

Preparation of La_2NiO_4 catalyst and catalytic performance for partial oxidation of methane

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Abstract

The performance of La_2NiO_4 perovskite catalysts, prepared using a citric acid complexation method, for the partial oxidation of methane to synthesis gas has been studied. The catalysts were characterized by X-ray diffraction (XRD), specific surface area measurements, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The experimental studies 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 850 °C with a molar ratio of $\text{La}:\text{Ni}:\text{CA}=2:1:3$ exhibited the best activity and excellent stability as well as very low coke formation. © 2007 Elsevier B.V. All rights reserved.

Keywords: Partial oxidation of methane; Perovskite; La_2NiO_4 catalyst; Preparation

1. Introduction

The partial oxidation of methane (POM) to synthesis gas has attracted both academic and industrial interest. Compared with conventional steam reforming, which is very energy and capital intensive, POM is more energy efficient and can be carried out with a much lower investment of capital. POM produces synthesis gas with a H_2/CO ratio of ca. 2, which is suitable for use in the production of methanol and Fisher-Tropsch synthesis.

The catalysts reported to be active for the POM to synthesis gas are either noble metal catalysts, like Ir, Pt, Pd, Rh and Ru, particularly Ru [1–4], or Ni-based catalysts. Despite the high activity of noble metal based catalysts, the high cost of such systems limits their widespread industrial application. Ni catalysts, usually supported on alumina and silica, have been most extensively studied [5–11], the major drawback of this reaction, however, is the rapid deactivation caused by carbon deposition. One promising method for the inhibition of carbon deposition over Ni catalysts is using perovskite-type oxides. Lago et al. [12] observed that a series of LnCoO_3 ($\text{Ln}=\text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{or Gd}$) perovskites gave high activity and selectivity for the POM to synthesis gas. Choudhary et al. [13] reported that complex

oxides with a perovskite structure, like LaNiO_3 , $\text{La}_{0.8}\text{Ca}$ (or $\text{Sr})_{0.2}\text{NiO}_3$ and $\text{LaNi}_{1-X}\text{Co}_X\text{O}_3$ ($X=0.2-1.0$), were resistant to coking. Takehira et al. [14] found that Ni supported on perovskites like $\text{Ni}_{0.2}/\text{ATiO}_3$ ($A:\text{Ca}, \text{Sr or Ba}$), which were prepared by solid phase crystallization, showed good activity and selectivity as well as very low coke formation. In addition, carbon deposition can be suppressed by the use of alkaline oxides or rare earth oxides in catalysts [15,16]. Tsipouriari et al. [17,18] investigated the partial oxidation of methane to synthesis gas over a $\text{Ni}/\text{La}_2\text{O}_3$ catalyst. They found that CH_4 conversion and H_2 selectivity were close to thermodynamic predictions. However, Ni catalysts suffer from the problem of coke formation. To inhibit carbon deposition, one must keep the size of the metal clusters smaller than the critical size needed for coke formation [19]. In this paper, the Ni catalyst from K_2NiF_4 -type perovskite oxides La_2NiO_4 exhibits 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 partial oxidation of methane were studied.

2. Experimental

2.1. Catalyst preparation

The La_2NiO_4 catalyst was prepared by a citric acid complexation method. Stoichiometric amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

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and $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved completely in de-ionized 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 formed. The gel was then dried at 110°C for 12 h, and subsequently calcined at different temperature 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 $\text{Co K}\alpha$ radiation, at 40 kV and 40 mA. The diffraction angle (2θ) was scanned from 10° to 90° . 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°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. Activity measurement

The partial oxidation of methane (POM) was carried out in a fixed bed quartz reactor (8 mm i.d.) at atmospheric pressure. A 100 mg sample of the catalysts was diluted with SiC (SiC/catalyst = 1) in order to avoid hot spots and was placed between quartz-wool swatches in the middle of the reactor. The reactor was kept in a tubular furnace and its temperature was controlled by a thermocouple, which was placed in the center of the catalyst bed. The catalyst was reduced in a flow of H_2 at 500°C for 1 h before the reaction. The reaction mixture was fed by mass-flow controllers at a total flow rate of 98 mL/min with a molar ratio of $\text{CH}_4:\text{O}_2:\text{N}_2 = 2:1:4$. The products were analyzed on-line by a GC900 gas chromatograph equipped with a thermal conductivity detector (TCD) using a TDX-01 column. The conversion of CH_4 , the selectivities of CO and H_2 are defined as follows:

$$X_{\text{CH}_4}(\%) = \frac{[\text{CH}_4]_o}{[\text{CH}_4]_i - [\text{CH}_4]_o} \times 100$$

$$S_{\text{H}_2}(\%) = \frac{[\text{H}_2]_o}{2 \times \{[\text{CH}_4]_i - [\text{CH}_4]_o\}} \times 100$$

$$X_{\text{CO}}(\%) = \frac{[\text{CO}]_o}{[\text{CH}_4]_i - [\text{CH}_4]_o} \times 100$$

where $[\text{CH}_4]_i$ are inlet flow rates, and $[\text{CH}_4]_o$, $[\text{H}_2]_o$ and $[\text{CO}]_o$ are outlet flow rates.

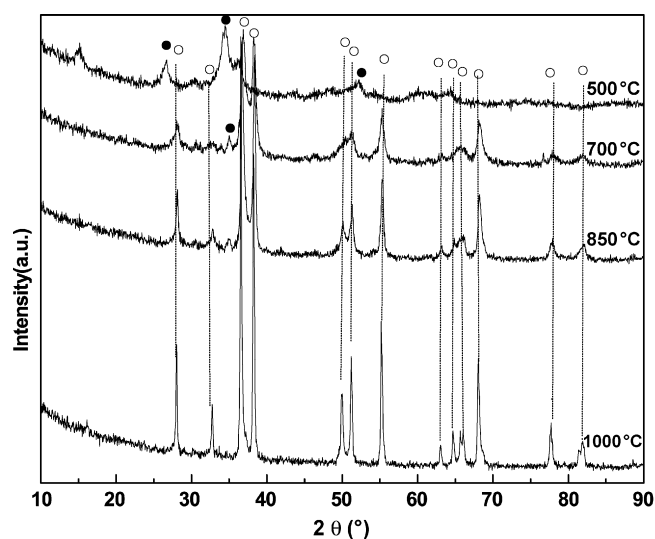


Fig. 1. XRD patterns of La_2NiO_4 calcined at different temperatures. (○) La_2NiO_4 ; (●) La_2O_3 .

3. Results and discussion

3.1. Influence of the calcination temperature

The XRD patterns of La_2NiO_4 samples calcined at different temperature are shown in Fig. 1. After the amorphous precursor was calcined at 500°C for 4 h, intense peaks for La_2O_3 were observed. When the temperature was increased to 700°C , typical diffraction peaks for the perovskite-like oxide La_2NiO_4 , which is identified as single phase with a tetragonal K_2NiF_4 structure, as well as a small amount of La_2O_3 were observed. When the calcination temperature was increased to 1000°C , the diffraction peaks for the spinel structure significantly intensified and became sharper, which suggests that the crystalline phase of La_2NiO_4 became more perfect. This result indicates that La_2NiO_4 with pure spinel structure can be formed by complexing citric acid with a mixture of La^{3+} and Ni^{2+} and calcining the obtained gel above 700°C .

The specific surface areas and crystal sizes of the La_2NiO_4 , calculated from the half-width of a diffraction peak using Scherrer's formula, are listed in Table 1. Upon increasing calcination temperature, the particle sizes increased, and the specific surface area decreased dramatically, especially for the La_2NiO_4 catalyst calcined at 1000°C . The drop in specific surface area may originate from the aggregate of the perovskite phase, which indicates the structure properties are significantly dependent on the calcination temperature.

Table 1
Specific surface area and crystal size of La_2NiO_4 calcined at different temperatures

Calcination temperature ($^\circ\text{C}$)	Surface area (m^2/g)	Particle size (nm)
700	11.18	23.0
850	7.58	23.6
1000	3.00	75.1

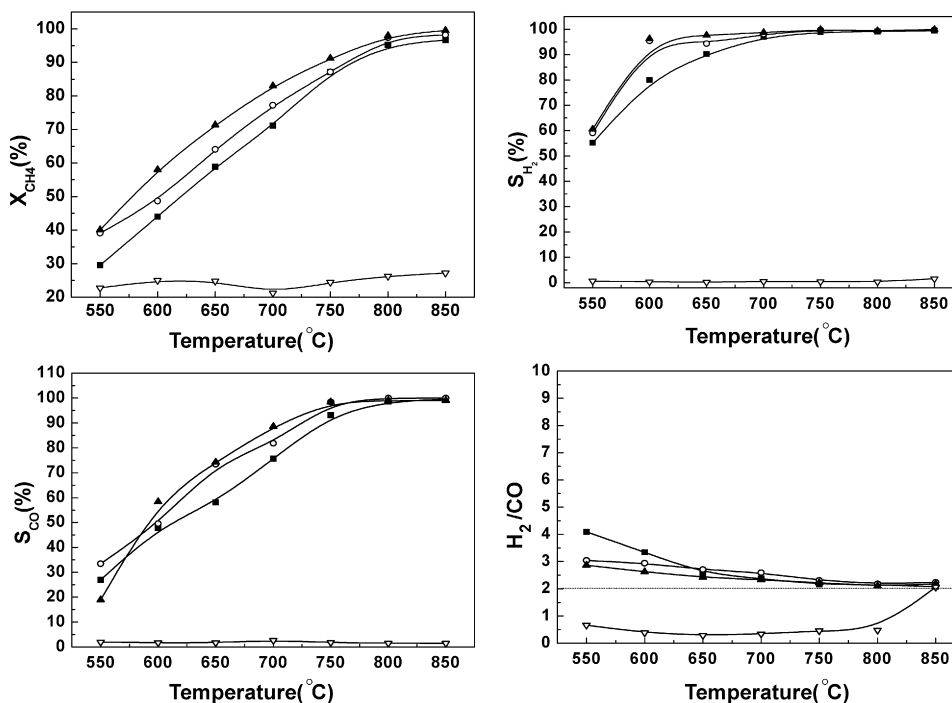


Fig. 2. Activity of La_2NiO_4 calcined at different temperatures. Calcinations temperatures: (—■—) 500 °C; (—○—) 700 °C; (—▲—) 850 °C; (—▽—) 1000 °C.

Fig. 2 shows the conversion of CH_4 , the selectivities of H_2 and CO and the H_2/CO ratio over La_2NiO_4 catalysts which have been calcined at different temperatures. The activity of the La_2NiO_4 catalyst increases with the increase in calcination temperature from 500 to 850 °C, but the activity

of the La_2NiO_4 catalyst calcined at 1000 °C was remarkably lower than those calcined at 500 °C, 700 °C or 850 °C. The La_2NiO_4 catalyst calcined at 850 °C showed the highest POM activity and remained constant during the 80 h test (Fig. 7). These results suggest that the activity of the La_2NiO_4 catalysts

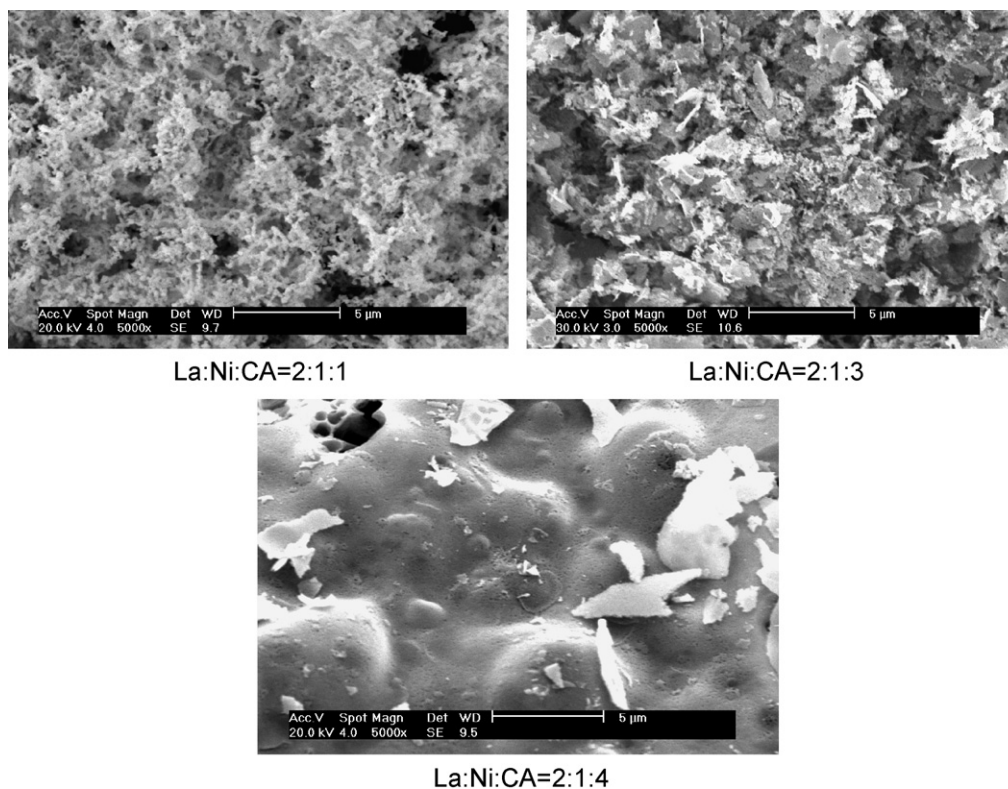


Fig. 3. SEM of La_2NiO_4 catalysts prepared with different La:Ni:CA ratios.

for the POM is sensitive to the calcination temperature of the precursors.

3.2. Influence of the amount of citric acid

Citric acid (CA) was used as a chelating reagent in the synthesis of the La_2NiO_4 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:Ni:CA are shown in Fig. 3. An homogeneous phase is visible (Fig. 4) when molar ratios of La:Ni:CA is 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 La:Ni:CA = 2:1:4 have the relatively large average granularity due to significant agglomeration of fine powders.

Fig. 4 shows the XRD patterns of the La_2NiO_4 catalysts calcined at 850°C with different mole ratios of La:Ni:CA. All these catalysts exhibit the characteristic diffraction lines for the La_2NiO_4 spinel structure. Weak diffraction lines of NiO are also observed in the catalysts with La:Ni:CA = 2:1:1 and La:Ni:CA = 2:1:4. This phenomenon indicates that the optimal amount of citric acid needed to obtain a pure perovskite structure of La_2NiO_4 is La:Ni:CA = 2:1:3.

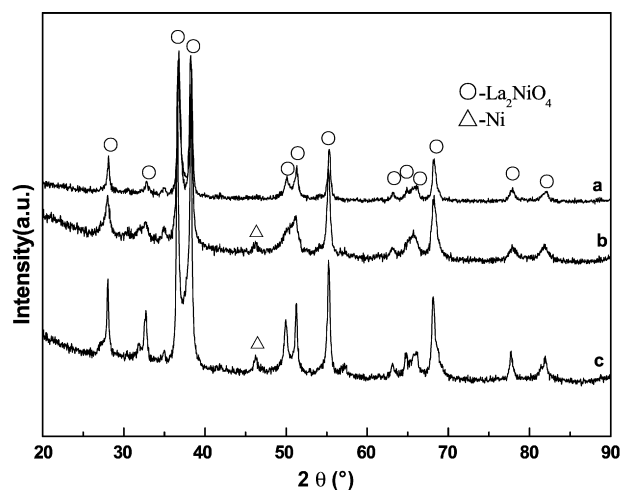


Fig. 4. XRD patterns of La_2NiO_4 prepared with different La:Ni:CA ratios. (a) La:Ni:CA = 2:1:3; (b) La:Ni:CA = 2:1:1; (c) La:Ni:CA = 2:1:4.

The surface areas of fresh and used La_2NiO_4 catalysts prepared with different amount of citric acid are listed in Table 2. As the amount of citric acid increases from La:Ni:CA = 2:1:1 to 2:1:4, the specific surface area of the fresh catalysts decreased from 7.78 to $6.48\text{ m}^2/\text{g}$. After the POM reaction, the specific surface area for La:Ni:CA = 2:1:1 decreased dramatically, and that for La:Ni:CA = 2:1:4 decreased slightly, but the specific surface area for La:Ni:CA = 2:1:3 was almost the same. This suggests that the La_2NiO_4 catalyst with La:Ni:CA = 2:1:3 has the most stable structure.

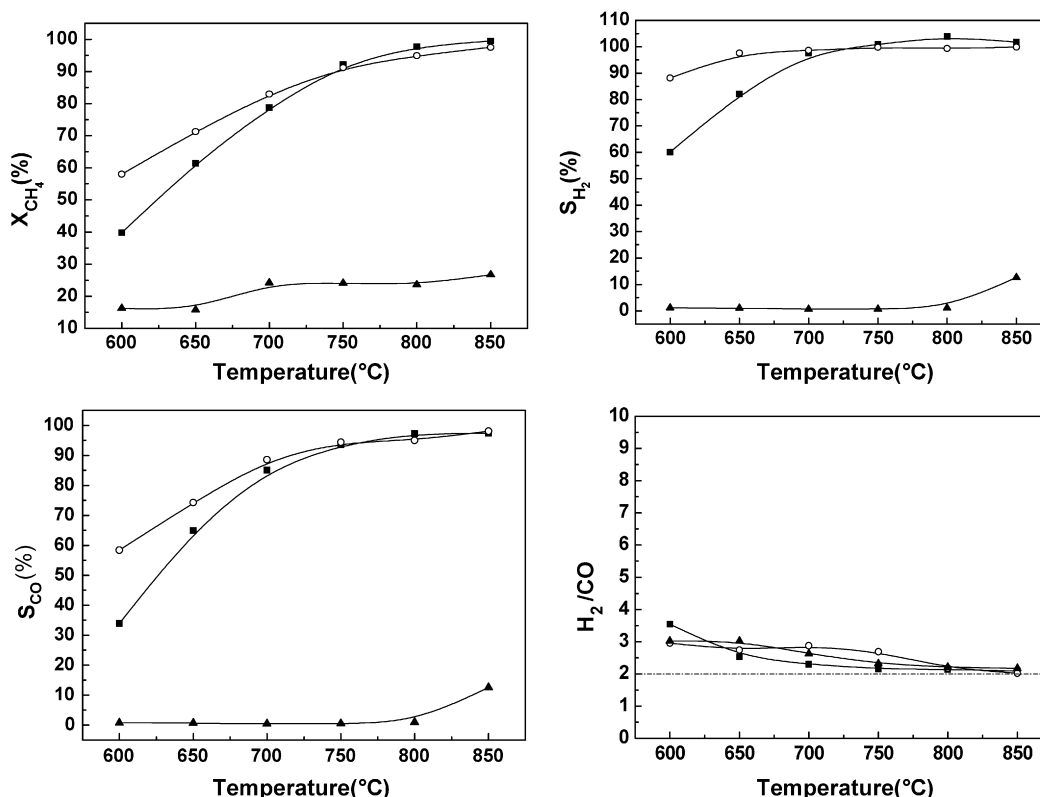


Fig. 5. Activity of La_2NiO_4 prepared with different molar ratios of La:Ni:CA. (■) La:Ni:CA = 2:1:1; (○) La:Ni:CA = 2:1:3; (▲) La:Ni:CA = 2:1:4.

Table 2
Specific surface area of La_2NiO_4 prepared with different La:Ni:CA ratios

La:Ni:CA	S_{BET} (m^2/g) (Fresh sample)	S_{BET} (m^2/g) (Used sample)
2:1:1	7.78	5.31
2:1:3	7.58	7.58
2:1:4	6.48	6.27

The conversion of CH_4 , the selectivities of H_2 and CO and the H_2/CO ratio over La_2NiO_4 with different molar ratios of La:Ni:CA were studied and the results are shown in Fig. 5. In the temperature range of 600–850 °C, the catalysts with La:Ni:CA = 2:1:1 and 2:1:3 exhibited fairly good conversion of CH_4 and good selectivities for H_2 and CO . The ratio of H_2/CO produced was close to 2. In contrast, the catalyst with La:Ni:CA = 2:1:4 had very low activity. When the reaction temperature was below 750 °C, the conversion and the selectivities are higher for La:Ni:CA = 2:1:3 than for La:Ni:CA = 2:1:1.

3.3. Stability of La_2NiO_4 catalyst

Fig. 6 shows the conversion of CH_4 , and selectivities for CO and H_2 as a function of time on stream over a La_2NiO_4 catalyst using a feed molar ratio of $\text{CH}_4:\text{O}_2:\text{N}_2 = 2:1:4$. Over a period of 80 h, the CH_4 conversion was above 97%, and CO and H_2 selectivities remained above 98% and 95%, respectively, which suggests that the La_2NiO_4 catalyst is quite stable and catalytically highly active.

The X-ray diffraction patterns of the fresh, reduced and used La_2NiO_4 catalysts are shown in Fig. 7. For the fresh La_2NiO_4 catalyst, typical diffraction peaks for the La_2NiO_4 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_2NiO_4 disappeared, whereas those belonging to La_2O_3 appeared, and nickel exists chiefly as Ni^0 , and the average crystal size of Ni^0 (21 nm) for La_2NiO_4 (after reduction), obtained from the XRD line broadening, is found to be much smaller than that (125 nm) for $\text{Ni-La}_2\text{O}_3$ [20]. This suggests that the La_2NiO_4 has

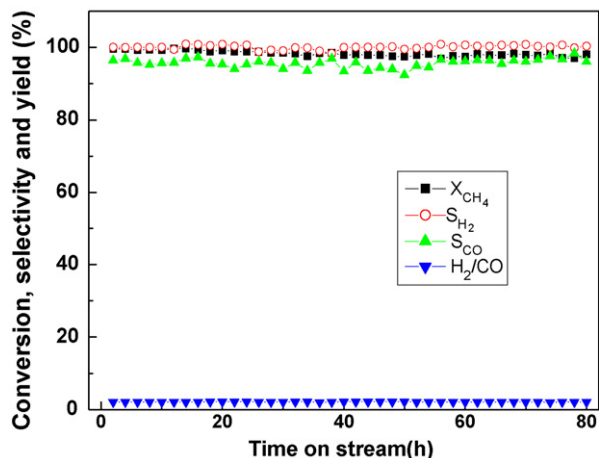


Fig. 6. Stability testing of La_2NiO_4 catalyst for POM. Reaction conditions: 800 °C, $\text{CH}_4:\text{O}_2:\text{N}_2 = 2:1:4$, flow rate of 98 mL/min.

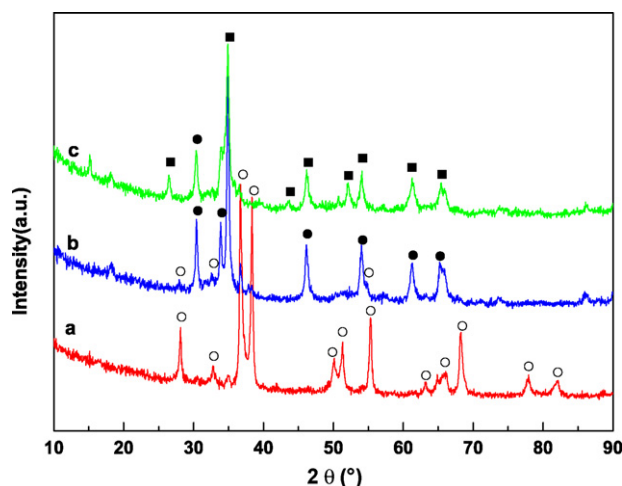


Fig. 7. X-ray diffraction patterns of the La_2NiO_4 . (a) after calcination at 850 °C; (b) after 1 h reduction at 500 °C; (c) after reaction. (○) La_2NiO_4 ; (●) La_2O_3 ; (■) $\text{La}_2\text{O}_2\text{CO}_3$.

been reduced and decomposed by hydrogen to form nanoscale Ni particles, which are segregated by La_2O_3 . Liu [21] suggested that La_2O_3 can prevent transition metals from agglomeration and promote the dispersion of nanoscale Ni^0 particles, resulting in an enhancement of catalytic activity and stability. After reaction the catalysts showed similar patterns with the results of Zhang and Verykios [22] and Nam et al. [23]. The La_2O_3 phase that existed in the reduced catalysts disappeared, the $\text{La}_2\text{O}_2\text{CO}_3$ phase was formed due to the adsorption of CO_2 on La_2O_3 ($\text{CO}_2 + \text{La}_2\text{O}_3 \rightarrow \text{La}_2\text{O}_2\text{CO}_3$). The $\text{La}_2\text{O}_2\text{CO}_3$ phase that existed in the used La_2NiO_4 catalyst is mainly hexagonal. Ni^0 particles were not observed, thus, Ni^0 particles might be present in an amorphous form or they are highly dispersed. Zhang and Verykios have noted that the carbon species formed on the Ni sites were easily removed by the oxygen species originating from $\text{La}_2\text{O}_2\text{CO}_3$ ($\text{La}_2\text{O}_2\text{CO}_3 + \text{C}^* \rightarrow \text{La}_2\text{O}_3 + 2\text{CO} + *$) and thus produces an active and stable catalyst due to the existence of synergetic sites which consist of Ni and La elements. As indicated in this experiment, $\text{La}_2\text{O}_2\text{CO}_3$ may play a crucial role in the POM using La containing catalyst prepared from perovskite precursors.

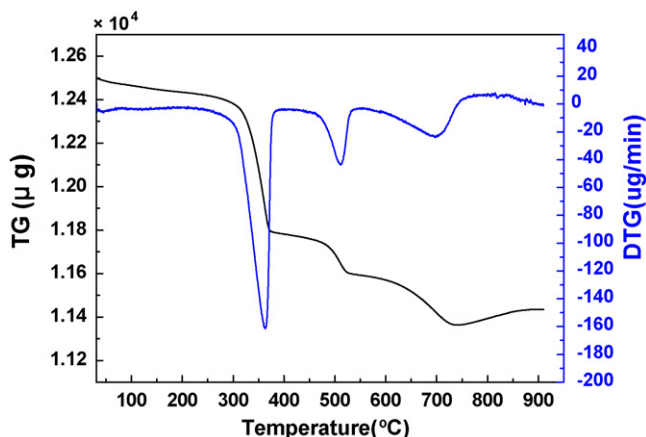


Fig. 8. TG/DTG profiles of La_2NiO_4 catalysts after POM at 800 °C for 80 h.

The TG/DTG curves for the La_2NiO_4 catalyst after POM at 800°C for 80 h are shown in Fig. 8. The DTG curve of the used catalyst distinctly indicates a weight loss due to the removal of carbon. Three DTG features were observed at 363, 513 and 700°C . This indicates that at least three kinds of carbon deposition were formed on the La_2NiO_4 . One of the carbon depositions is likely attributed to $\text{La}_2\text{O}_2\text{CO}_3$, which had been verified by XRD. $\text{La}_2\text{O}_2\text{CO}_3$, formed by the interaction of La_2O_3 with 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 partial oxidation of methane to synthesis gas. This has been confirmed by Tsipouriari and Verykios [18].

4. Conclusion

A series of La_2NiO_4 catalysts were prepared by a citric acid complexation method, and their catalytic performance for the partial oxidation of methane to synthesis gas were evaluated. The result showed that better catalytic performances can be achieved using the perovskite La_2NiO_4 as catalysts precursor. Among the catalysts tested, the catalyst La_2NiO_4 prepared with La:Ni:CA = 2:1:3 and calcined at 850°C exhibits the best activity with excellent stability. The XRD results confirmed that La_2NiO_4 exhibited a typical spinel structure. During the POM, the active Ni^0 particles did not aggregate and sinter, and the catalyst showed good stability within an on-stream time of 80 h.

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