Effect of Partial Substitution of Ni by Cu in LaNiO_3 Perovskite Catalyst for Dry Methane Reforming

G. R. MORADI*, F. KHOSRAVIAN, M. RAHMANZADEH

Catalyst Research Center, Chemical Engineering Department, Faculty of Engineering, Razi University, Kermanshah 67149-67346, Iran

Abstract: A series of ternary perovskite type oxides $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.2, 0.4, 0.6, 0.8$, and 1.0) were synthesized via the sol-gel method in propionic acid. Partial substitution of Ni by Cu showed higher activities and selectivities towards syngas products. $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ was the most active toward the CH_4 and CO_2 conversions, and was selective for syngas products. Temperature-programmed reduction results showed that the addition of Cu facilitates the reduction of Ni^{3+} to Ni^0 , which is the main reason for the higher performance of this catalyst.

Key words: dry reforming of methane; perovskite; lanthanum; nickel; sol-gel method

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*Corresponding author. Tel: +98-9123895988; Fax: +98-8314274542; E-mail: gmoradi@razi.ac.ir

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Dry reforming of methane has attracted many academic and industrial researchers as it produces synthesis gas with a low H_2/CO ratio while converting two major greenhouse gases to valuable products [1–4]. For dry reforming, noble metals are known to be active and stable catalysts and the order of activity for these metals and nickel are $\text{Ru} > \text{Rh} > \text{Ni} \sim \text{Ir} > \text{Pt} > \text{Pd}$. Despite the high activities and low sensitivities to carbon deposits of the noble metals, costs and limited availability of these metals discourage their widespread industrial applications. Ni is more promising since Ni-based catalysts are relatively inexpensive [5,6]. Nickel is more susceptible to coking and deactivates more rapidly than noble metals so many studies have been done to reduce this issue. Dispersing the active metal on a high surface area support along with the use of promoters, improves the stability and activity of the catalyst. The better dispersed the metal, the higher the catalytic activity [7,8].

Efforts have been made to synthesize Ni catalysts resistant to carbon deposition by introducing the metal into perovskite type oxides (ABO_3). These are well defined structures which can produce very small metal particles after reduction, with the metal well dispersed at the surface of a basic support. This small particle size helps avoid carbon formation and increases the activity and stability of the catalyst. Another advantage of the perovskite type structure is the possibility of total or partial substitution of its cations, modifying their oxidation state, mobility within the oxygen lattice, and the redox properties that can modify the catalytic activity and stability [9–12]. Partial substitution at the A site can strongly affect the catalytic activity through sta-

bilization of unusual oxidation states at the B site and the simultaneous formation of structural defects. Interactions created by the formation of bonds between Ni oxide and rare earth elements, increase in the reduction temperature of nickel oxide. However, particularly for LaNiO_3 , the thermal stability of the perovskite is low in a reducing atmosphere and coke formation can be important [13]. Thermodynamic calculations of graphitic carbon deposition suggest that carbon formation can be avoided by working at high temperatures (e.g., 1000°C) as well as using an excess of CO_2 , H_2O , or O_2 . Also, coke formation can be suppressed by the addition of alkaline earth metals with high basicity.

There are some published articles reporting improved activity, selectivity, and stability of LaNiO_3 in the dry reforming of methane by adding basic or noble promoters for Ni substitution such as in $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ (where $\text{M} = \text{Co}$ [12], Mg [11,14], Rh [15], Ru [8,16], Fe [13], Al [17]). The presence of cobalt enhances in situ formation of $\text{Ni}^0\text{-Co}^0$ particles highly dispersed on the $\text{La}_2\text{O}_2\text{CO}_3$ matrix that inhibits coke formation in spite of the severe reaction conditions. These perovskite-type oxides ($\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$) produce very active catalysts when $x \leq 0.8$ [12]. A small portion of Mg substituted into a perovskite, also decreases the amount of coke produced during the reaction. Partial substitution of nickel by rhodium (5% mol, $\text{LaNi}_{0.95}\text{Rh}_{0.05}\text{O}_3$) increases the catalytic activity. Characterization of the solids reveal the complete decomposition of the perovskite type structure after reduction with the formation of metallic species such as Ni and Rh, and the presence of a considerable amount of $\text{La}_2\text{O}_2\text{CO}_3$. The presence of rhodium not only modifies the

catalyst surface but also improves the catalytic performance by enhancing nickel reduction and dispersion [15]. The partial replacement of nickel by ruthenium in the perovskite structure makes the metal reduction more difficult due to the stronger Ru–O–La bond as compared with the Ni–O–La bond. The most promising catalyst was the partially substituted perovskite $\text{LaNi}_{0.8}\text{Ru}_{0.2}\text{O}_3$ which, in spite of being less active than the other samples, showed the highest resistance to carbon deposition [8]. The partial substitution of Ni by Fe in the perovskite structure, $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ decreased the rate of conversion of both reactants. However, the stability of the catalyst during the reaction was much increased [13]. Also, the addition of aluminum to LaNiO_3 resulted in an efficient catalyst in steam and the dry reforming of methane and generated a change in the temperature of nickel reduction and stabilized the structure under reaction conditions [17].

In this work, Cu was chosen for partial substitution of Ni in LaNiO_3 perovskite. There is not any comprehensive study on the effects on catalysis of Cu substitution into a LaNiO_3 perovskite in the literature. Therefore, a series of $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ perovskites were synthesized by a sol-gel method and were used as catalyst precursors in dry methane reformation.

1 Experimental

1.1 Synthesis of perovskite-type oxides

The ternary oxides $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.2, 0.4, 0.6, 0.8$, and 1.0) were synthesized by a sol-gel method in propionic acid. These were then used as catalyst precursors in the dry reforming of methane to syngas. In the synthesis, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and propionic acid ($\text{C}_3\text{H}_6\text{O}_2$) were used. All reagents were purchased from Merck. The initial sources of each metal were individually dissolved in additional hot propionic acid until the solution was clear at reflux. These salts were lightly warmed on a metal sheet with constant agitation until the dissolution of the solids was achieved. After complete dissolution, the solutions were mixed and agitated constantly for about 4 h at reflux. The propionic acid was then evaporated by increasing the temperature of metal sheet above the boiling point of the solvent, forming a resin, which hardened on cooling. The resulting gel was dried at $120\text{ }^\circ\text{C}$ for 24–48 h, ground to a fine powder and then calcined at $750\text{ }^\circ\text{C}$ for 4 h. Catalysts were calcined by increasing the temperature from ambient to $750\text{ }^\circ\text{C}$ at a rate of $3\text{ }^\circ\text{C}/\text{min}$ and maintained at that temperature for 4 h in order to obtain the perovskite phases with the same order of crystallinity [12]. The calcined precursors were grounded to a fine powder and used as fresh catalysts in the dry reforming reaction.

1.2 Catalytic activity

The experiments were carried out with a feed composition of $\text{CH}_4:\text{CO}_2:\text{He} = 1:1:1$ and a total flow of $30\text{ ml}/\text{min}$. All gases used were special purity grade ($> 99.9999\%$). An appropriate mixture of reactants was injected through a mass flow controller (MFC, Brooks 5850 TR series) to a fixed bed quartz tubular micro reactor which was 50 cm long and had an inner diameter of 5 mm , containing 0.01 g of sample. The samples were diluted with quartz particles with a mesh size between 30 and 60. The reactor was imbedded in an insulated electric furnace, equipped with a programmable temperature controller. The sample was fixed by two layers of quartz wool at the center of reactor to prevent the catalyst from moving and to reduce the free volume. The exhausted gas stream entered a condenser to remove water before entering a gas chromatograph. Exhaust gases were analyzed using a thermal conductivity detector. The catalytic properties have been evaluated in terms of CH_4 and CO_2 conversions, H_2 and CO yields, and H_2/CO ratio, as follows:

$$X(\text{CH}_4) = (n_{\text{in}}(\text{CH}_4) - n_{\text{out}}(\text{CH}_4))/n_{\text{in}}(\text{CH}_4) \times 100\% \quad (1)$$

$$X(\text{CO}_2) = (n_{\text{in}}(\text{CO}_2) - n_{\text{out}}(\text{CO}_2))/n_{\text{in}}(\text{CO}_2) \times 100\% \quad (2)$$

$$Y(\text{CO}) = n(\text{CO})/(n_{\text{in}}(\text{CH}_4) + n_{\text{in}}(\text{CO}_2)) \times 100\% \quad (3)$$

$$Y(\text{H}_2) = n(\text{H}_2)/2n_{\text{in}}(\text{CH}_4) \times 100\% \quad (4)$$

$$\text{H}_2/\text{CO} = n_{\text{out}}(\text{H}_2)/n_{\text{out}}(\text{CO}) \quad (5)$$

A schematic view of the dry reforming setup is shown in reference [18]. Each experiment took about 20 h to produce the active catalyst. The temperature was increased from room temperature to $750\text{ }^\circ\text{C}$ at a rate of $14.5\text{ }^\circ\text{C}/\text{min}$, and maintained at this temperature for the desired reaction time. In all experiments the perovskite catalyst was used without previous reduction. The stability of the catalysts was measured at $750\text{ }^\circ\text{C}$ for 20 h.

1.3 Catalyst characterization

X-ray powder diffraction (XRD) analyses were performed to determine the internal structure of the synthesized solids, using a SIEMENS D5000 equipment with a copper anode ($K_\alpha\text{ Cu}$, 0.15406 nm), operating at 40 kV and 30 mA . Phase recognition was obtained by comparison with JCPDS files.

Temperature-programmed reduction (TPR) of the catalysts were carried out in a stream of 5.1% H_2 balanced with Ar at a flow rate of $50\text{ ml}/\text{min}$ using a Micromeritics Pulse Chemisorb 2705 instrument. A catalyst sample (20 mg) placed in a quartz tube was degassed for 2 h at $120\text{ }^\circ\text{C}$ under a N_2 stream, and then cooled to room temperature. After the stream was switched from N_2 to the reducing gas, the sample was heated linearly at a rate of $5\text{ }^\circ\text{C}/\text{min}$. The water which formed during the reduction was trapped by cooling

in a mixture of ethylene glycol and liquid nitrogen. The hydrogen concentration in the effluent was continuously monitored by a thermal conductivity detector.

2 Results and discussion

2.1 Catalytic activity

To find the effects of partial substitution of Cu for Ni in the LaNiO₃ perovskite structure and its optimum value, the ternary oxides LaNi_{1-x}Cu_xO₃ were prepared with different degrees of substitution with $x = 0.2, 0.4, 0.6, 0.8$, and 1.0 and tested in the micro-reactor. The results of the catalytic tests for LaNi_{1-x}Cu_xO₃ series are shown in Fig. 1.

Fig. 1. Catalytic performance for LaNi_{1-x}Cu_xO₃ series as a function of time on stream. (a) Methane conversion; (b) CO₂ conversion; (c) H₂/CO ratio.

Figure 1(a) shows the methane conversion of the LaNi_{1-x}Cu_xO₃ series perovskites. This value is greater than that of perovskite LaNiO₃ when $x \leq 0.6$. Among this series,

LaNi_{0.8}Cu_{0.2}O₃ showed the greatest increase in the conversion of methane. CO₂ conversion of LaNi_{1-x}Cu_xO₃ series perovskites is illustrated in Fig. 1(b). Again, when $x \leq 0.6$, this value is greater than that of LaNiO₃ ($x = 0.0$).

For the partially substituted perovskites LaNi_{1-x}Cu_xO₃ where $x = 0.2, 0.4$, and 0.6 , the CH₄ and CO₂ conversions are close to the parent LaNiO₃, changing by ~4%. For $x > 0.6$, these conversions decrease intensely to the values lower than 30%.

Figure 1(c) illustrates the H₂/CO ratio of the LaNi_{1-x}Cu_xO₃ series. For $x \leq 0.6$, this value is similar to that of the parent LaNiO₃. For $x \geq 0.8$, this value decreases to between 0.5 and 0.7. Among this series, LaNi_{0.8}Cu_{0.2}O₃ showed the greatest conversions of CH₄ and CO₂ reactants. Comparing the conversions of CH₄ and CO₂ shown in Figs. 1(a) and (b), CO₂ conversion is uniformly higher than CH₄. This occurs because of the reverse water gas shift (RWGS) reaction (Equation 6), which is thermodynamically possible at these temperatures, and consumes CO₂, occurs simultaneously with the CO₂ reformation of CH₄. For this reason, the H₂/CO ratio attained is less than unity.

2.2 XRD results

Figure 2 shows the XRD patterns of perovskite-type oxide LaNiO₃ after calcination and after on-stream operation. As seen in Fig. 2(1), the main diffraction peaks of the calcined perovskite can be attributed to the perovskite structure. The diffraction patterns of the activated LaNiO₃ (Fig. 2(b)) are completely different from the patterns after calcination. It is obvious that after activation of this sample, the perovskite phase is lost to form two new phases which correspond to lanthanum oxide (La₂O₃) and nickel (Ni). Focusing on the 2θ between 32° and 35°, which correspond to the more intense diffraction of LaNiO₃, shows a split characteristic of rhombohedra symmetry. The position of the peak of maximum intensity of LaNiO₃ was located at

Fig. 2. XRD patterns for perovskite LaNiO₃ after calcination (1) and after on-stream operation (2) [10].

33.168°.

Figure 3 shows the XRD patterns of perovskite-type oxide $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ after calcination and after on-stream operation. In Fig. 3(1), the main diffraction peaks appear at 23.13°, 32.77°, 33.9°, 47.27°, and 58.67°, characteristic of the LaNiO_3 rhombohedra structure (JCPDF 33-711) that confirms the presence of a perovskite-type structure. Comparing with the XRD pattern of the perovskite LaNiO_3 , a progressive shift of the most intensive diffraction peak to lower angles is observed when nickel is partially substituted by copper ($x = 0.2$), accompanied of a small increase in its intensity. This shift indicates that a solid solution of LaNiO_3 is formed. Characterization of the after reaction catalyst used in the dry reforming of methane shows that the structure is completely different from that of the calcined counterpart (Fig. 3(2)). After on-stream operation, the perovskite phase is again lost to form two new phases which correspond to La_2O_3 and Ni. The XRD pattern shows the main diffraction peaks at 29.97°, 39.51°, 46.08°, 52.13°, and 55.44° characteristic of La_2O_3 hexagonal structure (JCPDF 5-602) and main diffraction peaks at 44.12° and 51.37° characteristic of the Ni cubic structure (JCPDF 3-1043). This La_2O_3 phase has been claimed to be responsible for the removal of carbonaceous material developed at the interface with the Ni^0 crystallites.

Figure 3(3) shows the XRD pattern of the perovskite-type oxide $\text{LaNi}_{0.2}\text{Cu}_{0.8}\text{O}_3$ after calcination. In this pattern, the partial substitution of nickel by copper at $x = 0.8$, gives rise to two new phases which correspond to CuO and La_2CuO_4 , as well as the original perovskite LaNiO_3 . The main diffraction peaks at 24.31°, 31.16°, 43.49°, and 47.66° are characteristic of La_2CuO_4 face-centered orthorhombic structure (JCPDF 38-709). Peaks at 32.75°, 33.21°, and 58.1° are characteristic of LaNiO_3 rhombohedra structure (JCPDF 33-711), and peaks at 35.56°, 38.71°, and 65.24° are char-

Fig. 3. XRD patterns for perovskite $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$. (1) After calcination ($x = 0.2$); (2) After on-stream operation ($x = 0.2$); (3) After calcination ($x = 0.8$).

acteristic of the CuO monoclinic structure (JCPDF 5-661).

By applying the Scherrer's equation to the most intense diffraction peaks in the XRD patterns, the average crystallite sizes in the calcined and activated samples were calculated. The main crystalline phases and the average crystallite sizes of the precursors LaNiO_3 (calcined), $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (calcined and after the activation process), and $\text{LaNi}_{0.2}\text{Cu}_{0.8}\text{O}_3$ (calcined) are shown in Table 1. The crystallite sizes of the calcined samples are on the order of 20–62 nm. As the substitution increases, the mean particle size of calcined perovskites increases.

Table 1 Mean particle sizes and main phases for analyzed precursors

Catalyst precursor	Mean particle size (nm)		Main phase	
	Calcined	Activation	Calcined	Activation
LaNiO_3	22.00	22.00	LaNiO_3	LaNiO_3 , $\text{La}_2\text{O}_2\text{CO}_3$
$\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$	25.42	50.48	LaNiO_3	LaNiO_3 , La_2O_3 , Ni^0
$\text{LaNi}_{0.2}\text{Cu}_{0.8}\text{O}_3$	62.52	—	CuO , La_2CuO_4 , LaNiO_3	—

For the perovskite LaNiO_3 , the mean particle sizes for calcined sample and the sample after activation are similar, indicating that no sintering of the metal particles occurs during activation process [10]. For $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$ the mean particle size after the activation process is greater than after calcination. It is possible that the sintering of the metal particles has occurred during this process. For the calcined samples, the mean particle size increases as the substitution degree increases.

2.3 TPR results

Figure 4(1) displays the TPR profile of the perovskite LaNiO_3 . LaNiO_3 shows two main reduction peaks: the first peak at 390 °C is assigned to the reduction of the Ni^{3+} to Ni^{2+} with concomitant formation of $\text{La}_2\text{Ni}_2\text{O}_5$; another reduction at 522 °C is due to the reduction of Ni^{2+} species in

Fig. 4. TPR profiles for $\text{LaNi}_x\text{Cu}_x\text{O}_3$ precursor. (1) LaNiO_3 ; (2) $\text{LaNi}_{0.8}\text{Cu}_{0.2}\text{O}_3$.

the brownmillerite phase to Ni⁰ and La₂O₃ in agreement with XRD patterns as suggested by Valderrama et al. [10] and Martinez et al. [19]. The resulting Ni⁰ metal particles, which are the active phase in the dry methane reformation, remain highly dispersed on the lanthanum oxide phase (Ni⁰/La₂O₃). A third smaller broad H₂ component overlaps the first main peak and extends over 350–370 °C was also observed. If LaNiO₃ is the only phase present the intensity of the second peak should be twice the first peak, however, the observed 1.41 value suggests that a small amount of a separate NiO phase is also present (NiO→Ni⁰).

Based on these results, the reduction steps are written as follows:

It was reported that the propionic acid synthesis method favors reduction of the solids at lower temperatures. According to some reports [10], the XRD patterns that do not show the formation of an alloy between nickel and added promoter to the perovskite structure have highly disperse metals. No alloy formation was observed in our XRD patterns, implying the metal is highly disperse.

Figure 4(2) displays the TPR profile of the perovskite LaNi_{0.8}Cu_{0.2}O₃. Two reduction peaks can be observed. The first peak at 365 °C shows a shift of ~25 °C to lower temperatures, compared with the LaNiO₃ perovskite. The second reduction peak at 510 °C shows a smaller shift of 12 °C to lower temperatures again compared with the LaNiO₃ perovskite. Thus the Cu²⁺ reduces to Cu⁰ at lower temperatures than either Ni³⁺ or Ni²⁺, and the Cu⁰ crystallites favor the reduction of nickel cations. A similar behavior was observed by Rivas et al. [15] for the LaNi_{0.95}Rh_{0.05}O₃ perovskite-type oxide.

Comparing Figs. 6(1) and (2), the area under the first reduction peak of the perovskite LaNi_{0.8}Cu_{0.2}O₃ is greater than that of the perovskite LaNiO₃. It is possible that NiO and La₂O₃ were formed, as well as the LaNiO₃ perovskite. This NiO can be reduced to Ni⁰ simultaneously with the formation of La₂Ni₂O₅, resulting in hydrogen consumption larger than the expected. The lower ratio of the area under the second peak area compared with the first indicates the amount of compounds other than the perovskite structure that were not observed by XRD and contribute to hydrogen consumption.

3 Conclusions

After partial substitution of Ni in the LaNiO₃ perovskite structure by Cu, perovskites exhibit high conversions of CH₄ and CO₂ reactants and high yields of H₂ and CO products. In the LaNi_{1-x}Cu_xO₃ perovskite series for $x \leq 0.6$, the partial substituted perovskites were found to be highly ac-

tive toward the production of valuable syngas product during the dry reformation of methane. Among these perovskites, LaNi_{0.8}Cu_{0.2}O₃, was the most active. Characterization of the catalysts revealed the complete decomposition of the perovskite-type structure after the activation process and the high activities are attributed to the in situ formation of metallic species including Ni⁰ and Cu⁰ which highly dispersed on a La₂O₃ matrix. Cu²⁺ reduces to Cu⁰ at lower temperatures than either Ni³⁺ or Ni²⁺, and the generated Cu⁰ crystallites favor the reduction of nickel cations. The stability of the prepared catalysts is due to the presence of the La₂O₃ phase.

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