Zn 掺杂的 LaCoO_3 钙钛矿用于乙醇水蒸气重整制氢反应

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摘要: 利用一步柠檬酸络合法合成了钙钛矿 $\text{LaCo}_{1-x}\text{Zn}_x\text{O}_3$ ($x=0, 0.05, 0.1, 0.2, 0.3, 0.5$), 并将其用于乙醇水蒸气重整反应. 利用 X 射线衍射、程序升温还原和 X 射线光电子能谱对催化剂进行了表征. 结果表明, Zn 的加入不利于形成 $\text{LaCo}_{1-x}\text{Zn}_x\text{O}_3$ 钙钛矿结构, 当 $x \geq 0.1$ 时产生了一些分离相. 新鲜 $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ 催化剂中意外发现存在 Co_3O_4 相, 这有利于催化剂反应性能的提高. 反应后的催化剂结构发生变化, 形成了 $\text{La}_2\text{O}_2\text{CO}_3$, 而该物质有利于积炭的消除和甲烷的重整.

关键词: 一步柠檬酸络合法; 钙钛矿; 多样纳米核; 锌; 乙醇; 蒸气重整; 积炭

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Steam Reforming of Ethanol over Zn-Doped LaCoO_3 Perovskite Nanocatalysts

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Abstract: Nanostructured $\text{LaCo}_{1-x}\text{Zn}_x\text{O}_3$ ($x=0, 0.05, 0.1, 0.2, 0.3$ and 0.5) perovskites were synthesized by a one-step citric acid-complexing method for hydrogen production by the steam reforming of ethanol. For comparison, 8% CoO/ZnO and 8% $\text{CoO}/\text{La}_2\text{O}_3$ were prepared by impregnation and evaluated. The catalyst samples were characterized by X-ray diffraction, temperature-programmed reduction, and X-ray photoelectron spectroscopy. The results indicated that zinc did not favor the formation of the $\text{LaCo}_{1-x}\text{Zn}_x\text{O}_3$ perovskite and the structures of the substituted samples were less weakening than that of LaCoO_3 . Some segregation was observed for $x \geq 0.1$. The reactivity of the studied samples was sensitive to the zinc content and lower substitution values were found to be better. An unexpected phase (Co_3O_4) appeared in the fresh $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ sample. The presence of the Co_3O_4 phase increased the reactivity toward hydrogen production by the steam reforming of ethanol. The presence of $\text{La}_2\text{O}_2\text{CO}_3$ is responsible for the low carbon deposition and the CH_4 selectivity in the aged samples.

Key words: one-step citric acid-complexing method; perovskite; multiple nanosized-cores; zinc; ethanol; steam reforming; carbon deposition

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An increasing amount of interest has been shown in the catalytic steam reforming of ethanol (SRE) recently, not only because of its high hydrogen production ratio, but also because ethanol is nontoxic, of renewable origin and is conveniently transported and stored. This process is represented by Eq. (1), and consists of a complex network of

reactions giving hydrogen and several by-products, such as ethylene, acetaldehyde, methane, carbon oxides, and coke. Among these products, coke is undesirable, as it causes the deactivation of the reforming catalysts [1], and a large number of studies have shown that the SRE is thermodynamically feasible [2–4]. Many catalysts containing Ni [5],

Co [6,7], and noble metals [8–10] have been reported to show good activity and selectivity for ethanol steam reforming reactions. Nickel-based catalysts are active in breaking C–C and C–H bonds, while cobalt, as a base metal, shows outstanding reforming activity. Cobalt supported on various oxides, such as Al₂O₃ [11], SiO₂ [12], MgO [13], CeO₂ [14], and ZnO [15–17], has been investigated extensively, and the Co/ZnO catalyst has excellent activity and a desirable product distribution. These reports suggest that cobalt catalysts are attractive and potentially applicable, and that the supports play an important role in their catalytic performance.

However, some challenges still exist for the application of Co-based catalysts to the SRE because of their low stability, which is caused by the sintering of metallic cobalt and coke deposition. To address these concerns the supports are crucial. As shown in previous reports, alkaline supports [18], redox active supports [19–21], or those produced by doping with other components that react with coke [22–24] can relieve sintering and/or coke deposition.

Perovskites are known highly stable compounds and show high catalytic activities in many fields, and their application as SRE catalysts has been reported [25–27]. The stability and activities of the catalysts have been determined, but metal formation is limited by the very high stability of the perovskite. Furthermore, the perovskite framework allows for partial substitution by other metal ions at the A sites or the B sites, which can lead to the modification of catalytic activity, redox properties, and structural properties of the perovskite. A report about a LaCo_xFe_{1-x}O₃ series of perovskites [28] pointed out that the amount of extractable metal can reach 2.1 wt% for LaCo_{0.4}Fe_{0.6}O₃ upon calcination at 750 °C. A later study on this series by Bedel et al. [29] revealed the presence of an Fe₂O₃ phase in multiple nanosized-cores dispersed in the La_{1-y}Co_{0.4}Fe_{0.6}O_{3-δ} perovskite phase by Mössbauer spectroscopy. Reducible Co has also been found in a LaCoO₃ perovskite upon substitution by copper [30,31]. Some segregation in single oxides has also been found in partially substituted-perovskites, and this promotes catalytic activity because of their interaction with the main structure. The separate ZnO phase from LaZn_xFe_{1-x}O₃ is crucial in increasing the performance of toluene combustion reactions [32].

Our current work has focused on LaCo_{1-x}Zn_xO₃ ($x = 0, 0.05, 0.1, 0.2, 0.3$, and 0.5) and their structures. We also describe the reducibility of the zinc-substituted perovskite. The catalytic performance toward the SRE, carbon deposition, and the reactivity as a result of the catalyst's structure as well as its catalytic performance is discussed.

1 Experimental

1.1 Catalyst preparation

The perovskites were prepared by the one-step citrate method [26]. La(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, and citric acid were used as reagents. The metal nitrates, in specific stoichiometric ratios, were first dissolved in deionized water and 20% excess citric acid (in terms of the total molar amount of the metal cations) was dissolved in deionized water in a different beaker. A certain amount of polyethylene glycol 400 (20% of the molar amount of citric acid) was added to the solution, and then the metal nitrate solution was added. The solution was stirred at 80 °C at atmospheric pressure until a gel formed. This gel was dried in an oven at 120 °C over 24 h, and thus the catalyst precursors were obtained and calcined at 750 °C for 3 h. These perovskite catalysts are expressed by LaCo_{1-x}Zn_xO₃ where $x = 0, 0.05, 0.1, 0.2, 0.3$, and 0.5 , although the actual composition may be non-stoichiometric and some other phase may exist.

8% CoO/ZnO and 8% CoO/La₂O₃ were prepared by impregnation and used for comparison.

1.2 Catalyst characterization

All the X-ray diffraction (XRD) experiments were performed on a Philips X'pert Pro automated powder diffractometer with graphite-monochromated Cu K_α radiation in a Bragg-Brentano parafocusing geometry. The spectra were collected between 20° and 90° (2θ range) with a scanning speed of 4°/min.

Transmission electron microscopy (TEM) was operated on a Tecnai G2F20. The samples were deposited on copper grids with a holey-carbon-film support after the ultrasonic dispersion of the catalysts in absolute ethanol.

X-ray photoelectron spectra (XPS) were recorded on a XSAM800 spectrometer with an Al K_α ($h\nu = 1486.6 \text{ eV}$) X-ray source. The charging effects were corrected by adjusting the binding energy of the C 1s peak from carbon contamination to 284.6 eV.

The specific surface areas, total pore volumes, and average pore diameters were determined using N₂ adsorption/desorption isotherms at -196 °C with an automated gas sorption system (Quantachrome NOVA 1000e apparatus). Before each measurement, the sample was degassed in vacuum at 300 °C for 3 h.

The temperature-programmed reduction (TPR) of the catalysts was carried out on a Thermo-Finnigan instrument in a 5% H₂-95% Ar gas mixture at a flow rate of 37 ml/min. In each run, the catalyst (50 mg) was loaded in a quartz tube reactor. The catalyst was heated in the gas mixture from

room temperature to 800 °C at a heating rate of 10 °C/min.

Fourier transform infrared (FT-IR) spectra of the samples were obtained using sol-gel methods and a System 2000 FTIR Perkin Elmer spectrometer equipped with a DTGS detector. The spectra were collected at a resolution of 4 cm⁻¹ using 32 scans in the range 4000–400 cm⁻¹. All the samples were prepared as KBr pellets.

1.3 Catalytic performance test

The catalytic tests were performed on a fixed-bed quartz reactor at atmospheric pressure. In each run, the catalyst (100 mg, 60–80 mesh) was diluted with SiO₂ (40–60 mesh) at a mass ratio of 1:8. The diluted catalysts were then loaded into the reactor and reduced in 5% H₂-95% Ar at 550 °C for 1 h and then cooled to the initial reaction temperature of 400 °C with N₂ flow protection. 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 gas hourly space velocity (GHSV) was 50000 h⁻¹. The reaction products were analyzed on-line by gas chromatography (GC). A TDX-01 packed column was used to separate H₂, N₂, CO, CH₄, and CO₂. Water, ethanol, acetaldehyde, and acetone were separated using a porapak Q column. As a result of product variation, the catalyst performance was characterized using two parameters. S_i represents the product distribution of i . Ethanol and water conversion is denoted as X_{EtOH} and $X_{\text{H}_2\text{O}}$, respectively. These were calculated according to Eqs. (2)–(5):

$$X_{\text{EtOH}} = (F_{\text{EtOH},\text{in}} - F_{\text{EtOH},\text{out}}) / F_{\text{EtOH},\text{in}} \quad (2)$$

$$X_{\text{H}_2\text{O}} = (F_{\text{H}_2\text{O},\text{in}} - F_{\text{H}_2\text{O},\text{out}}) / F_{\text{H}_2\text{O},\text{in}} \quad (3)$$

$$S_{\text{H}_2} = F_{\text{H}_2,\text{produced}} / [3(F_{\text{EtOH},\text{in}} - F_{\text{EtOH},\text{out}}) + (F_{\text{H}_2\text{O},\text{in}} - F_{\text{H}_2\text{O},\text{out}})] \quad (4)$$

$$S_{\text{C}} = \text{moles } C_i / \sum_{i=0}^n \text{moles } C_i \quad (5)$$

2 Results and discussion

2.1 XRD results

Figure 1 shows the XRD patterns of the catalysts. Each crystalline phase was identified using JCPDS. All samples have similar diffraction peaks to that of LaCoO₃, which is characterized by rhombohedral perovskite-type reflections, except for LaCo_{0.5}Zn_{0.5}O₃. Some segregation occurs for $x \geq 0.1$, however, the reflection peaks that correspond to Co₃O₄ are only found in LaCo_{0.9}Zn_{0.1}O₃. As the x value increases to 0.2, the reflection peaks of the ZnO phase ($2\theta = 34.43^\circ$ and 36.24°) appear, and they have an increasing trend. Furthermore, the average particle sizes (calculated by the Scherrer equation) of the separate phases ranged from 10–40 nm and this is shown in Table 1.

Fig. 1. XRD patterns of the LaCo_{1-x}Zn_xO₃ nanocatalysts. (1) LaCoO₃; (2) LaCo_{0.95}Zn_{0.05}O₃; (3) LaCo_{0.9}Zn_{0.1}O₃; (4) LaCo_{0.8}Zn_{0.2}O₃; (5) LaCo_{0.7}Zn_{0.3}O₃; (6) LaCo_{0.5}Zn_{0.5}O₃.

Table 1 Physical properties of the prepared catalysts

Sample	Crystalline size (nm)		Surface area (m ² /g)	Impurity
	ZnO	Co ₃ O ₄		
LaCoO ₃	—	—	8.2	—
LaCo _{0.95} Zn _{0.05} O ₃	—	—	9.1	—
LaCo _{0.9} Zn _{0.1} O ₃	—	16.9	8.5	Co ₃ O ₄
LaCo _{0.8} Zn _{0.2} O ₃	21.2	—	7.4	ZnO
LaCo _{0.7} Zn _{0.3} O ₃	18.6	—	4.6	ZnO
LaCo _{0.5} Zn _{0.5} O ₃	17.1	—	2.3	ZnO, LaO

The XRD results show that zinc is unfavorable for the formation of LaCo_{1-x}Zn_xO₃, and the single perovskite (LaCoO₃) was observed only in LaCo_{1-x}Zn_xO₃ with low Zn substitution ($x < 0.1$). The diffraction peaks are broader and lower for higher amounts of zinc. The patterns for the LaCo_{1-x}Zn_xO₃ perovskite are similar to those of the LaCoO₃ perovskite without any shift. Therefore, the introduced zinc can result in a weakening of the LaCoO₃ perovskite structure.

2.2 FT-IR spectra

The FT-IR spectra of the prepared samples are shown in Fig. 2. The two strong bands around 600 and 420 cm⁻¹ are assigned to a Co–O [33] stretching vibration and an O–Co–O [34] bending vibration from the CoO₆ octahedra in perovskite LaCoO₃, respectively. An IR band at 670 cm⁻¹ was observed for LaCo_{0.9}Zn_{0.1}O₃ and is attributed to the stretching vibration mode of M–O, in which M is Co²⁺ and is tetrahedrally coordinated [35]. This suggests that Co²⁺ originates from Co₃O₄ [36], which was shown by XRD. The bands around 1470 and 418 cm⁻¹ may correspond to CO₃²⁻

Fig. 2. FT-IR spectra of the LaCo_{1-x}Zn_xO₃ perovskites.

(the C–O stretching and C–O bending of CO₃²⁻ at 1476 and at 844 cm⁻¹, respectively [37].

2.3 Textural property

The BET surface area (listed in Table 1) shows conventional LaCoO₃ values, and low substitution leads to a slight increase (LaCo_{0.95}Zn_{0.05}O₃ and LaCo_{0.9}Zn_{0.1}O₃), which corresponds to the weakening of the LaCoO₃ perovskite and it decreases rapidly as the impurity ZnO occurs.

2.4 TPR results

The TPR results of the catalysts are shown in Fig. 3. Two successive reduction steps were observed for all the samples. The first step with double peaks has been described in the literature [38] as Co³⁺ being reduced to Co²⁺ to form a brownmillerite structure of LaCoO_{2.5}; the other peak suggests that some cobalt was reduced to metallic cobalt at the end of the first step. The second step can be attributed to the reduction of LaCoO_{2.5} as follows:

The amount of hydrogen consumption in the first step over the LaCo_{0.95}Zn_{0.05}O₃, LaCo_{0.9}Zn_{0.1}O₃, LaCo_{0.8}Zn_{0.2}O₃, and LaCo_{0.7}Zn_{0.3}O₃ samples was significantly higher than that of the LaCoO₃ and LaCo_{0.5}Zn_{0.5}O₃ samples. The LaCo_{0.9}Zn_{0.1}O₃ sample had the largest peak and the double peaks almost disappeared, which may be attributed to a weakening of the perovskite and the presence of Co₃O₄. LaCo_{0.5}Zn_{0.5}O₃ led to the weakest signal because of a lack of cobalt. By comparison with the LaCoO₃ sample, the reduction peaks of LaCo_{0.9}Zn_{0.1}O₃ and LaCo_{0.95}Zn_{0.05}O₃ shifted towards a lower temperature, suggesting a weakening of the

Fig. 3. TPR profiles of the LaCo_{1-x}Zn_xO₃ perovskites.

perovskite. The first LaCo_{0.9}Zn_{0.1}O₃ reduction step shifted towards a lower temperature, but the peak of the second step shifted to a higher temperature than that of LaCo_{0.8}Zn_{0.2}O₃, suggesting a strong interaction between the segregated phases and the perovskite structure.

2.5 XPS results

The Co 2p_{3/2} spectra of the LaCoO₃, LaCo_{0.9}Zn_{0.1}O₃, and reduced LaCo_{0.9}Zn_{0.1}O₃ samples (550 °C for 3 h) are shown in Fig. 4. These were obtained to determine the minor species that contribute to their superior catalytic activity. In the Co 2p_{3/2} spectrum of LaCo_{0.9}Zn_{0.1}O₃ the shake-up peaks at 790 eV suggest the presence of Co²⁺ in Co₃O₄ [39,40], while no shake-up peak was found in the LaCoO₃ sample. Similar behavior was observed in the high La/Co ratio LaCoO₃ perovskite [41]. This result is consistent with the XRD and FT-IR results. Figure 4 also shows the peaks of the reduced

Fig. 4. XPS spectra of Co 2p. (1) LaCoO₃; (2) LaCo_{0.9}Zn_{0.1}O₃; (3) Reduced LaCo_{0.9}Zn_{0.1}O₃; (4) Aged LaCo_{0.9}Zn_{0.1}O₃.

LaCo_{0.9}Zn_{0.1}O₃ sample. The peaks near 781.2 eV can be attributed to both the Co²⁺ and the Co³⁺ species, while the peak at 784.4 eV can be attributed to the Co²⁺ shake-up peak. The strong peak near 778.5 eV comes from Co metal [42], suggesting abundant extractable metallic cobalt in the SRE reaction.

Table 2 summarizes the atomic ratios of surface Co/La and the binding energies (BE) of the Co 2p_{3/2} shake-up peaks. We propose that the highly reducible cobalt is crucial for catalyst activity. Compared with the LaCoO₃ sample, LaCo_{0.9}Zn_{0.1}O₃ has a larger cobalt ratio on the surface, leading to a higher amount of extractable cobalt metal because of the weakening of the LaCoO₃ perovskite. However, the surfaces of the two catalysts have far less cobalt than could be inferred from the stoichiometry, because of the enrichment of La from the formation of LaCO₃ [43]. The Co 2p_{3/2} binding energy of LaCoO₃ (~778.0 eV) is close to the value reported in literature [44]. However, for LaCo_{0.9}Zn_{0.1}O₃ the Co 2p_{3/2} peak shifted to a higher binding energy (~780.3 eV) and for $x = 0.2$ the peak shifted back to 780.1 eV. This chemical shift reveals the partial variation in cobalt valence. Taguchi et al. [45] also reported that increasing the Co²⁺ ion content induced a shift toward the high binding energy site.

Table 2 Surface atomic ratios and binding energies of LaCoO₃, LaCo_{0.9}Zn_{0.1}O₃, LaCo_{0.8}Zn_{0.2}O₃, reduced LaCo_{0.9}Zn_{0.1}O₃ at 550 °C for 10 h, and aged LaCo_{0.9}Zn_{0.1}O₃ at 600 °C

Sample	Atom content (%)		Co/La ratio	BE of Co 2p _{3/2} (eV)
	La	Co		
LaCoO ₃	6.81	3.58	0.53	780.0
LaCo _{0.9} Zn _{0.1} O ₃	10.68	5.54	0.52	780.3
Reduced	11.08	8.20	0.74	780.7
LaCo _{0.9} Zn _{0.1} O ₃				
LaCo _{0.8} Zn _{0.2} O ₃	11.26	5.12	0.45	780.1
Aged LaCo _{0.9} Zn _{0.1} O ₃	10.87	8.58	0.79	781.2

2.6 Catalytic performance of the catalysts

2.6.1 Effects of substitution on the activity

To study the catalytic behavior of the LaCo_{1-x}Zn_xO₃ catalysts with temperature in the ethanol steam reforming reaction, catalytic tests were performed at seven different temperatures ranging from 400 to 700 °C. Figure 5 shows the variation in ethanol conversion in this temperature range for the different samples. The substituted catalysts perform much better in terms of sample activity than the LaCoO₃ sample. Eighty percent ethanol conversion was obtained at 500 °C and reached 100% at 600 °C, while water conversion (Fig. 6) showed an increasing trend with the reaction temperature up to 600 °C, and decreased somewhat at temperatures above 600 °C. The conversion of ethanol and wa-

Fig. 5. Effects of temperature on the conversion of ethanol over the LaCo_{1-x}Zn_xO₃ catalysts.

ter over the substituted catalysts are similar apart from LaCo_{0.5}Zn_{0.5}O₃, which shows visibly lower activity. This is probably because of the low cobalt content. The LaCo_{0.9}Zn_{0.1}O₃ sample gives the best ethanol conversion, since it has the highest amount of reducible Co. All the substituted samples show much better activity than the LaCoO₃ sample because of the absence of an active phase. These results indicate that the high stability of the LaCoO₃ perovskite-type structure and partial substitution modifies the LaCoO₃ perovskite to produce a less stable structure. For the LaCo_{1-x}Zn_xO₃ samples, we deduce that the presence of a Co₃O₄ phase and a ZnO phase is crucial for catalytic performance. Therefore, the generation of small cobalt particles takes place and the ethanol steam-reforming reaction progresses [46,47].

2.6.2 Effects of substitution on the product distribution

Figure 6 shows the hydrogen selectivity, CH₄ selectivity, and CO₂/CO_x ratios as a function of the reaction temperature over LaCo_{1-x}Zn_xO₃. We observed that LaCo_{0.9}Zn_{0.1}O₃ gave the highest hydrogen selectivity, while LaCo_{0.5}Zn_{0.5}O₃ gave the lowest. The hydrogen selectivity was a maximum of 81.4% at 650 °C on the LaCo_{0.9}Zn_{0.1}O₃ sample, which is close to the 80% obtained for the Pd-promoted cobalt catalyst at 600 °C [48] for an ethanol to steam ratio of 5:1 and a GHSV of 8400 h⁻¹. From 500–700 °C, all the substituted samples retain more than 50% of their hydrogen selectivity and this agrees with the performance of 10% Co/ZnO catalyst at an ethanol to steam ratio of 6:1 and at a lower GHSV [49]. Compared with La-Fe-Ni [26] these samples have lower CH₄ (0.5%–5%) selectivity and higher CO₂ to CO ratios (4:1); even for the Co catalyst [49,50] these values are greatly advantageous. These values are in line with the high water conversion shown in Fig. 5. Other important influencing factors for hydrogen selectivity are the water gas

Fig. 6. The product distribution and the water conversion ability of the $\text{LaCo}_{1-x}\text{Zn}_x\text{O}_3$ catalysts.

shift reaction (WGSR), methane reforming, and the reverse reaction [26]. In WGSR:

CO and H_2O produce CO_2 and H_2 and, therefore, the higher CO_2 selectivity and the lower CH_4 selectivity corresponds to a higher hydrogen selectivity.

2.6.3 Stability and deactivation of the catalyst

Figure 7 shows the stability test results of the catalyst that gave the best activity ($\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$) and this was carried out at a high space velocity of 50000 h^{-1} at 600°C and at a $\text{H}_2\text{O}/\text{EtOH}$ ratio of 6:1. Under these conditions only a small amount of deactivation for all the studied catalysts was observed, and the $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ catalyst had the highest ethanol conversion after 10 h. A small decrease in ethanol conversion was found for all the samples after 5 h. To in-

Fig. 7. Stability of the $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ catalyst.

vestigate the state and deactivation behavior of the used catalyst we obtained XRD, XPS, and TEM images of the spent $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ catalyst. Figure 8 shows XRD patterns of the reduced sample and the used sample. No peaks belonging to metallic cobalt are present in the XRD pattern of the reduced sample, but the XPS of the reduced sample indicates the existence of metallic Co^0 . Surprisingly, no Co peaks of the aged catalyst are present in the XRD pattern and the XPS results (Fig. 4(4)) also indicate that there is no metallic cobalt. However, from Table 2 the $\text{Co } 2p_{3/2}$ binding energy (around 780 eV), which consists of Co^{3+} and Co^{2+} , shift to a higher value (781.2 eV) than was the case for the other

Fig. 8. XRD patterns of the reduced $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ and the $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ obtained after the reaction. (1) Fresh; (2) Reduced at 550°C ; (3) After reaction at 600°C for 1 h; (4) After reaction at 600°C for 10 h.

binding energies, and we can deduce that the amount of Co^{2+} increased after the reaction. Therefore, we propose that the Co^{2+} species is still highly dispersed over the catalyst surface. Figure 9 shows TEM images of the aged catalyst and the CoO phase is present while multiple nanosized-cores are dispersed in the $\text{La}_2\text{O}_2\text{CO}_3$ phase. Catalyst sintering and carbon deposition is not significant. We propose that a small amount of catalyst deactivation occurred because of the collapse of the perovskite or the oxidation of metallic Co at high temperature. Therefore, the XRD patterns of $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ after a 1 h reaction was obtained, as shown in Fig. 8(3). Under these conditions the structure of the perovskite had collapsed. Valderrama et al. [51] showed that the active state of the $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ perovskite catalyst is $(\text{Ni},\text{Co})/\text{La}_2\text{O}_2\text{CO}_3$ while for the single perovskite LaCoO_3 it is $\text{Co}/\text{La}_2\text{O}_3$, which has poor activity toward the dry forming of CH_4 . It has been reported [52] that the interaction between Co^{2+} and Co^0 increases the activity in the SRE reaction and therefore the deactivation of the catalyst can be attributed to the disappearance of metallic Co , which has been shown to occur by XPS in Fig. 4. However, the activity of the catalyst after the 10 h test did not decrease obviously and this indicates that Co^{2+} is also active in the SRE.

Fig. 9. TEM micrographs of $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ after a 10 h catalytic test.

2.7 Discussion

As described above, Zn-doped LaCoO_3 perovskite results in a slight weakening of the perovskite structure. This weakening was confirmed by XRD and was helpful in increasing the amount of extractable cobalt as shown by XPS. The surface content of cobalt determined by XPS is 3.58% for LaCoO_3 , 5.54% for $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$, and 5.12% for $\text{LaCo}_{0.8}\text{Zn}_{0.2}\text{O}_3$, indicating about 2% extractable cobalt in relation to LaCoO_3 was produced, and this is in agreement with the research by Bedel et al. [28] into the La-Co-Fe perovskite. Interestingly, as a result of this weakening, metal oxides formed in the $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ sample, and this was shown by XRD, FT-IR, and XPS. We deduce that this weakening reaches a maximum when the Co_3O_4 phase appears. The TPR profiles also suggest that a weakening of the LaCoO_3 perovskite helps in the reduction of the catalysts, and a strong interaction exists between the segregated phases and the perovskite structure in the $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ sample. As the ratio of Zn increases the effect of the interaction surpasses the weakening effect. Zinc and cobalt are one of the most used combination catalysts for the SRE reaction. Therefore, $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ shows the best reforming activity. The presence of Zn seems to be sensitive to the activity and the amount of cobalt corresponds to the H_2 and CH_4 selectivity in the products.

As for carbon formation, the TEM images indicate that activity centers are abundant in this reaction, and that the carbon deposits are mainly carbon nanotubes, while carbon deposition on the catalyst surface is not obvious. This may be attributed to the enrichment of La in the form of a carbonate on the catalyst surface, which can eliminate carbon deposition by the following reaction [26]:

XRD analyses of the post-reaction solids reveal the presence of $\text{La}_2\text{O}_2\text{CO}_3$ (Fig. 8). The high amount of dispersion of the Co phases plays a very important role in ethanol steam reforming and the presence of $\text{La}_2\text{O}_2\text{CO}_3$ allows for a reaction with methane to regenerate La_2O_3 (Eq. (12)) and this inhibits coke deposition, which leads to low methane selectivity, as shown in Fig. 6 [51].

3 Conclusions

Zinc-doped $\text{LaCo}_{1-x}\text{Zn}_x\text{O}_3$ ($x = 0.05, 0.1, 0.2, 0.3$, and 0.5) perovskites were successfully synthesized using a one-step citric acid-complexing method. The substituted samples are promising candidates for the steam reforming of ethanol and the $\text{LaCo}_{0.9}\text{Zn}_{0.1}\text{O}_3$ catalyst had the highest reactivity and selectivity. The presence of zinc is not conducive to the formation of the perovskite structure and it can weaken the

LaCoO₃ perovskite to some extent. However, a strong interaction exists between ZnO and the perovskite as is clearly shown by XRD, XPS, and TPR. Moreover, the presence of Zn also contributes to high activity. Co²⁺ can act as an active center in the SRE and it can synergetically interact with Co⁰ to enhance the activity of the cobalt catalyst. The La₂O₂CO₃ phase has a positive influence on anti-carbon deposition and on CH₄ reforming.

References

- Vizcaino A J, Carrero A, Calles J A. *Catal Today*, 2009, **146**: 63
- Fishtika I, Alexandera A, Dattaa R, Geana D. *Int J Hydrogen Energy*, 2000, **25**: 31
- Ioannides T. *J Power Sources*, 2001, **92**: 17
- Rossi C C R S, Alonso C G, Antunes O A C, Guirardello R, Cardozo-Filho L. *Int J Hydrogen Energy*, 2009, **34**: 323
- Zhang L F, Liu J, Li W, Guo G L, Zhang J L. *J Natur Gas Chem*, 2009, **18**: 55
- Pereira E B, Homsa N, Martí S, Fierro J L G, de la Piscina P R. *J Catal*, 2008, **257**: 206
- Wang H, Ye J L, Liu Y, Li Y D, Qin Y N. *Catal Today*, 2007, **129**: 305
- Birrot A, Epron F, Descorme C, Duprez D. *Appl Catal B*, 2008, **79**: 17
- Cai W J, Wang F G, Zhan E S, Van Veen A C, Mirodatos C, Shen W J. *J Catal*, 2008, **257**: 96
- Zhang B C, Tang X L, Li Y, Cai W J, Xu Y D, Shen W J. *Catal Commun*, 2006, **7**: 367
- Profeti L P R, Ticianelli E A, Assaf E M. *J Power Sources*, 2008, **175**: 482
- Vizcaino A J, Carrero A, Calles J A. *Int J Hydrogen Energy*, 2007, **32**: 1450
- Frusteri F, Freni S, Spadaro L, Chiodo V, Bonura G, Donato S, Cavallaro S. *Catal Commun*, 2004, **5**: 611
- 王红, 刘鹏翔, 刘源, 秦永宁. 催化学报 (Wang H, Liu P X, Liu Y, Qin Y N. *Chin J Catal*), 2006, **27**: 976
- Llorca J, de la Piscina P R, Dalmon J A, Sales J, Homs N. *Appl Catal B*, 2003, **43**: 355
- Llorca J, Homs N, Sales J, Fierro J L G, de la Piscina P R. *J Catal*, 2004, **222**: 470
- Guil J M, Homs N, Llorca J, de la Piscina P R. *J Phys Chem B*, 2005, **109**: 10813
- Fatsikostas A N, Kondarides D I, Verykios X E. *Catal Today*, 2002, **75**: 145
- Song H, Ozkan U S. *J Catal*, 2009, **261**: 66
- Song H, Ozkan U S. *J Phys Chem A*, 2010, **114**: 3796
- Lin S S Y, Daimon H, Ha S Y. *Appl Catal A*, 2009, **366**: 252
- Tsipourari V A, Verykios X E. *J Catal*, 1999, **187**: 85
- Chen H Q, Yu H, Peng F, Yang G X, Wang H J, Yang J, Tang Y. *Chem Eng J*, 2010, **160**: 333
- Chen H Q, Yu H, Peng F, Wang H J, Yang J, Pan M Q. *J Catal*, 2010, **269**: 281
- de Lima S M, da Silva A M, da Costa L O O, Assaf J M, Jacobsc G, Davis B H, Mattos L V, Noronha F B. *Appl Catal A*, 2010, **377**: 181
- Chen S Q, Liu Y. *Int J Hydrogen Energy*, 2009, **34**: 4735
- Chen S Q, Wang H, Liu Y. *Int J Hydrogen Energy*, 2009, **34**: 7995
- Bedel L, Roger A C, Estournes C, Kiennemann A. *Catal Today*, 2003, **85**: 207
- Bedel L, Roger A C, Rehspringer J L, Zimmermann Y, Kiennemann A. *J Catal*, 2005, **235**: 279
- Tien-Thao N, Alamdari H, Zahedi-Niaki M H, Kaliaguine S. *Appl Catal A*, 2006, **311**: 204
- Huang L, Bassir M, Kaliaguine S. *Appl Surf Sci*, 2005, **243**: 360
- Hosseini S A, Sadeghi M T, Alemi A, Niaei A, Salari D, Kafi-Ahmadi L. 催化学报 (*Chin J Catal*), 2010, **31**: 747
- Khalil M S. *Mater Sci Eng A*, 2003, **352**: 64
- Rao G V S, Rao C N R, Ferraro J R. *Appl Spectrosc*, 1970, **24**: 436
- Salavati-Niasari M, Davar F, Mazaheri M, Shaterian M. *J Magn Magn Mater*, 2008, **320**: 575
- Salavati-Niasari M, Khansari A, Davar F, Salavati-Niasari M, Khansari A, Davar F. *Inorg Chim Acta*, 2009, **362**: 4937
- Worayingyong A, Kangvansura P, Ausadasuk S, Praserttham P. *Colloids Surf A*, 2008, **315**: 217
- Royer S, Bérubé F, Kaliaguine S. *Appl Catal A*, 2005, **282**: 273
- Guo Q, Liu Y. *Appl Catal B*, 2008, **82**: 19
- Navarro R M, Alvarez-Galvan M C, Villoria J A, González-Jiménez I D, Rosa F, Fierro J L G. *Appl Catal B*, 2007, **73**: 247
- Natile M M, Ugel E, Maccato C, Glisenti A. *Appl Catal A*, 2007, **72**: 351
- Khassin A A, Yurieva T M, Kaichev V V, Bukhtiyarov V I, Budneva A A, Paukshtis E A, Parmon V N. *J Mol Catal A*, 2001, **175**: 189
- Barbero B P, de Gamboa J A, Cadus L E. *Appl Catal B*, 2006, **65**: 21
- Wang Y G, Ren J W, Wang Y Q, Zhang F Y, Liu X H, Guo Y, Lu G Z. *J Phys Chem C*, 2008, **112**: 15293
- Taguchi H, Kido H, Tabata K. *Phys B*, 2004, **344**: 271
- Llorca J, Dalmon J A, de la Piscina P, Homs N. *Appl Catal A*, 2003, **243**: 261
- Llorca J, Homs N, de la Piscina P R. *J Catal*, 2004, **227**: 556
- Kwak B S, Kim J, Kang M. *Int J Hydrogen Energy*, 2010, **35**: 11829
- Casanovas A, Roig M, de Leitenburg C, Trovarelli A, Llorca J. *Int J Hydrogen Energy*, 2010, **35**: 7690
- Karim A M, Su Y, Sun J, Yang C, Strohm J J, King D L, Wang Y. *Appl Catal A*, 2010, **96**: 441
- Valderrama G, Kiennemann A, Goldwasser M R. *Catal Today*, 2008, **133**: 142
- Hyman M P, Vohs J M. *Surf Sci*, 2011, **605**: 383