponds to the reduction of Ni$^{2+}$ to Ni$^{0}$, forming metallic Ni particles.\textsuperscript{42,43} The restoration steps are as follows\textsuperscript{9}

\begin{equation}
2 \text{LaNiO}_3 + \text{H}_2 \rightarrow \text{La}_2\text{Ni}_2\text{O}_5 + \text{H}_2\text{O} \tag{1}
\end{equation}

\begin{equation}
\text{La}_2\text{Ni}_2\text{O}_5 + \text{H}_2 \rightarrow 2 \text{Ni}^0 + \text{La}_2\text{O}_3 + \text{H}_2\text{O} \tag{2}
\end{equation}

Figure 4 shows the reduction of La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Sm, and Ca) and LaNiO$_3$/SiO$_2$. For the LaNiO$_3$/SiO$_2$ sample, only two reduction peaks appear at 358 and 504 °C, which is consistent with the reduction of LaNiO$_3$ reported in the literature. The XRD results in Figure 1 also confirmed that the LaNiO$_3$/SiO$_2$ samples prepared had no other impurity phases. The three catalysts substituted with Ca, Sr, and Sm all showed two obvious reduction peaks and a weak shoulder peak. The low-temperature reduction peak near 370 °C is attributed to the reduction of LaNiO$_3$ to La$_2$NiO$_4$ and the reduction of free NiO at 500 °C. The weak small shoulder peak nearby is attributed to the reduction of NiO, formed outside the perovskite structure, to Ni$^{0}$, and the high-temperature reduction peak above 600 °C is attributed to the continued reduction of La$_2$Ni$_2$O$_5$ reduced to Ni$^{0}$ at 370 °C. The XRD results show that La$_{0.75}$Ca$_{0.25}$NiO$_3$/SiO$_2$ has a relatively obvious heterogeneous NiO diffraction peak, while the La$_{0.75}$Sr$_{0.25}$NiO$_3$/SiO$_2$ and La$_{0.75}$Sm$_{0.25}$NiO$_3$/SiO$_2$ substituted samples do not exhibit the NiO diffraction peaks. Corresponding to the temperature program reduction (TPR) results, the La$_{0.75}$Ca$_{0.25}$NiO$_3$/SiO$_2$ reduce the peak area is the largest at the 503 °C, and the reduction peak spans a wide temperature, presenting a stepped reduction, which is beneficial for the reduction of different types of Ni particles.
during the process of increasing the reaction temperature, thereby improving the catalytic activity of the catalyst. It is worth noting that the area of the first peak of the substituted La\textsubscript{0.75}A\textsubscript{0.25}NiO\textsubscript{3}/SiO\textsubscript{2} (A = Sr, Sm, and Ca) catalyst is significantly increased. Among them, the reduction peak of the Ca\textsuperscript{2+}-substituted La\textsubscript{0.75}Ca\textsubscript{0.25}NiO\textsubscript{3}/SiO\textsubscript{2} sample increases most obviously at around 370 °C. Combined with analysis of the XRD results, Ca\textsuperscript{2+} substitution leads to the formation of separate NiO phases on the surface, prompting the reduction peak at 370 °C to include LaNiO\textsubscript{3} to La\textsubscript{2}NiO\textsubscript{4} reduction and reduction of free NiO.

The Ni dispersions on La\textsubscript{0.75}A\textsubscript{0.25}NiO\textsubscript{3}/SiO\textsubscript{2} (A = Sr, Sm, and Ca) catalysts calculated by CO chemisorption are summarized in Table 3. All La\textsubscript{0.75}A\textsubscript{0.25}NiO\textsubscript{3}/SiO\textsubscript{2} (A = Sr, Sm, and Ca) catalysts exhibit a Ni dispersion of 27.46%−32.85%, resulting in a surface area of Ni metal (1.59−3.30 m\textsuperscript{2}/g sample). In contrast, the Sr-doped catalyst has better Ni particle dispersion, which is consistent with the XRD characterization of the reduced catalyst.

It is reported that A-site substitution can change the B-site valence and oxygen defect concentration, thereby changing the oxidation–reduction performance of the catalyst.\textsuperscript{9} The reduction peaks of the three La\textsubscript{0.75}A\textsubscript{0.25}NiO\textsubscript{3}/SiO\textsubscript{2} (A = Sr, Sm, and Ca) catalysts after substitution all moved in the high-temperature direction. The increase in the low-temperature reduction temperature is due to the formation and separation of free NiO, which leads to the corresponding Ni\textsuperscript{3+} and Ni\textsuperscript{2+} reduction peak moving to the high-temperature direction. Compared with LaNiO\textsubscript{3}, the high-temperature reduction temperature of the substituted catalysts increased above 600 °C. The high-temperature reduction peak of the Ca\textsuperscript{2+}-substituted La\textsubscript{0.75}Ca\textsubscript{0.25}NiO\textsubscript{3}/SiO\textsubscript{2} catalyst was the highest at 658 °C. Furthermore, the substitution of Ca\textsuperscript{2+} and Sr\textsuperscript{2+} for La\textsuperscript{3+} represents a metamorphic substitution. The replacement of the lower oxidation state with the
A-site cation will increase the high-valence ratio of the Ni B-site ion, aggravate the deformation of the perovskite octahedral crystal phase, modulate the oxygen behavior of the catalyst and surface oxygen species, increase the difficulty of the reduction of lattice oxygen, and produce oxygen vacancies. The binding activity test showed that Ca\(^{2+}\) and Sr\(^{2+}\) replaced the A-site element La\(^{3+}\), which is an effective strategy to generate oxygen vacancies to improve the mesothermal activity. However, the binding energy of the substituted catalyst Ni\(^{2+}\) will be enhanced, weakening the covalent bond of A–O and increasing the ionic bond of Ni–O, which is consistent with the X-ray photoelectron spectroscopy (XPS) results.

By fitting the XPS curve, the XPS spectra of the La\(_{0.75}A_{0.25}\)NiO\(_3\)/SiO\(_2\) (A = Sr, Sm, and Ca) and LaNiO\(_3\)/SiO\(_2\) catalyst samples are given. As shown in Figure 5, the XPS spectrum of La3d shows two double peaks, La3d\(_{3/2}\) and La3d\(_{5/2}\), which are similar in form to standard trivalent La3d compounds. The XPS spectrum was fitted to four peaks, located at 834, 838.1, 851.0, and 854.9 eV, which correspond to the La3d\(_{3/2}\) and La3d\(_{5/2}\) bond, the La3d\(_{3/2}\) and La3d\(_{5/2}\) bond, and belong to La2O3 and LaNiO3. It is proved that each catalyst has an obvious La\(^{3+}\) compound and a LaNiO\(_3\) crystal phase, which indicates that the doped Sm, Sr, and Ca elements can be substituted at the A position, which is also consistent with the XRD characterization.

The XPS spectrum of Ni shows that many of the peaks are similar to the standard Ni2p peaks, which are typical Ni2p peaks (Figure 5(b)). The Ni2p peaks of the LaNiO\(_3\)/SiO\(_2\) catalyst at 853.6 and 855.8 eV correspond to Ni\(^{2+}\) and Ni\(^{3+}\), respectively.\(^{13}\) The Ni ions in LaNiO\(_3\) coexist as Ni\(^{2+}\) and Ni\(^{3+}\). When La\(^{3+}\) is partially replaced with low-valence Ca\(^{2+}\) and Sr\(^{2+}\), the peak area of Ni\(^{3+}\) increases, the content of high-valence Ni\(^{3+}\) increases, and the ratio of Ni\(^{3+}/Ni^{2+}\) increases (Table 4). Compared with the undoped LaNiO\(_3\) catalyst, the electron-binding energy of doped Ca, Sr, and Sm elements moves to a higher binding energy direction than that of undoped LaNiO\(_3\), which indicates that the ionic bond of Ni–O is enhanced, the interaction force is enhanced, and that the result of TPR consistent.

The activity of perovskite-type oxides is strongly affected by the properties of near-surface oxygen species. It can be seen from the O1s spectrum (Figure 5(c)) that in the La\(_{0.75}A_{0.25}\)NiO\(_3\)/SiO\(_2\) (A = Sr, Sm, and Ca) and LaNiO\(_3\)/SiO\(_2\) catalyst samples, three obvious O1s binding energy peaks appear. The peak at 528–529 eV is regarded as the surface oxygen species O\(_{ad}\), which corresponds to the lattice perovskite O\(^{2-}\). and the peak near 530–531 eV corresponds to the surface adsorbed oxygen O\(_{lat}\). The peak near 532.4 eV corresponds to the Si–O bond between SiO\(_2\). The Si–O position at 532.4 eV did not change significantly, indicating that the structure of the SiO\(_2\) support remained stable before and after doping and was not destroyed. Comparing the peak positions and peak areas of the catalysts, it can be seen that after doping with Sr, Ca, and Sm elements, the peak areas and peak positions of 528.7 and 530.4 eV all move to a high-binding energy, indicating that the doped perovskite ore is more difficult to reduce, which is consistent with the H\(_2\)-TPR results. At the same time, the area ratio of lattice oxygen and adsorbed oxygen has changed, indicating that doping with different elements affects the existence of oxygen species.

In Table 5, it can be seen that the percentage of lattice oxygen O\(_{lat}\) and surface adsorbed oxygen O\(_{ad}\) decreases on doping with different elements. Among them, the ratio of O\(_{ad}/O_{lat}\) in the Ca-doped catalyst decreased significantly, and the content of adsorbed oxygen O\(_{ad}\) increased. This is due to the substitution of Ca\(^{2+}\) for La\(^{3+}\), which distorted the perovskite structure and broke the internal balance of LaNiO\(_3\), thereby resulting in the distribution of oxygen not being uniform, and more unsaturated nickel ions and oxygen vacancies are formed. The oxygen vacancies have a promoting effect on the adsorption of oxygen, causing changes in the adsorption of oxygen and lattice oxygen, and conversion between the two.\(^{44}\)

From the results of TPR and XRD combined with the performance test data, it can be concluded that doping with different elements has a significant impact on the structure and performance of the prepared catalyst. Doping with Ca\(^{2+}\), Sr\(^{2+}\), and Sm\(^{2+}\) whose ion radius is close to La\(^{3+}\), doping elements can enter the LaNiO\(_3\) lattice and partially replace the A-site element La. After substitution, the reduction temperature increases, the interaction between the active material and the support is enhanced, and the reduced Ni\(^0\) is beneficial to improve the mid-temperature activity of the methanation reaction. However, doping with 0.25 wt% Ce\(^{3+}\) cannot successfully replace La at the A-site to form LaCeNiO\(_3\), but enters the La\(_2\)O\(_3\) lattice to cause the lattice to shrink, forming NiO and La–Ce–O solid solutions. In XPS, compared with the undoped LaNiO\(_3\)/SiO\(_2\) catalyst, the catalyst doped with Ca, Sr, and Sm moves to a higher binding energy direction, which enhances its interaction force and promotes the covalent double bond and electron interaction. The interaction promotes the dissociation and adsorption of CO.\(^{45–47}\) The perovskite catalysts doped with Ca and Sr elements are more likely to generate oxygen vacancies and have better oxygen adsorption, storage and migration capabilities.

### Table 3. CO nickel dispersion, nickel surface areas, and of La\(_{0.75}A_{0.25}\)NiO\(_3\)/SiO\(_2\) (A = Sr, Sm, and Ca) catalysts.

| Sample | Catalyst | Ni dispersion (%) | Ni surface area (m\(^2/\)g sample) | Ni surface area (m\(^2/\)g metal) | Ni particle diameter (nm) |
|--------|----------|-------------------|-----------------------------------|-----------------------------------|--------------------------|
| 1      | LaNiO\(_3\)/SiO\(_2\) | 27.46            | 3.30                              | 173.15                            | 2.72                     |
| 2      | La\(_{0.75}Sr_{0.25}\)NiO\(_3\)/SiO\(_2\) | 32.85            | 3.81                              | 136.06                            | 3.83                     |
| 3      | La\(_{0.75}Ca_{0.25}\)NiO\(_3\)/SiO\(_2\) | 28.37            | 3.79                              | 158.84                            | 2.69                     |
| 4      | La\(_{0.75}Sm_{0.25}\)NiO\(_3\)/SiO\(_2\) | 33.29            | 1.59                              | 139.75                            | 3.08                     |
Stability tests

In order to study the stability of the catalysts prepared by doping with different elements, the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Sm, and Ca) and LaNiO$_3$/SiO$_2$ catalysts were tested for their stability at 700 °C, the 0.1 MPa, and 15,000 mL$^{-1}$ g$^{-1}$ h (Figure 6). It can be observed from Figure 6 that the La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Sm, and Ca) and LaNiO$_3$/SiO$_2$ catalysts show good stability at 700 °C for 30 h, and the CO conversion remains above 85%.

Catalyst structures after the stability tests

After 30 h of high-temperature catalytic reaction, the diffraction peaks of La$_2$O$_3$ of each catalyst disappeared, and La$_2$O$_2$CO$_3$ appeared at 22.3°, 25.1°, 25.8°, 30.3°, 33.8°, and 56.9° (22-0642) (Figure 7). The diffraction peak of the crystalline phase, La$_2$O$_2$CO$_3$ is formed because La$_2$O$_3$ absorbs the by-product CO$_2$ produced in the reaction. At the same time, La$_2$O$_2$CO$_3$ can react with carbon deposits on the active site, thus playing an important role in removing carbon deposits.

After the stability test, each catalyst has diffraction peaks due to Ni metal element (PDF no. 01-1260) at 44.5° and 51.8°. The size of the Ni nanoparticles after the reaction was estimated by the Scherrer formula. The results are shown in Table 6. It can be seen from the table that the catalyst prepared by doping elements Ca, Sr, and Sm reacted at 700 °C for 30 h, and the Ni particles became larger, indicating that it is easier to migrate and slightly aggregate in high-temperature environment, but it has little effect on the activity of the catalyst.

The LaNiO$_3$/SiO$_2$ and La$_{0.75}$Ce$_{0.25}$NiO$_3$/SiO$_2$ catalysts showed obvious weight gains in the range of 300–600 °C (Figure 8(a)), accompanied by an exothermic peak at the
same temperature in the DSC chart, which is due to Ni^0 in the catalyst after the reaction reacting with CO2 in the air to form nickel carbonate. As the temperature rises further, the substance decomposes. The catalyst prepared by doping with Ca and Sr shows an obvious exothermic peak at about 600 °C, which is attributed to the burning of graphitic carbon. The catalyst prepared by doping with Ca and Sr shows a significant exothermic peak at about 600 °C, which is also attributed to the burning of graphitic carbon. From Figure 8(a), there is a significant weight loss at about 600 °C, indicating that the catalyst has produced more carbon deposits after the stability test. The catalyst prepared by doping with Sm has no obvious weight loss stage or exothermic peak in Figure 8(a) and 8(b). This is because the lanthanide element Sm has the best plasticity among rare earth metals. The addition of rare earth Sm promotes the conversion of NiO into Ni^0, and the presence of elements in the silicon dioxide lattice will generate oxygen vacancies to maintain its electron neutrality. These vacancies make it easier to activate

Table 4. The binding energy values and Ni concentrations of La_{0.75}A_{0.25}NiO_3/SiO_2 and LaNiO_3/SiO_2.

| Sample | Catalyst               | Ni2p3/2 binding energy (eV) | Ni^2+/Ni^3+ (%) | Ni atom content (%) |
|--------|------------------------|-----------------------------|-----------------|---------------------|
| 1      | LaNiO_3/SiO_2          | 853.6                       | 855.7           | 72.1                | 4.66                |
| 2      | La_{0.75}Sr_{0.25}NiO_3/SiO_2 | 853.7                       | 855.8           | 76.0                | 5.10                |
| 3      | La_{0.75}Ca_{0.25}NiO_3/SiO_2 | 853.7                       | 855.8           | 75.1                | 4.05                |
| 4      | La_{0.75}Sm_{0.25}NiO_3/SiO_2 | 853.7                       | 855.8           | 73.2                | 4.58                |

Table 5. The binding energy values and O atomic ratio of the La_{0.75}A_{0.25}NiO_3/SiO_2 and LaNiO_3/SiO_2.

| Sample | Catalyst               | O1s binding energy (eV) | O_ad/O_lat (%) |
|--------|------------------------|-------------------------|----------------|
| 1      | LaNiO_3/SiO_2          | 528.7                   | 38.2           |
| 2      | La_{0.75}Sr_{0.25}NiO_3/SiO_2 | 528.9                   | 10.6           |
| 3      | La_{0.75}Ca_{0.25}NiO_3/SiO_2 | 529.0                   | 9.5            |
| 4      | La_{0.75}Sm_{0.25}NiO_3/SiO_2 | 528.8                   | 15.3           |

Figure 6. The stability testing of the La_{0.75}A_{0.25}NiO_3/SiO_2 (A = Sr, Sm, and Ca) and LaNiO_3/SiO_2 catalysts at 700 °C, 0.1 MPa, 15,000 mL g^{-1} h^{-1}, 30 h (a) CO conversion and (b) CH4 selectivity.

Figure 7. XRD patterns of the La_{0.75}A_{0.25}NiO_3/SiO_2 (A = Sr, Sm, and Ca) and LaNiO_3/SiO_2 catalysts after stability sting at 700 °C for 30h, space velocity of 15,000 h^{-1}.
NiO, and weaken the bond between Ni–O, thereby promoting the formation of Ni⁰, and eliminating carbon deposition.

**Conclusion**

In this paper, an La₀.₇₅A₀.₂₅NiO₃/SiO₂ (A = Sr, Ce, Sm, and Ca) catalyst was prepared by the citric acid complexation method. The elements Ca, Sr, and Sm successfully partially replaced the A-site element La in LaNiO₃. After reduction, the perovskite structure is destroyed, forming hexagonal La₂O₃ and Ni crystal phases. The Ce element failed to enter the perovskite structure in the Ce element-doped catalyst, but was doped into the La₂O₃ lattice to form the cubic La–Ce–O solid solution and the NiO separated phase. After reduction, the structure of the La–Ce–O solid solution remained unchanged.

Compared with undoped LaNiO₃/SiO₂, the catalyst prepared by partially replacing the A-site elements in LaNiO₃ with Ca, Sr, and Sm had significantly improved catalytic performance at medium temperature. Among these, the La₀.₇₅Ca₀.₂₅NiO₃/SiO₂ catalyst showed the best catalytic performance. When the temperature reached about 550 °C, the CO conversion rate reached more than 90%. This is due to the use of low-valent Ca²⁺ instead of high-valent La³⁺ to cause distortion of the catalyst lattice, producing oxygen vacancies so that it exhibits better oxygen adsorption, storage, and mobility. In addition, it has a wide reduction temperature, allowing Ni to interact with the support in various ways. Combined with the XRD and thermogravimetric (TG)-DSC results of each catalyst after the stability test, it can be seen that the catalyst prepared by doping with Sm shows the best anti-sintering and anti-carbon deposition performance, which is related to the small size and high dispersion of Ni particles after reduction of the La₀.₇₅Sm₀.₂₅NiO₃/SiO₂ catalyst. This also shows that the substitution of different elements produces different electronic effects, which significantly affect the size of Ni particles and the interaction between Ni and La₂O₃, as confirmed by Figures 2 and 3.

**Experimental**

**Preparation of SiO₂ supports**

Commercial silicon oxide was calcined at 700 °C for 5 h at a heating rate of 2 °C/min, and the obtained powder granular material was used as the support.

**Preparation of the catalysts**

The catalysts are prepared by the citric acid complex method: La(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Ca(NO₃)₂·4H₂O, SmN₃O₉·6H₂O, Sr(NO₃)₂, and other nitrates are measured in the proportions: n(La⁺):n(Ni) = 1, n(La):n(A) = 3:1 (A = Ce, Ca, Sm, and Sr) dissolved in distilled water, add the molar ratios of total metal cations: citric acid:ethylene glycol were 1:2:4. After the sample had completely dissolved, it was immersed in an equal volume on the carrier SiO₂, stirred and evaporate to a green gel at 80 °C, and at room temperature, dried at 80 °C for 6 h and then heated up to 120 °C for 12 h. The resulting powder was calcined at 350 °C at a heating rate of 2 °C/min for 2 h, and then at 700 °C for 5 h at the same heating rate. The SiO₂-supported perovskite catalyst is

**Table 6. Ni particle size in the catalysts before and after the reaction.**

| Sample | Catalyst                           | Ni average grain size/nm Before reaction | After stability test | Rate of change (%) |
|--------|------------------------------------|----------------------------------------|---------------------|--------------------|
| 1      | LaNiO₃/SiO₂                        | 17.29                                  | 18.40               | 6.42               |
| 2      | La₀.₇₅Sr₀.₂₅NiO₃/SiO₂              | 15.62                                  | 18.02               | 15.36              |
| 3      | La₀.₇₅Ca₀.₂₅NiO₃/SiO₂              | 20.70                                  | 24.12               | 16.52              |
| 4      | La₀.₇₅Sm₀.₂₅NiO₃/SiO₂              | –                                      | 14.86               | –                  |

**Figure 8.** TG-DSC patterns of the La₀.₇₅A₀.₂₅NiO₃/SiO₂ (A = Sr, Sm, and Ca) and LaNiO₃/SiO₂ catalysts after stability text at 700 °C for 30 h, space velocity of 15,000 h⁻¹. (a) TG patterns of the catalysts and (b) DSC patterns of the catalysts.
obtained, expressed as La$_{0.75}$A$_{0.25}$NiO$_3$/SiO$_2$ (A = Sr, Ce, Sm, and Ca) and LaNiO$_3$/SiO$_2$.

Catalytic performance evaluation

The performance tests were carried out using a WF5M-3060DL catalytic evaluation instrument (Tianjin Xianquan Co., Ltd, China). The powdered catalyst (200 mg) of 40–60 mesh particle size was mixed with quartz sand and then placed in a tubular quartz microreactor. First, the catalysts was purged with N$_2$ for 2 h to remove the impurities on the surface, and then reduced at 400 °C for 50 min using hydrogen. Second, the reaction gases (H$_2$:CO = 3, volume ratio) and Ar as a balance gas were switched into the microreactor after the catalyst had been cooled to 200 °C. The hourly space velocity was 10,000 h$^{-1}$, and the temperature of catalytic evaluation was from 250 to 700 °C with a temperature interval of 50 °C at 0.10 MPa. The reactants and products were analyzed on line using on online SP-2100A gas chromatograph equipped with a thermal conductivity detector (TCD). The details of the catalytic performance were calculated based on formulas (3)–(5) as follows:

$$X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\% \quad (3)$$

$$S_{CH_4} = \frac{[CH_4]_{out}}{[CO]_{in} - [CO]_{out}} \times 100\% \quad (4)$$

$$Y_{CH_4} = \frac{[CH_4]_{out}}{[CO]_{in}} \times 100\% \quad (5)$$

Characterization of the catalysts

The XRD characterization was performed using a SmartLab 9 KW model X-ray diffractometer produced by Rigaku Corporation. It adopts the Cu target configuration (wavelength 0.154 nm) and is equipped with a high-sensitivity D/teX Ultra 250 detection system, tube voltage is 40 kV, and the tube current is 40 mA. The catalyst scanning is characterized by the STA409PC synchronous thermal analyzer produced by NETZSCH in Germany, and the amount of carbon deposited on the spent catalyst is analyzed from the TG curve obtained. During the TG test, the sample was heated from 40 to 1000 °C at a heating rate of 10 °C/min in an air atmosphere.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the National Natural Science Foundation of China (no. 21962014) and the Inner Mongolia Autonomous Region Science and Technology plan project (2020GG066).

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