

## Preparation and properties of $K_2NiF_4$ -type perovskite oxides $La_2NiO_4$ catalysts for steam reforming of ethanol

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**Abstract:** The performance of  $La_2NiO_4$  perovskite catalysts, prepared using a citric acid complexation method, for the steam reforming of ethanol was studied. The catalysts were characterized by X-ray diffractometry (XRD), specific surface area measurements (BET), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The experimental results show that the calcination temperature and the amount of citric acid (CA) have a significant influence on the characteristics of the catalysts and their catalytic activity. Among the catalysts tested, the  $La_2NiO_4$  catalyst calcined at 700 °C with  $n(La):n(Ni):n(CA)$  of 2:1:3 exhibits the best activity and excellent stability as well as very low coke formation.

**Key words:** hydrogen; ethanol; perovskite-like oxides;  $La_2NiO_4$

### 1 Introduction

In the wake of the growing demand for carbon-neutral and zero-emission alternative fuels, considerable attention has been paid to transform the biomass-derived compounds into hydrogen-rich gas. Of special interest among such compounds is bioethanol obtained by biomass fermentation, in view of the increasing availability of raw material, ease of handling in the liquid state, high hydrogen content and low toxicity[1–3]. The biomass-derived ethanol, an aqueous solution containing 12%–15% ethanol, requires the distillation for direct use. Hydrogen manufacture by the catalytic steam reforming of ethanol without the distillation can thus be considered to be one of the most effective ways for the utilization of the biomass-derived ethanol. Catalysts using a wide variety of transition metals and supports have previously been reported for the steam reforming of ethanol[4–8]. Among the catalysts reported so far, rhodium, cobalt and nickel are considered to be the most promising metals[9]. Although rhodium seems to be most active, the use of noble metal is considered to be economically unfavorable. On the other hand, more inexpensive nickel catalysts often suffer from catalyst deactivation due to coke formation and sintering. One promising method for the inhibition of carbon deposition over Ni catalysts is

using perovskite-type oxides. CHOUDHARY et al[10] reported that complex oxides with a perovskite structure, like  $LaNiO_3$ ,  $La_{0.8}Ca(or Sr)_{0.2}NiO_3$  and  $LaNi_{1-x}Co_xO_3$  ( $x=0.2-1.0$ ), were resistant to coking for the partial oxidation of methane to synthesis gas. To inhibit carbon deposition, one must keep the size of the metal clusters smaller than the critical size needed for coke formation. In this work, the Ni catalysts from  $K_2NiF_4$ -type perovskite oxides  $La_2NiO_4$  exhibit high activity and a rather high stability. The effects of calcination temperature and citric acid concentration on the structure and the catalytic activity for the steam reforming of ethanol are studied.

### 2 Experimental

#### 2.1 Catalyst preparation

The  $La_2NiO_4$  catalysts were prepared by a citric acid complexation method. Stoichiometric amounts of  $Ni(NO_3)_2 \cdot 6H_2O$  and  $La(NO_3)_3 \cdot 6H_2O$  were dissolved completely in deionized water, and a stoichiometric amount of citric acid was mixed into the solution. The solution was then heated to 80 °C with constant stirring until a gel was formed. The gel was then dried at 110 °C for 12 h, and subsequently calcined at different temperatures for 5 h. The calcined samples were pressed, crushed and sieved to obtain a particle size of 0.40–0.50 mm.

## 2.2 Catalyst characterization

The powder X-ray diffraction (XRD) experiments were carried out on Philips PANalytical apparatus with Co  $K_{\alpha}$  radiation, at 40 kV and 40 mA. The diffraction angle ( $2\theta$ ) was scanned from  $10^{\circ}$  to  $90^{\circ}$ . Specific areas were calculated using the BET method from the nitrogen adsorption isotherms, recorded at the temperature of liquid nitrogen on a NOVA-2000 instrument. The thermogravimetric analysis (TGA) was carried out under an oxidative atmosphere with a Pyris Diamond Analyzer. About 10 mg of sample was heated from room temperature to  $850^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$ . Scanning electron microscopy (SEM) was performed with a PHILIPS XL30 scanning electron microscope operating at 20 kV.

## 2.3 Catalytic tests

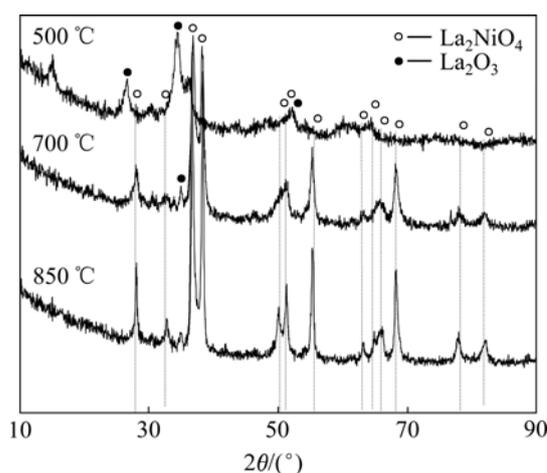
Steam reforming tests were performed in a fixed-bed flow quartz tubular reactor (12 mm of inner diameter) operating at atmospheric pressure. The catalyst (0.10 g) was first subjected to in situ reduction under pure hydrogen flow (3 mL/min) at  $500^{\circ}\text{C}$  for 1 h. Following reduction, hydrogen was replaced by argon (20 mL/h) and temperature was adjusted to reaction temperature. The liquid ethanol-water solution was fed by means of a syringe pump into a heating chamber ( $150^{\circ}\text{C}$ ) and vaporized completely in the stream of argon. The ethanol feed rate was  $5.8 \times 10^{-5}$  mol/min in all tests and the ethanol-to-water-to-argon molar ratio of 1:9:14.3 was used. The gas products were analyzed on-line by gas chromatography using both flame ionization and thermal conductivity detector. Results were expressed in terms of molar composition in the gas phase for  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ .

## 3 Results and discussion

### 3.1 Influence of calcination temperature

The XRD patterns of  $\text{La}_2\text{NiO}_4$  samples calcined at different temperatures are shown in Fig.1. After the amorphous precursor was calcined at  $500^{\circ}\text{C}$  for 4 h, intense peaks for  $\text{La}_2\text{O}_3$  were observed. When the temperature was increased to  $700^{\circ}\text{C}$ , typical diffraction peaks for the perovskite-like oxide  $\text{La}_2\text{NiO}_4$ , which was identified as single phase with a tetragonal  $\text{K}_2\text{NiF}_4$  structure, as well as a small amount of  $\text{La}_2\text{O}_3$  were observed. When the calcination temperature was increased to  $850^{\circ}\text{C}$ , the diffraction peaks for the spinel structure significantly intensified and became sharper, which suggests that the crystalline phase of  $\text{La}_2\text{NiO}_4$  became more perfect. This result indicates that  $\text{La}_2\text{NiO}_4$  with pure spinel structure can be formed by complexing citric acid with a mixture of  $\text{La}^{3+}$  and  $\text{Ni}^{2+}$  and calcining the obtained gel above  $700^{\circ}\text{C}$ . The specific surface areas and crystal sizes of the  $\text{La}_2\text{NiO}_4$ , calculated from the

half-width of a diffraction peak using Scherrer formula, are listed in Table 1. Upon increasing calcination temperature, the particle sizes increased, and the specific surface area decreased dramatically. The drop in specific surface area may originate from the aggregation of the perovskite phase, which indicates the structure properties are significantly dependent on the calcination temperature.



**Fig.1** XRD patterns of  $\text{La}_2\text{NiO}_4$  calcined at different temperatures

**Table 1** Specific surface area and crystal size of  $\text{La}_2\text{NiO}_4$  calcined at different temperatures

Calcination temperature/ $^{\circ}\text{C}$	Specific surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$	Crystal size/nm
700	11.18	23.0
850	7.58	23.6

Steam reforming tests were performed at  $500^{\circ}\text{C}$  and  $650^{\circ}\text{C}$  over  $\text{La}_2\text{NiO}_4$  catalysts calcined at different temperatures. Total ethanol conversion took place all along the 3 h runs at both reaction temperatures. The typical gaseous products  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  were obtained in all cases while other common intermediates or by-products like ethylene, diethylether and acetaldehyde were detected only in negligible amounts ( $<0.10\%$ ). Table 2 shows the typical molar composition of the gaseous mixture obtained with the  $\text{La}_2\text{NiO}_4$  catalysts calcined at different temperatures. For every catalyst, the  $\text{H}_2$  content was found to increase with temperature. At  $650^{\circ}\text{C}$ , it was found to be 70.3%–71.6%, approaching the theoretical reaction stoichiometry ( $\text{H}_2$ : 75%). Also in agreement with stoichiometry, the  $\text{H}_2$ -to- $\text{CO}_2$  molar ratio was found to approach 3.0 for the catalysts tested at  $650^{\circ}\text{C}$ . In contrast, the  $\text{CH}_4$  molar fraction showed a decreasing trend, which is consistent with a higher reaction rate of the reforming reaction

**Table 2** C<sub>2</sub>H<sub>5</sub>OH reforming using La<sub>2</sub>NiO<sub>4</sub> catalysts calcined at different temperatures

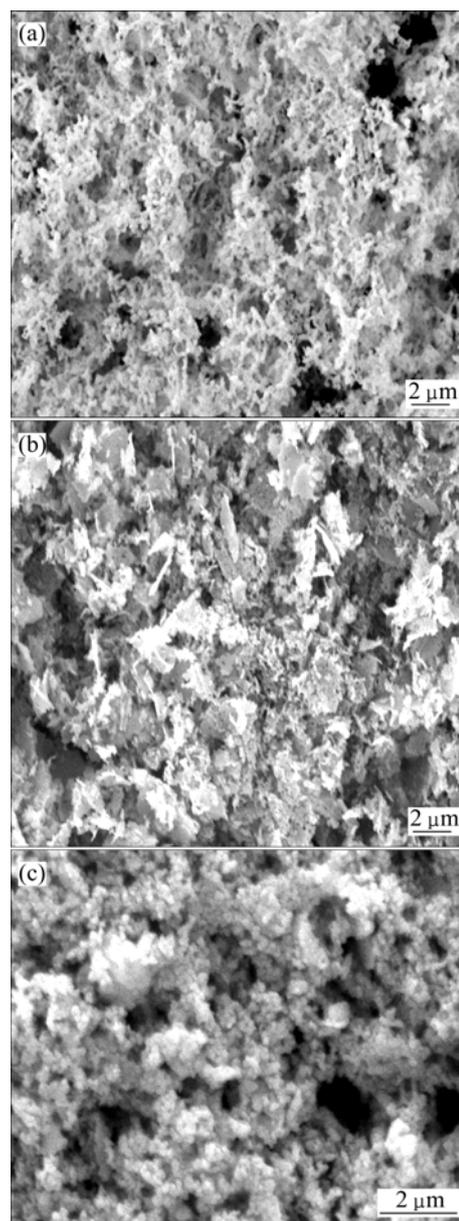
Catalyst	Ethanol conversion (in molar fraction)/%	Reaction product (in molar fraction)/%							
		H <sub>2</sub>		CO		CO <sub>2</sub>		CH <sub>4</sub>	
		500 °C	650 °C	500 °C	650 °C	500 °C	650 °C	500 °C	650 °C
La <sub>2</sub> NiO <sub>4</sub> (500)	100	66.9	70.3	1.7	4.1	26.6	24.4	4.8	1.2
La <sub>2</sub> NiO <sub>4</sub> (700)	100	67.4	71.6	1.4	3.2	28.5	25.1	2.7	0.10
La <sub>2</sub> NiO <sub>4</sub> (850)	100	66.9	71.0	1.8	5.2	26.8	23.6	4.5	0.16

(CH<sub>4</sub>+2H<sub>2</sub>O → CO<sub>2</sub>+4H<sub>2</sub>), which is favored both thermodynamically and kinetically by the temperature increment. The CO and CO<sub>2</sub> contents were found to have opposite trends with increasing temperature, which is consistent with the temperature dependence of the thermodynamic equilibrium constant of the exothermic water gas shift reaction (WGSR) (CO+H<sub>2</sub>O→CO<sub>2</sub>+H<sub>2</sub>). Ni is known as a not very active catalyst for the WGSR[11]. Thus, under the experimental conditions here the CO-to-CO<sub>2</sub> molar ratios used could be far from the equilibrium values and more dependent on kinetics parameters and textural properties of La<sub>2</sub>NiO<sub>4</sub> catalysts. Thus, these La<sub>2</sub>NiO<sub>4</sub> catalysts could be explained by differences in the influence of textural properties on the rate of the direct and reverse WGSR.

By comparing the performance of catalysts at the same reforming temperature, the catalyst La<sub>2</sub>NiO<sub>4</sub> (700 °C) led to a higher H<sub>2</sub> content (71.6%) and a lower CH<sub>4</sub> content (0.10%) in the gaseous mixture than the catalysts La<sub>2</sub>NiO<sub>4</sub> (500 °C) and La<sub>2</sub>NiO<sub>4</sub> (85 °C) at 650 °C. This is ascribed not only to a higher rate of the CH<sub>4</sub> reforming reaction being linked to a higher surface specific area, but also to that being closely linked to the smaller La<sub>2</sub>NiO<sub>4</sub> crystal size in the case of La<sub>2</sub>NiO<sub>4</sub> (700 °C).

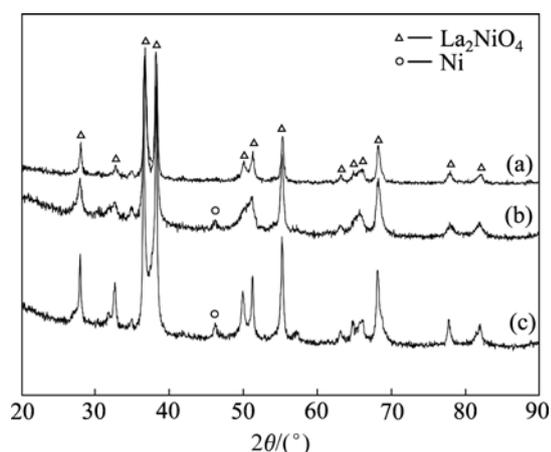
### 3.2 Influence of amount of citric acid

Citric acid (CA) is used as a chelating reagent in the synthesis of the La<sub>2</sub>NiO<sub>4</sub> powders. The amount of citric acid plays an important role in the morphology and activity of the catalysts. If the amount of citric acid is too low, some of the ions may not chelate with the citric acid and resulting gel may not be homogeneous. On the other hand, too much citric acid causes waste and precipitation from unchelated citrate. The SEM micrographs of the catalysts with different molar ratios of La to Ni to CA are shown in Fig.2. An homogeneous phase is visible when molar ratios are 2:1:1 and 2:1:3. Thus, we propose that this technique is a good and convenient method to disperse the active metal. While the catalyst powders with *n*(La):*n*(Ni):*n*(CA) of 2:1:4 have the relatively large average granularity due to significant agglomeration of fine powders.



**Fig.2** SEM images of La<sub>2</sub>NiO<sub>4</sub> catalysts prepared with different *n*(La):*n*(Ni):*n*(CA): (a) 2:1:1; (b) 2:1:3; (c) 2:1:4

Fig.3 shows the XRD patterns of the La<sub>2</sub>NiO<sub>4</sub> catalysts calcined at 700 °C with different molar ratios of La to Ni to CA. All these catalysts exhibited the characteristic diffraction peaks for the La<sub>2</sub>NiO<sub>4</sub> spinel structure. Weak diffraction lines of NiO were also



**Fig.3** XRD patterns of  $\text{La}_2\text{NiO}_4$  prepared with different  $n(\text{La}):n(\text{Ni}):n(\text{CA})$ : (a) 2:1:3; (b) 2:1:1; (c) 2:1:4

observed in the catalysts with  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:1$  and  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:4$ . This phenomenon indicates that the optimal amount of citric acid needed to obtain a pure perovskite structure of  $\text{La}_2\text{NiO}_4$  is  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:3$ .

The surface areas of fresh and used  $\text{La}_2\text{NiO}_4$  catalysts prepared with different amounts of citric acid are listed in Table 3. As the amount of citric acid increased from  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:1$  to 2:1:4, the specific surface areas of the fresh catalysts decreased from 7.78 to 6.48  $\text{m}^2/\text{g}$ . After the ethanol steam reforming reaction, the specific surface area for  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:1$  decreased dramatically, and that for  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:4$  decreased slightly, but the specific surface area for  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:3$  was almost the same. This suggests that the  $\text{La}_2\text{NiO}_4$

**Table 3** Specific surface area of  $\text{La}_2\text{NiO}_4$  prepared with different  $n(\text{La}):n(\text{Ni}):n(\text{CA})$

$n(\text{La}):n(\text{Ni}):n(\text{CA})$	Specific surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$	Specific surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$
	(Fresh sample)	(Used sample)
2:1:1	7.78	5.31
2:1:3	7.58	7.58
2:1:4	6.48	6.27

**Table 4**  $\text{C}_2\text{H}_5\text{OH}$  reforming using  $\text{La}_2\text{NiO}_4$  catalysts prepared with different  $n(\text{La}):n(\text{Ni}):n(\text{CA})$

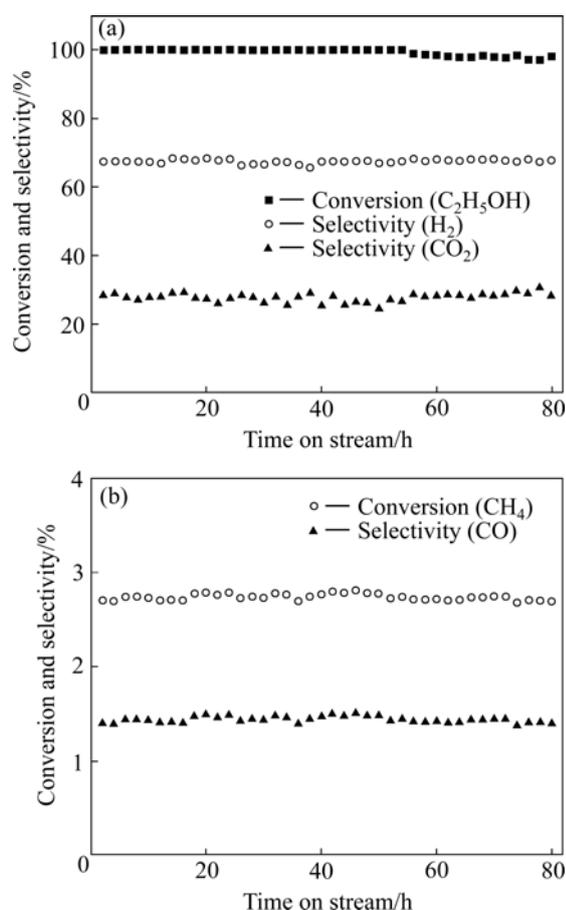
$n(\text{La}):n(\text{Ni}):n(\text{CA})$	Ethanol conversion (in molar fraction)/%	Reaction product (in molar fraction)/%							
		$\text{H}_2$		$\text{CO}$		$\text{CO}_2$		$\text{CH}_4$	
		500 °C	650 °C	500 °C	650 °C	500 °C	650 °C	500 °C	650 °C
2:1:1	100	64.4	66.2	3.8	6.5	24.7	21.1	7.1	6.2
2:1:3	100	67.4	71.6	1.4	3.2	28.5	25.1	2.7	0.10
2:1:4	100	61.6	63.8	6.2	8.9	20.4	18.3	11.8	9.0

catalyst with  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:3$  has the most stable structure.

The conversion of  $\text{C}_2\text{H}_5\text{OH}$  and the content of products at 500 °C and 650 °C over  $\text{La}_2\text{NiO}_4$  with different molar ratios of La to Ni to CA were studied and the results are shown in Table 4. Total ethanol conversion took place all along the 3 h runs at both reaction temperatures. The typical gaseous products  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  were obtained in all cases while other common intermediates or by-products like ethylene, diethylether and acetaldehyde were detected only in negligible amounts ( $<0.10\%$ ). For every catalyst, the  $\text{H}_2$  content was found to increase with temperature. By comparing the performance of catalysts at the same reforming temperature, the catalyst  $\text{La}_2\text{NiO}_4$  with  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:3$  led to a higher  $\text{H}_2$  content (71.6%) and a lower  $\text{CH}_4$  content (0.10%) in the gaseous mixture than the catalysts  $\text{La}_2\text{NiO}_4$  with  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:1$  and 2:1:4 at 650 °C. This is ascribed to a higher rate of the  $\text{CH}_4$  reforming reaction linked to a higher active metal dispersion degree seen from Fig.2.

### 3.3 Stability of $\text{La}_2\text{NiO}_4$ catalyst

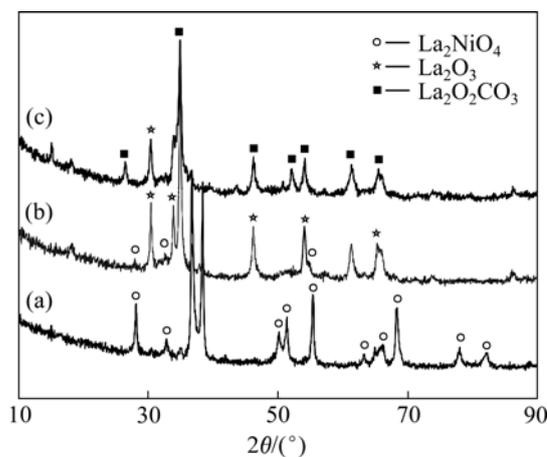
Fig.4 shows the conversion of  $\text{CH}_4$ , and the content of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{CO}_2$  as a function of time on stream at 500 °C with the ethanol feed rate of  $5.8 \times 10^{-5}$  mol/min and the ethanol-to-water-to-argon molar ratio of 1:9:14.3 over a  $\text{La}_2\text{NiO}_4$  catalyst calcined at 700 °C with  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:3$ . It is clear that during the first 55 h reaction ethanol was completely converted. When the operation time was longer than 56 h, the ethanol conversion started to decrease slightly and arrived about 97.5% at 80 h, and the selectivities of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{CO}_2$  were stable at around 67.5%, 1.44%, 2.73% and 28.3%. Meanwhile, other common intermediates or by-products like ethylene, diethylether and acetaldehyde were detected only in negligible amounts ( $<0.10\%$ ) in the whole 80 h, which suggests that the  $\text{La}_2\text{NiO}_4$  catalysts are quite stable and catalytically highly active. In agreement with these results, Ni-La catalysts also showed constant activity under the same reforming conditions[12].



**Fig.4** Stability of La<sub>2</sub>NiO<sub>4</sub> catalyst for ethanol steam reforming reaction at 500 °C

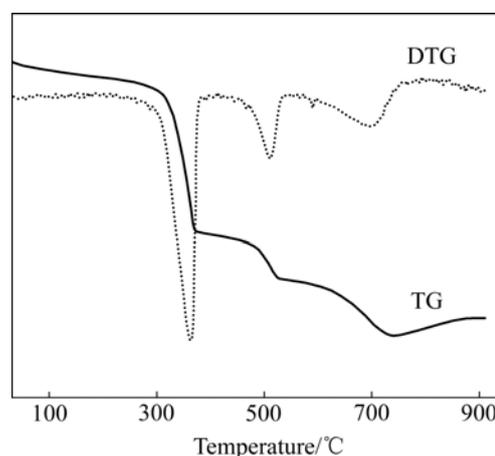
The X-ray diffraction patterns of the fresh, reduced and used La<sub>2</sub>NiO<sub>4</sub> catalysts are shown in Fig.5. For the fresh La<sub>2</sub>NiO<sub>4</sub> catalyst, typical diffraction peaks for the La<sub>2</sub>NiO<sub>4</sub> spinel structure were observed. After the catalyst was reduced by hydrogen at 500 °C for 1 h, most of the diffraction peaks attributed to La<sub>2</sub>NiO<sub>4</sub> disappeared, whereas those belonging to La<sub>2</sub>O<sub>3</sub> appeared. And nickel existed chiefly as Ni<sup>0</sup>, and the average crystal size of Ni<sup>0</sup> (21 nm) for La<sub>2</sub>NiO<sub>4</sub> (after reduction), obtained from the XRD line broadening, was found to be much smaller than that (125 nm) for Ni-La<sub>2</sub>O<sub>3</sub>[13]. This suggests that the La<sub>2</sub>NiO<sub>4</sub> has been reduced and decomposed by hydrogen to form nanoscale Ni particles, which are segregated by La<sub>2</sub>O<sub>3</sub>. LIU and AU[14] suggested that La<sub>2</sub>O<sub>3</sub> can prevent transition metals from agglomeration and promote the dispersion of nanoscale Ni<sup>0</sup> particles, resulting in an enhancement of catalytic activity and stability. After reaction, the catalysts showed similar patterns with the results of ZHANG and VERYKIOS[15]. The La<sub>2</sub>O<sub>3</sub> phase that existed in the reduced catalysts disappeared, and the La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phase was formed due to the adsorption of CO<sub>2</sub> on La<sub>2</sub>O<sub>3</sub> (CO<sub>2</sub>+La<sub>2</sub>O<sub>3</sub>→La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>). The La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phase that existed in the used La<sub>2</sub>NiO<sub>4</sub> catalyst was mainly

hexagonal. Ni<sup>0</sup> particles were not observed, thus, Ni<sup>0</sup> particles might be present in an amorphous form or they were highly dispersed. ZHANG and VERYKIOS[15] have noted that the carbon species formed on the Ni sites were easily removed by the oxygen species originating from La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>+C\*→La<sub>2</sub>O<sub>3</sub>+2CO+\*), thus producing an active and stable catalyst due to the existence of synergetic sites which consist of Ni and La elements. As indicated in this experiment, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> may play a crucial role in the ethanol steam reforming reaction using La containing catalyst prepared from perovskite precursors.



**Fig.5** X-ray diffraction patterns of La<sub>2</sub>NiO<sub>4</sub>: (a) After calcination at 850 °C; (b) After 1 h reduction at 500 °C; (c) After reaction

The TG/DTG curves for the La<sub>2</sub>NiO<sub>4</sub> catalyst after ethanol steam reforming reaction at 500 °C for 80 h are shown in Fig.6. The DTG curve of the used catalyst distinctly indicated a mass loss due to the removal of carbon. Three DTG features were observed at 363, 513 and 700 °C. This indicated that at least three kinds of carbon depositions were formed on the La<sub>2</sub>NiO<sub>4</sub>. One of the carbon depositions was likely attributed to La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>,



**Fig.6** TG/DTG profiles of La<sub>2</sub>NiO<sub>4</sub> catalysts after ethanol steam reforming reaction at 500 °C for 80 h

which had been verified by XRD.  $\text{La}_2\text{O}_2\text{CO}_3$ , formed by the interaction of  $\text{La}_2\text{O}_3$  with  $\text{CO}_2$ , may decompose into CO and produce oxygen species, which react with the surface carbon species on the Ni sites, thus giving active and stable catalytic performance for the ethanol steam reforming reaction, indicating  $\text{La}_2\text{NiO}_4$  catalyst has higher resistance to coke formation, as well as higher catalytic stability as shown in Fig.4 and Fig.6.

## 4 Conclusions

1) Better catalytic performances can be achieved using the perovskite  $\text{La}_2\text{NiO}_4$  as catalyst precursor. Among the catalysts tested, the catalyst  $\text{La}_2\text{NiO}_4$  prepared with  $n(\text{La}):n(\text{Ni}):n(\text{CA})=2:1:3$  calcined at  $700\text{ }^\circ\text{C}$  exhibits the best activity with excellent stability.

2) The XRD results confirm that  $\text{La}_2\text{NiO}_4$  exhibits a typical spinel structure.

3) During the ethanol steam reforming reaction, the active  $\text{Ni}^0$  particles do not aggregate and sinter, and the catalyst shows good stability as well as higher resistance to coke formation within an on-stream time of 80 h.

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