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Article

Preparation of LaXCoO_3 ($\text{X} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ce}$) catalysts and their performance for steam reforming of ethanol to hydrogen

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ABSTRACT

Perovskite nanocomposite catalysts LaXCoO_3 ($\text{X} = \text{Mg}, \text{Ca}, \text{Sr}, \text{or Ce}$; $n(\text{La}):n(\text{X}) = 3:2$) have been prepared by a citric acid-complexing method and used for steam reforming of ethanol (SRE), leading to hydrogen generation. The samples were characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, N_2 adsorption-desorption, and H_2 temperature-programmed reduction. The effects of elemental substitution in the LaCoO_3 perovskite were studied, and the catalytic performance and primary stability of the hydrogen production from SRE were investigated. In the highly substituted samples, only the Ce-doped sample was isolated as the pure perovskite phase. The presence of a Co_3O_4 phase in the Ca-doped or Sr-doped samples was beneficial for the reduction of the active Co component, while Sr-doped or Ce-doped samples showed good activity and stability. The sample incorporating Sr demonstrated better catalytic performance than those of other samples.

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1. Introduction

Hydrogen is an efficient and clean fuel [1,2] and is considered to be one of a small list of new energies capable of solving the human energy crisis in the 21st century. The rapid development of hydrogen-based fuel cells and fuel cell vehicles has led to an increase in the demand for hydrogen, which will continue to increase in the future. At present, most hydrogen used in industry is derived from fossil fuel reforming and water electrolysis. In these processes, the former consumes fossil fuels, and the latter requires higher energy than it produces. These problems present significant barriers to the widespread application of hydrogen. Because of this, the reforming of lower

alcohols has been studied extensively; the steam reforming of ethanol (SRE) has attracted attention because the raw material of 10% (v/v) biomass ethanol can be obtained directly from the production industry without distillation. The reaction process is expressed as:

The SRE to hydrogen is endothermic [3], with complex reactions and numerous by-products, including acetaldehyde, acetone, ethylene, CO, and carbon deposition [4]. Hence, it is particularly important that catalysts have good catalytic performance and high selectivity and stability over the whole process of producing hydrogen from ethanol. According to the literature, many catalysts containing Ni [5,6], Co [7,8], and other

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metals [9,10] in the SRE reaction show superior performance and selectivity. Ni-based catalysts show excellent activity in breaking the C–C and C–H bonds in ethanol; however, they suffer from significant carbon deposition, while Co-based catalysts exhibit outstanding reforming performance.

Supported on various oxides such as Al_2O_3 [11], SiO_2 [12], MgO [13], CeO_2 [14], and La_2O_3 [15], cobalt has been investigated widely, and CeO_2 and La_2O_3 have proved to be catalyst supports with excellent activity and desirable reaction products. However, some challenges still exist for the application of Co-based catalysts in SRE because of their low stability, which is caused by the sintering of metallic Co and coke deposition. In particular, higher-content cobalt generally leads to more serious sintering. Rare earth elements on the surface of the supports have been shown to react with CO_2 [7] to form carbonate, which could eliminate surface coke. CeO_2 can generate lattice oxygen, which reacts with surface carbon deposits to eliminate carbon. Therefore, the supports also play important roles in the SRE reaction [14].

ABO_3 perovskite is known to be stable and shows good catalytic activity in many fields. In recent years, researchers have found that perovskites in SRE demonstrate catalytic performance, but the amount of active metal is limited. Therefore, the ability to maximize the use of a metal in a perovskite becomes the most important problem. Partial substitution of the ABO_3 perovskite by another metal (alkali metal or rare earth element) at the A site forms $\text{A}_{1-x}\text{A}_x\text{BO}_3$ -type materials, which can change the oxidation state of the B site ion and the oxygen vacancy density, indirectly affecting the catalytic performance of perovskite.

LaCoO_3 perovskite catalyst in SRE does not tend to form CH_4 and CO, but its activity is too low, and appropriate substitution at the A or B sites is required to improve its catalytic performance [16–20]. Cui et al. [21] found that Ce-doped LaCoO_3 perovskite significantly promoted the catalytic performance of the methane combustion reaction. Sr-doped $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ ($0 < x < 0.4$, $M = \text{La, Ca, Fe}$) compares favorably with the noble metal catalyst 0.5 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ in the catalytic combustion of methane [22]. The catalytic performance of Cu-doped $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ perovskite is significantly higher in the synthesis of lower alcohols [23]. Bedel et al. [24] confirmed that in the Fischer-Tropsch (F-T) reaction the peak amount of metallic cobalt, produced by the reduction of $\text{La}_{1-y}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ perovskite, could reach 2.1%. Zn-doping of the LaCoO_3 perovskite as studied by Chu et al. [7] enhanced the catalytic performance of SRE remarkably.

This paper examines the effect of LaXCoO_3 ($X = \text{Mg, Ca, Sr, Ce}$), formed by the substitution of four different metal ions in LaCoO_3 at the A sites, on both the perovskite structure and the valence Co at the B sites. These catalysts were characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), N_2 adsorption-desorption (BET), and H_2 temperature-programmed reduction (TPR). The substitution effects of four elements on the LaCoO_3 perovskite structure and performance have been studied, and the catalytic performance and stability of the catalysts for hydrogen production by SRE

were investigated.

2. Experimental

2.1. Catalyst preparation

Perovskite composite catalysts, LaXCoO_3 ($X = \text{Mg, Ca, Sr, Ce}$), were prepared by the citric acid-complexing method. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and citric acid (CA) were used as reagents. The six metal nitrates, in the required stoichiometric ratios ($n(\text{La}+X)/n(\text{Co}) = 1$, $n(\text{La})/n(X) = 3:2$), and citric acid ($n(\text{CA})/n(M) = 1.2$), were dissolved in deionized water in separate beakers. The appropriate amount of PEG 400 ($n(\text{PEG 400})/n(\text{CA}) = 0.2$) was added to the citric acid solution, and then the metal nitrate solution was added. The mixed solutions were stirred at 80 °C at atmospheric pressure until a gel formed. This gel was dried in an oven at 120 °C for 24 h to give the precursor materials, and these were calcined at 750 °C for 3 h to obtain the catalyst samples LaCoO_3 , $\text{La}_{0.6}\text{Mg}_{0.4}\text{CoO}_3$, $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, and $\text{La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$, which are denoted L-C, L-Mg-C, L-Ca-C, L-Sr-C, and L-Ce-C, respectively.

2.2. Catalyst characterization

The crystal phase of the catalysts was measured on a Philips X'pert pro MPD X-ray diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation, operating at a voltage of 40 kV and current of 50 mA. The scattering angles were between 20° and 80°.

The catalysts were also characterized with the TENSOR 27 infrared spectrometer (IR, Bruker, Germany). The catalyst was diluted 100 times with KBr before being ground and formed into a tablet. These samples were scanned at room temperature (32 scans) from 4000 to 400 cm^{-1} .

The morphologies of the catalysts were recorded using a Hitachi S-3400 field emission scanning electron microscope (FE-SEM) with the accelerating voltage 20 kV.

The surface elements of the catalysts were analyzed on a XSAM800 spectrometer (XPS, Kratos, UK) with an $\text{Al K}\alpha$ ($h\nu = 1486.6 \text{ eV}$) X-ray radiation source. Charging effects were corrected by referencing the binding energy of the C 1s peak from carbon contamination at 284.6 eV.

The specific surface area and average pore diameter of catalysts were determined on a NOVA 1000e surface area and pore size distribution analyzer (Quantachrome, USA). The nitrogen adsorption volume of the loaded catalyst (200 mg) was measured with cryogenic liquid nitrogen at -196 °C. The specific surface area of the catalyst was calculated by the BET equation, and the pore size distribution of catalyst was measured using the BJH model.

For H_2 -TPR experiment, H_2 consumption of catalyst (50 mg) was recorded online on an SC-200 gas chromatograph with a thermal conductivity detector (TCD) in a 5% H_2/N_2 gas mixture at a heating rate of 10 °C/min.

2.3. Catalyst activity measurements

The catalyst activity was measured using a fixed-bed microreactor. In each run, the catalyst (100 mg, 60–80 mesh) was diluted with quartz sand (800 mg, 40–60 mesh) and loaded into the reactor. Prior to reaction, the catalysts were heated to the required temperature in 5% H₂/Ar and then cooled to the initial reaction temperature under a flow of N₂. A liquid reaction mixture, with a water to ethanol molar ratio of 6:1, was fed into the reactor through a DDB-300 electronic peristaltic pump at a rate of 4.8 mL/h before mixing with N₂ (as a carrier gas, 60 mL/min), and then vaporized at 150 °C. The total space velocity was 50 000 h⁻¹. The catalyst reactivity was measured at 600 °C for 10 h. The reaction products were analyzed online on an SC-200 gas chromatograph with a TCD. H₂, N₂, CO, CO₂, CH₄, and other permanent gases were separated on a TDX-01 column using 30 mL/min pure Ar as the carrier, while H₂O, ethanol, acetone, and acetaldehyde were separated on a Porapak-Q column.

3. Results and discussion

3.1. The structure and surface elements of catalysts

3.1.1. Phase analysis of catalysts

Figure 1 shows the XRD patterns of the prepared catalysts. All samples show diffraction peaks attributed to the LaCoO₃ rhombohedral crystalline phase. When other elements are substituted into the perovskite, the samples contained hybrid phases. Only the L-Ce-C sample displayed a pure perovskite crystal phase. The characteristic reflection peaks of the MgCo₂O₄ phase appeared in L-Mg-C ($2\theta = 43^\circ$ and 62.5°). A Co₃O₄ phase was observed in both L-Sr-C and L-Ca-C ($2\theta = 31.3^\circ$, 36.8° , and 65.7°), but L-Sr-C also contained lanthanum oxide and a strontium carbonate impurity. Figure 1 also shows a shift in the characteristic peaks of the perovskite as different elements were substituted into LaCoO₃. Around the characteristic peak of perovskite ($2\theta = 33^\circ$), the peaks of L-Mg-C, L-Sr-C, and L-Ca-C were slightly shifted to lower angles (-0.1°), while the same peak in L-Ce-C was shifted to a higher angle ($+0.3^\circ$). Thus, substituting different elements affected the LaCoO₃ perovskite structure, of which L-Ce-C had the greatest change. To further investigate, the cell parameters of the samples were calculated and are listed in Table 1.

Table 1 shows that the lattice parameters of L-Mg-C, L-Sr-C, and L-Ca-C are similar or slightly larger than L-C (0.5436 nm), whereas L-Ce-C is 0.0017 nm smaller. In terms of ionic radius, Mg²⁺ (0.068 nm) and Ca²⁺ (0.118 nm) are smaller than La³⁺ (0.136 nm). The Ce³⁺ (0.134 nm) is quite similar to La³⁺, and only Sr²⁺ (0.144 nm) is larger than La³⁺. Because of the different ionic radii, substituted elements into the perovskite lattice led to the differences in the lattice parameters [25,26]. Although the ionic radius of Mg²⁺ or Ca²⁺ is much less than that of La³⁺, the differences in the lattice parameters between L-Mg-C, L-Ca-C, and L-C are very small. L-Mg-C contains the MgCo₂O₄ phase, while L-Ca-C contains the Co₃O₄ phase, which indicates that most of the Mg and Ca did not enter the LaCoO₃ perovskite lattice. L-Ce-C is significantly different from the single crystalline phase, indicating that Ce has more extensively entered the

Fig. 1. XRD patterns of the LaCoO₃ catalysts with different cations. (1) L-C; (2) L-Mg-C; (3) L-Sr-C; (4) L-Ca-C; (5) L-Ce-C.

perovskite lattice. This is why Ce substitution has a greater impact than Mg and Ca substitution on the main structure of the LaCoO₃ perovskite [27]. However, the data from the L-Sr-C sample showed the coexistence of an additional phase or phases. To further analyze the influence of substitution on the main structure of the perovskite, more parameters of samples were characterized.

The FT-IR spectra of the prepared samples are displayed in Fig. 2. Two strong bands at around 600 and 420 cm⁻¹ have been assigned to a Co–O [28] stretching vibration and an O–Co–O [29] bending vibration from the CoO₆ octahedra in perovskite LaCoO₃, respectively. As shown in Fig. 2, all the samples contain this structure. A peak at 670 cm⁻¹ was observed in the L-Ca-C and L-Sr-C samples, which has been attributed to the M–O stretching vibration in the tetrahedral structure of Co²⁺ [30]. This Co²⁺ could be from the Co₃O₄ [31], seen in the XRD

Table 1
Physical characters of the catalysts.

Sample	S_{BET} (m ² /g)	Lattice parameter (nm)	Segregation phase	Crystallite size (nm)
L-C	8.3	0.5436	—	—
L-Mg-C	3.3	0.5435	MgCo ₂ O ₄	26.5
L-Ca-C	9.8	0.5438	Co ₃ O ₄	23.5
L-Sr-C	9.5	0.5442	Co ₃ O ₄	20.3
L-Ce-C	6.8	0.5419	—	—

Fig. 2. FT-IR spectra of the LaXCoO_3 ($X = \text{Mg, Ca, Sr, Ce}$) samples. (1) L-C; (2) L-Sr-C; (3) L-Ca-C; (4) L-Mg-C; (5) L-Ce-C.

data. A CO_3^{2-} peak at around 1470 and 814 cm^{-1} was observed in the L-Sr-C sample (the C–O stretching and C–O bending vibrations at 1476 and 844 cm^{-1} , respectively), indicating that carbonate is present in L-Sr-C, which is consistent with the XRD results. Compared with the L-C data around 600 cm^{-1} , the vibration peaks of L-Mg-C, L-Ca-C, and L-Ce-C are shifted to a low wavenumber, among which L-Ce-C shows the largest change and is further evidence of the larger substitution into the perovskite structure.

Table 1 displays the specific surface area of the samples. From these results, the specific surface area of the samples is quite small, less than 10 m^2/g , which is due to the high calcination temperature. This high temperature is required for the formation of the perovskite structure. The specific surface area of L-Mg-C was the smallest of the five samples (3.3 m^2/g), and those of the L-Sr-C (9.5 m^2/g) and L-Ca-C (9.8 m^2/g) samples

Fig. 4. XPS Co 2p spectra of the five samples. (1) L-C; (2) L-Ce-C; (3) L-Sr-C; (4) L-Ca-C; (5) L-Mg-C.

were slightly larger than the L-C sample (8.3 m^2/g), while the specific surface area of L-Ce-C was lower than the L-C sample.

3.1.2. The morphologies of catalysts

To show the effect of different element substitutions on the surface morphology, SEM images of the new samples are shown in Fig. 3. L-Mg-C and L-Ca-C have a surface morphology similar to the L-C sample. However, L-Mg-C has a smaller specific surface area due to a denser surface morphology. L-Sr-C and L-Ce-C had a similar structure to that of L-C perovskite, but L-Sr-C had a new acicular phase and L-Ce-C had a bulk crystal phase, embedded on the perovskite structure.

3.1.3. Surface properties of the catalysts

The Co 2p spectra of the five catalysts are shown in Fig. 4. The samples exhibited similar XPS spectra to the perovskite

Fig. 3. SEM images of the five samples. (a) L-C; (b) L-Ca-C; (c) L-Sr-C; (d) L-Mg-C; (e) L-Ce-C.

Table 2

Surface atomic ratios and binding energies of catalysts.

Sample	Atom concentration (at%)		Co/La	Co 2p _{3/2} (eV)
	La	Co		
L-C	6.81	3.58	0.53	780.0
L-Mg-C	8.18	10.61	1.29	780.8
L-Ca-C	9.26	8.30	0.90	780.6
L-Sr-C	4.59	8.23	1.79	780.6
L-Ce-C	6.67	15.01	2.25	780.3

LaCoO₃. As shown in Table 2, compared with the L-C sample, the Co 2p_{3/2} peak of the four substitution catalysts are shifted to higher binding energies, indicating that the charge on the cobalt had changed. The Co³⁺ binding energy in MgCo₂O₄ is 780.8 eV [32,33], and in the L-Mg-C sample, the Co 2p_{3/2} peak was 0.8 eV higher than LaCoO₃, which is mainly due to the inclusion of the MgCo₂O₄ phase. For the L-Ca-C and L-Sr-C samples, the Co 2p_{3/2} peak shifted to a higher energy by 0.6 eV because of the presence of the Co₃O₄ phase. The binding energy was 0.3 eV higher in the L-Ce-C sample [27]. From the ratio of Co/La, the substitution of Sr or Ce into the sample increased the content of the surface cobalt in the catalyst, which should increase catalytic activity.

3.2. TPR results

The H₂-TPR profiles of the catalysts are shown in Fig. 5. At

Fig. 5. H₂-TPR profiles of the LaXCoO₃ (X = Mg, Ca, Sr, Ce) catalysts. (1) L-C; (2) L-Mg-C; (3) L-Ca-C; (4) L-Sr-C; (5) L-Ce-C.

least two reduction peaks are observed for the catalysts except for L-Mg-C. Relative to the L-C sample, the first reduction peaks of the Ca, Sr, and Ce-substituted samples are shifted to lower temperatures, thus the La-O-Co interaction is weaker, which therefore lowered the energy of the cobalt reduction. Because of the partial reduction of Co³⁺ to Co²⁺ [7], the first reduction

Fig. 6. Ethanol conversion and product distribution versus reaction time on stream at 600 °C. (a) L-Sr-C; (b) L-Ce-C; (c) L-Ca-C; (d) L-Mg-C.

peak of the Sr-substituted sample exhibited a larger shift. However, in the Mg-substituted sample, the first reduction peak almost disappeared, and the higher-temperature reduction peak shifted to a higher temperature. This is due to the formation of a new phase MgCo_2O_4 , which makes the reduction of cobalt more difficult.

3.3. Catalytic performance of catalysts

The performance of the four catalysts for SRE are shown in Fig. 6, where X_{ethanol} indicates the ethanol conversion and X_{water} the water conversion. From Fig. 6, the Sr substitution catalyst exhibited the highest catalytic performance with 100% ethanol conversion, which did not change during the 10 h on stream, and the water conversion remained above 30%. The catalytic performance of the Ce-substituted catalyst was slightly lower than that of the Sr substitution sample, with an ethanol conversion of 95% at 600 °C. However, in the entire test time range, its performance did not decline and even slightly improved, and the water conversion was higher than 20%. The activity of the Ca-substituted sample was significantly lower, with only 50% ethanol conversion within the first hour, and this decreased with the reaction time, with a final value less than 40%. The Mg-substituted sample showed the lowest activity with an ethanol conversion of only 40%. According to the literature [7], under the same conditions, the ethanol conversion for the La- CoO_3 catalyst is about 50%. Therefore, the Sr and Ce-substituted samples provide a more active phase and improve the catalyst performance significantly. The Ca-substituted sample weakened the cobalt-support interaction but did not enhance its activity.

The XRD patterns of the used catalysts for 10 h are shown in Fig. 7. After the reaction, L-Mg-C and L-Ca-C had a brownmillerite structure, which limits the reduction of the cobalt species in the perovskite, and thereby lowers the activity. The perovskite structure in the L-Ce-C sample was destroyed, leaving the La, Sr, and Ce as $\text{La}_2\text{O}_2\text{CO}_3$, SrCO_3 , and CeO_2 , respectively. A CoO phase was detected in L-Ce-C, but this could not be confirmed in the L-Sr-C sample because of the obscuring diffraction peaks of SrCO_3 .

Fig. 7. XRD patterns of the catalysts after aging for 10 h. (1) L-Ce-C; (2) L-Sr-C; (3) L-Ca-C; (4) L-Mg-C.

XPS spectra of the fresh and aged L-Sr-C and L-Ce-C samples are shown in Fig. 8. Co exists in a number of valence states in the aged L-Sr-C sample with Co $2p_{3/2}$ binding energies of 778.9, 781.4, and 787.1 eV. The peaks at 778.9 and 781.4 eV could be attributed to the Co^0 species and the Co^{2+} shake-up peak, respectively, while the more complex peak at 787.1 eV is due to either Co^{2+} or Co^{3+} [17]. However, for the aged L-Ce-C sample, there were only peaks near 781 and 787 eV, indicating the presence of Co^{2+} and the absence of Co^0 . According to the literature [34], the interaction of Co^0 and Co^{2+} promotes catalytic activity in the SRE reaction, with Co^{2+} acting as the active center. This would explain why the catalytic performance of L-Sr-C was better than L-Ce-C.

4. Conclusions

The four LaXCoO_3 ($X = \text{Mg, Ca, Sr, or Ce}$) catalysts, formed by the substitution of different elements into LaCoO_3 at the A site, were prepared and investigated, and their catalytic performance in SRE was also examined. The results showed that the

Fig. 8. XPS Co $2p$ spectra of the two samples after reaction.

Graphical Abstract

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Preparation of LaXCoO_3 ($\text{X} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ce}$) catalysts and their performance for steam reforming of ethanol to hydrogen

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Compared with the perovskite LaCoO_3 , the Sr-doped or Ce-doped catalyst demonstrated significantly better catalytic performance, while better cobalt reduction enabled the effects.

L-Ce-C sample had a purely perovskite crystal phase, while L-Mg-C, L-Ca-C, and L-Sr-C appeared to have some separation phases to different degrees. L-Sr-C and L-Ce-C samples have acicular and bulk crystal phases on the catalyst surface, respectively. Mg substitution strengthened the cobalt-support interaction, making the cobalt reduction more difficult. The Sr and Ce substitution weakened the cobalt-support interaction, which made the cobalt reduction easier. The L-Sr-C sample exhibited the higher activity, with better cobalt reduction, while there was also a separation phase besides the perovskite structure. Both L-Sr-C and L-Ce-C showed high activity and stability in the steam reforming of ethanol. However, the catalytic performance of the former was better.

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LaXCoO₃ (X = Mg, Ca, Sr, Ce) 催化剂的制备及其催化乙醇水蒸气重整制氢

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摘要: 以PEG 400为分散剂, 采用一步柠檬酸络合法制备了LaXCoO₃ (X = Mg, Ca, Sr, Ce; La:X = 3:2)复合催化剂. 采用X射线衍射、红外光谱、扫描电镜、X射线光电子能谱、N₂吸附-脱附和H₂程序升温还原等技术对复合催化剂进行了表征, 考察了不同元素A位取代对LaCoO₃钙钛矿结构的影响, 进而研究了其对乙醇水蒸气重整制氢的催化性能和稳定性. 结果表明, 在高含量取代时, 只有Ce取代的样品能够保持单一的钙钛矿晶型; Ca或Sr取代的样品产生的Co₃O₄分离相有利于复合催化剂活性中心钴的还原; Sr或Ce取代的样品在反应中表现出较好的活性和稳定性, Sr取代的样品活性更高.

关键词: 柠檬酸络合法; 钙钛矿; 钴; 复合催化剂; 乙醇水蒸气重整; 氢气

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1. 前言

氢气作为一种高效、清洁的能源^[1,2], 被认为是解决21世纪人类社会能源危机的新能源之一. 特别是随着以氢气为原料的燃料电池及燃料电池汽车的快速发展, 预计未来对氢能源的需求会逐渐增大. 目前工业上氢气主要来源于化石燃料重整和电解水, 然而前者仍以消耗化石能源为代价, 后者能耗较高, 因此在应用方面受到一定的限制. 低碳醇重整制取氢因其高产氢比而成为广泛研究对象, 乙醇水蒸气重整制氢(SRE)更是因其原料含10% (v/v)左右的生物质乙醇, 可直接从工业得到不需蒸馏浓缩而备受关注. 该反应过程可表示如下:

该反应过程为吸热反应^[3], 存在一系列复杂的副反应生成乙醛、丙酮、乙烯、CO和积碳等^[4], 因此选择具有高活性、高选择性和高稳定性的催化剂是整个乙醇制氢过程中的关键. 据文献报道, 含有Ni^[5,6]、Co^[7,8]和贵金属^[9,10]的催化剂在SRE反应中表现出较好的活性和选择性. 以Ni为活性中心的催化剂对乙醇中C–C键和C–H键断裂表现出很强的活性, 但积碳现象严重; 而Co基催化剂表现出优异的重整性能. 因此, 人们对不同载体负载的Co基催化剂进行了广泛研究, 包括Al₂O₃^[11], SiO₂^[12], MgO^[13], CeO₂^[14]和La₂O₃^[15]等. 研究表明, 以CeO₂或La₂O₃为载体的催化剂都表现出较好的活性并且得到了

理想的反应产物. 然而, Co基催化剂稳定性不高, 在应用上还存在很大挑战. 高温时金属Co粒子的烧结和积碳对催化剂稳定性的影响非常大; Co含量越高, 烧结越严重. 稀土载体表面的元素能与CO₂发生反应生成碳酸盐, 可消除积碳^[7]; CeO₂能够产生晶格氧, 并与表面积碳发生反应. 因此, 载体的选择同样对SRE反应影响很大.

钙钛矿ABO₃因其稳定性而在很多反应中表现出非常好的催化活性, 且在SRE反应中也具有一定的催化活性, 但钙钛矿中用作活性中心的金属量有限. 因此, 最大限度地利用钙钛矿中的金属比较困难. 钙钛矿结构中A位用其他元素(碱金属或稀土元素)部分取代形成A_{1-x}A_xBO₃, 可以改变B位离子的氧化状态以及阳离子缺陷密度和氧空位量, 从而间接影响ABO₃钙钛矿的催化性能.

钙钛矿型LaCoO₃催化剂材料应用于乙醇水蒸气重整反应时具有低CH₄和CO选择性的优势, 但是单一的LaCoO₃钙钛矿的活性还远不够, 适当的A位或者B位取代能够提高其催化性能^[16–20]. 崔梅生等^[21]发现掺入Ce的LaCoO₃可明显提高其催化甲烷燃烧反应活性. 用Sr取代的La_{1-x}Sr_xMO₃ (0 < x < 0.4, M = La, Ca, Fe)在甲烷燃烧反应中的催化活性可与贵金属催化剂0.5 wt% Pt/Al₂O₃媲美^[22]. 而Cu取代的钙钛矿LaCo_{1-x}Cu_xO_{3-δ}在低碳醇合成反应中的催化性能也有显著提高^[23]. Bedel等^[24]证实了在F–T合成反应中从La_(1-y)Co_{0.4}Fe_{0.6}O_{3-δ}钙钛矿

还原出来的金属Co的最大量可达2.1%。马飞等^[7]研究的Zn掺杂的LaCoO₃钙钛矿显著提高了其催化SRE反应活性。

本文制备了四种金属离子取代LaCoO₃钙钛矿A位而得到的LaXCoO₃ (X = Mg, Ca, Sr, Ce)系列钙钛矿结构催化剂, 并通过X射线衍射(XRD)、红外光谱(FT-IR)、扫描电镜(SEM)、X射线光电子能谱(XPS)、N₂吸附-脱附(BET)和H₂程序升温还原(H₂-TPR)等技术进行了表征, 考察了催化剂在SRE反应中的催化性能及其稳定性。

2. 实验部分

2.1. 催化剂的制备

采用柠檬酸络合法制备LaXCoO₃ (X = Mg, Ca, Sr, Ce)钙钛矿复合催化剂, 用La(NO₃)₃·6H₂O, Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Sr(NO₃)₂·4H₂O, Ce(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O和柠檬酸作为反应试剂。首先将按计量比($n(\text{La}+\text{X}):n(\text{Co}) = 1$, $n(\text{La}):n(\text{X}) = 3:2$)的金属硝酸盐溶解在去离子水中, 将金属总摩尔量1.2倍的柠檬酸溶解在另一个烧杯中, 加入0.2倍柠檬酸摩尔量的PEG 400, 然后把金属盐溶液逐滴加到柠檬酸溶液, 在80 °C常压下搅拌蒸发至形成胶状。将胶状物于120 °C干燥24 h, 形成的疏松海绵状固体于750 °C焙烧3 h, 得到催化剂样品LaCoO₃, La_{0.6}Mg_{0.4}CoO₃, La_{0.6}Ca_{0.4}CoO₃, La_{0.6}Sr_{0.4}CoO₃和La_{0.6}Ce_{0.4}CoO₃, 分别记为L-C, L-Mg-C, L-Ca-C, L-Sr-C和L-Ce-C。

2.2. 催化剂的表征

采用飞利浦X'pert pro MPD型XRD仪分析催化剂的晶相, Cu K α 射线, 石墨单色器, 管电压40 kV, 管电流50 mA, 测试范围 $2\theta = 20^\circ\text{--}80^\circ$ 。采用德国Bruker公司的TENSOR 27型红外光谱仪测定催化剂的FT-IR谱。将15 mg样品用100倍的KBr稀释, 研磨混合均匀后压片, 然后在室温下进行测试, 扫描范围400–4000 cm⁻¹。

催化剂的形貌采用Hitachi公司的S-3400型FE-SEM进行分析, 加速电压20 kV。

采用英国Kratos公司的XSAM800型能谱仪对催化剂表面元素进行分析。激发光源采用Al K α 射线($h\nu = 1486.6$ eV), 样品的电荷效应以C 1s (284.6 eV)为内标加以校正。

催化剂的比表面积和孔性质采用美国康塔公司的NOVA 1000e型比表面积和孔径分布测定仪测量。催化剂装量为200 mg, 在-196 °C时测定N₂的吸附-脱附曲线, 利用BET公式求得催化剂的比表面积, 用BJH方法求得

孔径分布。

催化剂的还原性能用TPR实验进行测量。样品用量为50 mg, 还原气为5% H₂/N₂混合气, 升温速率10 °C/min。采用SC-200型气相色谱仪热导检测器(TCD)对床层出口的尾气进行在线分析。

2.3. 催化剂的评价

催化剂评价在微型固定床石英反应器上进行, 每次装入100 mg催化剂(60–80目)和800 mg石英砂(40–60目)的混合样品, 用5 vol% H₂/Ar混合气在特定温度下还原。还原后在氮气吹扫下降至最初反应温度, 通入乙醇水混合溶液($n(\text{H}_2\text{O})/n(\text{C}_2\text{H}_5\text{OH}) = 6$)和N₂, 溶液流量为4.8 mL/h, 用DDB-300型电子蠕动泵打入汽化室并于150 °C汽化, N₂流量为60 mL/min, 总的空速为50 000 h⁻¹。在600 °C下连续反应10 h以考察催化剂的反应活性。采用SC-200型气相色谱仪TCD在线分析反应产物。H₂, N₂, CO, CO₂和CH₄等永久性气体用TDX-01分子筛柱分离, 以30 mL/min高纯Ar为载气; H₂O、乙醇、乙醛和丙酮等产物用Porapak-Q柱分离。

3. 结果与讨论

3.1. 催化剂的物相结构和表面元素分析

3.1.1. 催化剂的物相分析

图1为不同元素取代A位的钙钛矿型样品的XRD谱。所有样品都出现了LaCoO₃斜方晶体的特征衍射峰, 但只有Ce取代的LaCoO₃表现出单一的钙钛矿晶相。Mg取代的样品在 $2\theta = 34.3^\circ$ 和 62.5° 处出现MgCo₂O₄的特征峰; Ca和Sr取代的样品在 $2\theta = 31.3^\circ$, 36.8° 及 65.7° 处出现Co₃O₄的特征峰; 而Sr取代的样品还出现了镧的氧化物及碳酸盐等杂相。图1还示出了不同元素对钙钛矿的取代导致其特征峰的移动情况。相对于 $2\theta = 33^\circ$ 附近的钙钛矿特征峰, Mg, Ca和Sr取代的样品向低角度偏移0.1°, Ce取代的样品则向高角度偏移0.3°, 表明不同元素取代均对钙钛矿结构有影响, 其中以Ce取代影响较大。

根据实验结果计算了样品的晶胞参数, 如表1所示。相对于L-C样品的晶胞参数(0.5436 nm), Mg, Ca和Sr取代样品的略有变化, 而Ce取代的样品减少了0.0017 nm。然而就离子半径而言, Mg²⁺ (0.068 nm)和Ca²⁺ (0.0118 nm)均小于La³⁺ (0.136 nm); Ce³⁺ (0.134 nm)与La³⁺的基本相当; Sr²⁺ (0.144 nm)大于La³⁺。由于离子半径不同, 取代元素进入到钙钛矿晶格之中会导致晶胞参数的差异^[25,26]。尽管Mg²⁺和Ca²⁺的离子半径远小于La³⁺, 但取代样品的晶胞参数和L-C差距很小, 且分别检测到

MgCo₂O₄相和Co₃O₄相,表明Mg或Ca的添加没有影响LaCoO₃钙钛矿晶格。而Ce取代的样品只出现单一的晶相,表明Ce完全进入钙钛矿主体;离子半径相近和相似的性质可以解释实验现象^[27]。Sr取代的样品则表现出多种物相共存。为了进一步分析取代对钙钛矿结构和性质的影响,进一步对样品进行了表征。

图2为A位离子用不同元素取代的催化剂样品的FT-IR谱。在600和420 cm⁻¹附近的两个强峰分别归属于典型的LaCoO₃钙钛矿中Co-O六面体中的Co-O伸缩振动^[28]和O-Co-O弯曲振动^[29]。由图可见,所有样品都形成了这种结构。L-Ca-C和L-Sr-C样品在670 cm⁻¹处出现红外峰,对应于四面体结构中的Co²⁺形成的M-O的伸缩振动^[30]。可以推测这种Co²⁺来源于Co₃O₄^[31],与XRD结果一致。L-Sr-C样品还在1470和814 cm⁻¹处出现CO₃²⁻中的特征振动峰(C-O伸缩振动1476 cm⁻¹, C-O弯曲振动844 cm⁻¹),表明在Sr取代的样品中有碳酸盐,与XRD结果一致。还可以看到,相对于LaCoO₃钙钛矿在600 cm⁻¹附近的振动峰,Ca, Mg, Sr和Ce取代的样品振动峰红移,且Ce取代样品的偏移量较Ca和Sr取代样品的大。

五个样品的比表面积列于表1。可见各样品的比表面积均不足10 m²/g,这是由于形成钙钛矿结构所需的高温(750 °C)烧结造成的。Mg取代样品的比表面积最小(3.3 m²/g),Ca和Sr取代的样品略高于L-C样品(8.3 m²/g),Ce取代样品为6.8 m²/g。

3.1.2. 催化剂的表面形貌

图3为各取代样品的SEM照片。可以看出,Mg和Ca取代样品的表面形貌和L-C样品类似,但Mg取代的样品更加致密,因而比表面积较小;而Sr和Ce取代的样品表面有类似于L-C钙钛矿的结构,且分别出现了针状和块状晶相,镶嵌在主体钙钛矿结构上,可以直观地看到Ce和Sr取代对钙钛矿结构的影响。

3.1.3. 催化剂表面元素分析

图4为五个催化剂的Co 2p XPS谱。取代样品显示出类似于LaCoO₃钙钛矿的XPS谱。为了研究催化剂中Co物种被不同元素取代后Co价态的变化,表2列出了Co 2p_{3/2}的结合能。相对于L-C样品,取代的样品都向高结合能方向偏移,表明Co的价态有所变化^[18]。MgCo₂O₄中的Co³⁺结合能为780.8 eV^[32,33],Mg取代后的钙钛矿偏移值最大,为0.8 eV,这主要是由于出现的分离相MgCo₂O₄所致。同样地,出现分离相Co₃O₄的Ca和Sr取代的样品也表现出较大的偏移量,为0.6 eV。Ce取代的偏移最小,为0.3 eV,这是由于Ce主要以+3价形式存在,与LaCoO₃中La的

价态相同,但其本身存在+4价和+3价相互转换,其结合能也略高于纯的LaCoO₃钙钛矿^[32]。通过Co/La比发现,Sr和Ce取代能够增加钙钛矿表面的Co含量,有利于在SRE反应中表现出较高的催化活性。

3.2. TPR结果

图5为五个样品的H₂-TPR谱。由图可知,除了Mg取代的样品,其他样品都有低温和高温两个还原峰。相对于L-C样品,Ca, Sr和Ce取代的样品的第一个还原峰均向低温发生偏移,表明它们的取代削弱了钙钛矿结构中La-O-Co的作用,从而有利于Co的还原,其中以Sr取代样品的第一个还原峰向低温方向偏移最大,该峰可归属为部分Co³⁺还原为Co²⁺^[33]。而Mg取代样品的第一个还原峰几乎消失,可归结于Mg的加入形成了新的MgCo₂O₄相,使Co很难被还原。

3.3. 催化剂在SRE反应中的催化性能

图6为四种不同元素取代的LaCoO₃催化剂上SRE反应活性,其中X_{ethanol}和X_{water}分别表示乙醇转化率和水的转化率。由图可知,Sr取代的催化剂上,乙醇转化率能达到100%,且可保持10 h而活性几乎没有下降,水转化率达到30%以上;Ce取代样品的活性略低于Sr取代样品,600 °C时乙醇不能达到完全转化,最大只能达到95%,但在整个测试范围活性没有下降,反而呈上升趋势,水转化率高于20%;Ca取代的样品活性较低,在最初的1 h内乙醇转化率只有50%,且随着时间的增加明显下降,最终仅为40%;Mg取代的样品活性最低,整个过程中乙醇最大转化率只有40%。而据文献[7],在相同条件下,LaCoO₃催化剂对乙醇的转化率为50%左右。由此表明,Sr或Ce取代样品后能够产生较多的活性相,可以显著提高催化剂活性;Ca的取代对催化剂活性影响不大;而Mg的取代则降低了样品活性。

图7为反应后各催化剂的XRD谱。可以看到,Mg和Ca取代的样品在反应后仍存在钙铁石等结构,不利于钙钛矿中钴物种的还原,因而催化活性较低。反应后的Sr或Ce取代样品中钙钛矿结构遭到破坏,La主要以La₂O₂CO₃形式存在,Sr主要以SrCO₃形式存在,Ce主要以CeO₂形式存在。在Ce取代的样品中检测到了CoO相;而在该位置由于SrCO₃的衍射峰比较强,不能证明在Sr取代的样品中同样存在CoO相。

图8为Sr或Ce取代样品反应前后的XPS谱。可以看出,反应后的Sr取代样品中Co以多种价态形式存在,Co 2p_{3/2}的结合能分别是778.9, 781.4和787.1 eV。前两者可分别归属于Co⁰和Co²⁺的摇摆振动峰,而781.4 eV处的峰

比较复杂,既可能是 Co^{2+} 也可能是 Co^{3+} 的峰.而反应后Ce取代的样品只在781和787 eV附近出现峰,表明Co主要是以 Co^{2+} 存在.研究表明^[34], Co^0 与 Co^{2+} 相互作用能够促进SRE反应活性, Co^{2+} 也是活性中心之一.因此,Sr取代的样品活性比Ce取代样品的高.

4. 结论

研究了Mg, Ca, Sr和Ce在A位取代 LaCoO_3 形成 LaXCoO_3 对钙钛矿结构的影响,考察了催化剂在乙醇水蒸气重整制氢反应中的催化活性. Ce取代的样品能够

得到单一的钙钛矿晶型,没有观察到分离相;而Mg, Ca和Sr取代的样品在不同程度上出现了分离相. Mg取代的样品形成了致密的钙钛矿形态, Sr或Ce取代的样品在催化剂表面呈现针状或片状的分离相. Mg取代的样品增强了钙钛矿中钴的相互作用,不利于Co物种的还原. 而Ca, Sr和Ce取代削弱了钙钛矿中钴的结合程度,有利于Co物种的还原; Sr取代的样品由于其分离相的影响,表现出了更优的Co还原性能. 在乙醇水蒸汽重整反应中Sr或Ce取代的样品表现出了较高的活性和稳定性,其中以Sr取代的更优.