### Accepted Manuscript

Title: Effects of Fe partial substitution of  $La_2NiO_4/LaNiO_3$  catalyst precursors prepared by wet impregnation method for the dry reforming of methane

Author: Xiao Song Xiaolei Dong Shiliu Yin Meng Wang Ming Li Haiqian Wang



PII:	S0926-860X(16)30393-3
DOI:	http://dx.doi.org/doi:10.1016/j.apcata.2016.07.024
Reference:	APCATA 15961
To appear in:	Applied Catalysis A: General
Received date:	26-4-2016
Revised date:	6-7-2016
Accepted date:	27-7-2016

Please cite this article as: Xiao Song, Xiaolei Dong, Shiliu Yin, Meng Wang, Ming Li, Haiqian Wang, Effects of Fe partial substitution of La2NiO4/LaNiO3 catalyst precursors prepared by wet impregnation method for the dry reforming of methane, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2016.07.024

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Effects of Fe partial substitution of La<sub>2</sub>NiO<sub>4</sub>/LaNiO<sub>3</sub> catalyst precursors prepared by wet impregnation method for the dry reforming of methane

Xiao Song<sup>a</sup>, Xiaolei Dong<sup>a</sup>, Shiliu Yin<sup>a</sup>, Meng Wang<sup>a</sup>, Ming Li<sup>a</sup>, Haiqian Wang<sup>a,\*</sup>

<sup>a</sup> Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China

Corresponding author. Tel.: +86 551 63603770; Fax: +86 551 63606266.

E-mail address: hqwang@ustc.edu.cn

### Graphical abstract



#### **Highlights**

- Mixed perovskites precursors with the nominal compositions of La<sub>2</sub>NiO<sub>4</sub>, LaNiO<sub>3</sub>, La<sub>2</sub>Ni<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>4</sub> and LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> were prepared by a wet impregnation method.
- 2. LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> phase enhances the metal-support interaction and suppresses the agglomeration of small Ni particles.
- 3. A stable Ni-based catalyst with high carbon resistance for dry reforming of methane is obtained through the LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> precursor.

#### Abstract

Improving the carbon resistance of Ni-based catalysts for the dry reforming of methane (DRM) through the metal-perovskite interaction is an attractive strategy. Ni-based perovskite precursors with the nominal compositions of La<sub>2</sub>NiO<sub>4</sub> and LaNiO<sub>3</sub>, as well as their Fe partially substituted counterparts (La<sub>2</sub>Ni<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>4</sub> and LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub>), were prepared by a wet impregnation method. Perovskite structures in the samples without Fe partial substitution are unstable and completely reduced during the DRM test, forming catalysts composed of Ni as the active component and La<sub>2</sub>O<sub>3</sub> as the support. The stability of the perovskite structure is significantly enhanced by the Fe partial substitution, and improved carbon resistance are observed in these catalysts, which is attributed to the smaller particle size and better dispersion of Ni resulted from the stronger metal-support interaction. The LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> perovskite plays an important role in the structural stability of mixed perovskite catalysts in reducing atmosphere and the enhancement of metal-support interaction. Our results indicate that the LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> precursor synthesized by wet impregnation method is feasible to obtain stable Ni-based catalysts with high carbon resistance for DRM.

#### **Keywords**

Dry reforming of methane, Perovskite, Fe partial substitution, Wet impregnation, Reducibility, Carbon resistance

#### 1. Introduction

The reforming of methane by carbon dioxide (dry reforming of methane, DRM) attracts much attention because of its industrial and environmental potential. Two abundantly available green-house gases (CH<sub>4</sub> and CO<sub>2</sub>) are used as feed gas to produce industrially important syngas (H<sub>2</sub> and CO). The main reactions of DRM are[1]:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H_{298}^0 = 247.3 \text{ kJ/mol} (1)$$
  
 $CO_2 + H_2 \rightleftharpoons 2CO + H_2O \quad \Delta H_{298}^0 = 41.2 \text{ kJ/mol} (2)$ 

Eq. (1) suggests that DRM is endothermic, which needs high temperature to attain high equilibrium conversions to syngas. Ideally, it produces a syngas with a H<sub>2</sub>/CO ratio of 1: 1, but the reverse water gas shift reaction (RWGS, Eq. (2)) causes a decrease in H<sub>2</sub>/CO ratio to values < 1 [2, 3], which is more favored in the synthesis of oxygenated chemicals[4] and hydrocarbons from Fischer-Tropsch synthesis [5].

A main concern of DRM catalysts is the carbon deposition during the reaction[6] which causes catalyst deactivation, catalyst destruction, and reactor blockage [7, 8]. The carbon formation reactions [1] are mainly:

$$CH_4 \rightleftharpoons C(s) + 2H_2 \quad \Delta H^0_{298} = 74.9 \text{kJ/mol}$$
 (3)  
 $2C0 \rightleftharpoons C(s) + CO_2 \quad \Delta H^0_{298} = -173.5 \text{kJ/mol}$  (4)

The CH<sub>4</sub> decomposition (Eq. (3)) and the Boudouard reaction (Eq. (4)) depend on the operation temperature and partial pressures of reactants. These reactions occur on the catalyst surface and form solid carbon. On the other hand, under the high temperature operation condition, metal catalyst tends to deactivate due to the sintering [9] or the reaction between metal and support forming inactive species. Thus, a thermal stable catalyst that can resist degradation and carbon deposition is essential.

Although noble metals like Pt, Rh and Ru are more active towards DRM and more

resistant to carbon deposition than transition metals like Ni, Co, Fe[9-11], the high cost limits their applications on the industrial scale. The low cost transition metal Ni attracts much attention because of its high catalytic activity. However, the Ni-based catalyst suffers a severe carbon deposition issue which leads to catalyst deactivation [12]. Highly dispersed Ni particles with small size and strong metal-support interaction are proven effective for the improvement of the catalytic activity, stability and carbon resistance [13-19]. Such kind of catalyst can be obtained from perovskite type Ni-based catalyst precursors, like LaNiO<sub>3</sub>. After reduction, LaNiO<sub>3</sub> completely decomposes to Ni and La<sub>2</sub>O<sub>3</sub>, where small Ni particles (~2-50 nm) are well dispersed on  $La_2O_3$  support with a strong metal-support interaction [20-22]. Moreover, the reaction  $La_2O_3+CO_2 \rightarrow La_2O_2CO_3$  increases the activity of the lattice oxygen which is beneficial for the removal of carbon species adsorbed on Ni surface [23]. It is also reported that La<sub>2</sub>NiO<sub>4</sub>, as another type of perovskite (A<sub>2</sub>BO<sub>4</sub>), is more favored than LaNiO<sub>3</sub> as a DRM catalyst precursor because smaller Ni particles with the stronger Ni-La<sub>2</sub>O<sub>3</sub> interaction are accessible [24-26]. However, the Ni-La<sub>2</sub>O<sub>3</sub> interaction is still not strong enough to restrict Ni particles from sintering which leads to a carbon deposition during a long term operation of DRM [24].

The perovskite structure can be stabilized by B-site partial substitution under DRM reaction conditions, which is able to enhance the metal-support interaction [27-30]. According to recent investigations regarding self-regeneration of perovskite based catalyst, the sintering and agglomeration of metals are effectively inhibited because metal particles can evolve reversibly between the surface and the inside of perovskite in redox process [31-33]. Provendier et al. also reported that a LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> perovskite structure favors the metal-support interaction and effectively suppresses carbon deposition [34]. Arandiyan et al. studied the influences of Fe content in

LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> catalyst precursors on the catalytic performance of the steam reforming, and concludes that catalysts with high activity and stability can be achieved when x is between 0.4 to 0.6 [35].

In the present work, Ni-based perovskite precursors with the nominal compositions of La<sub>2</sub>NiO<sub>4</sub>, LaNiO<sub>3</sub>, La<sub>2</sub>Ni<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>4</sub> and LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> were prepared by a wet impregnation method. The samples were characterized before and after the DRM tests. Influences of Fe partial substitution in the La<sub>2</sub>NiO<sub>4</sub>/LaNiO<sub>3</sub> perovskite catalyst precursor on the DRM reactions and carbon deposition are discussed.

#### 2. Experimental

#### 2.1 Catalysts preparation

La<sub>2</sub>NiO<sub>4</sub> and LaNiO<sub>3</sub> catalyst precursors were prepared by wet impregnation method. Nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>• 6H<sub>2</sub>O) was dissolved in distilled water and stirred for 10 min. La<sub>2</sub>O<sub>3</sub> powder was added into the Ni(NO<sub>3</sub>)<sub>2</sub> solution under continues stirring for 30 min. Then the slurry was heated at 80 °C to vaporize the aqueous water. Finally the mixtures were ground and calcined at 800 °C for 4 h to obtain the catalyst precursors. The Fe partially substituted La<sub>2</sub>Ni<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>4</sub> and LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> precursors were prepared by the same method, except Fe(NO<sub>3</sub>)<sub>3</sub> was first mixed with Ni(NO<sub>3</sub>)<sub>2</sub> in the solution. For the convenience of discussions, the La<sub>2</sub>NiO<sub>4</sub>, LaNiO<sub>3</sub>, La<sub>2</sub>Ni<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>4</sub> and LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> catalyst precursors are denoted as L2N, LN, L2NF and LNF respectively in the following contents.

#### 2.2 Characterization of catalysts

X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer (TTR III, Rigaku Co., Japan) with a Cu target K $\alpha$ -ray ( $\lambda$ =1.5406 Å) as the X-ray source in the range of  $2\theta = 20 - 80^{\circ}$ . The microstructures of samples were obtained using scanning electron microscopy (SEM, JSM-6301F, Hitach, Japan) and transmission electron microscopy (TEM, JEM-2011, JEOL, Japan).

X-ray photoelectron spectroscopy (XPS) was performed using an electron spectrometer (ESCALAB 250, Thermo-VG Scientific, U.S.) with a monochromatized Al K X-ray source (1486.6 eV photons) at a pass energy of 30 eV. All binding energies were referenced to the C 1s peak at 284.8 eV.

Temperature programmed reduction (TPR) experiments were performed by a thermal conductivity detector (TCD) with a temperature programmed heating furnace. 100 mg catalyst precursor was set in a quartz tube of 6 mm inner diameter and heated from room temperature to 900 °C at a heating rate of 5 °C/min. A forming gas of 5.0 vol%  $H_2/N_2$  was introduced into the tube during the TPR test.

The carbon depositions of used samples were determined by thermogravimetric analysis (TGA) which was carried out with a simultaneous thermal analyzer (STA 449 F3, NETZSCH, Germany). 10-15 mg used sample was placed in an alumina crucible and heated from room temperature to 800 °C at a heating rate of 10 °C/min in N<sub>2</sub> at a flow rate of 10 ml/min to minimize the influence of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, and then held at 800 °C for 2 h in air at a flow rate of 60 ml/min to evaluate the amount of deposited carbon.

#### 2.3 Catalytic activity test

300 mg sample was placed in a fixed bed continuous flow quartz reactor (i.d. = 6 mm) at atmospheric pressure. The sample was reduced at 700 °C in H<sub>2</sub> with a flow

rate of 30 ml/min for 2 h before the test. Then the reactor was heated to 750 °C and an equimolecular  $CO_2/CH_4$  mixture at a flow rate of 60 ml/min (GHSV=1.2×10<sup>4</sup> mL g<sup>-1</sup> h<sup>-1</sup>) was introduced into the reactor. The reaction products were analyzed by a gas chromatography (GC9790, FULI, China). The conversions of CH<sub>4</sub> and CO<sub>2</sub> are defined as:

$$X_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100\%$$
$$X_{CO_2} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100\%$$

Where  $[CH_4]_{in}$  and  $[CO_2]_{in}$  refer to the flow rates of introduced CH<sub>4</sub> and CO<sub>2</sub>, while  $[CH_4]_{out}$  and  $[CO_2]_{out}$  refer to the flow rates of CH<sub>4</sub> and CO<sub>2</sub> in the tail gas.

#### 3. Results and discussion

#### 3.1 XRD analysis

Figure 1 (A) shows the XRD patterns of all the catalyst precursors. In the L2N and LN samples without Fe partial substitution, mainly La<sub>2</sub>NiO<sub>4</sub> (marked as P'), LaNiO<sub>3</sub> (marked as P), and La(OH)<sub>3</sub> (marked as "•") phases are observed. The appearance of La(OH)<sub>3</sub> is related to the hydration of La<sub>2</sub>O<sub>3</sub> in air [36]. In addition, a small amount of NiO (marked as N) is observed in LN. In the Fe partially substituted L2NF and LNF samples, ABO<sub>3</sub> type LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> perovskite, La(OH)<sub>3</sub> and NiO phases are identified, while no A<sub>2</sub>BO<sub>4</sub> type perovskite phase is evidenced. The compositions of samples are listed in Table 1. These results indicate that our catalyst precursors are multiphase composites. Considering the samples were prepared by a simple wet impregnation method with a moderate calcining temperature of 800 °C, the formation of multiphase composites is attributed to the incomplete reaction between the source materials.

Figure 1 (B) shows the XRD patterns of the catalysts after used for DRM tests. By operating under the DRM condition at 750 °C for 4 hours, the perovskite structures in both L2N and LN are completely decomposed that only Ni (Marked as Ni) and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (marked as •) are identified. The formation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is because of the reaction between La<sub>2</sub>O<sub>3</sub> and CO<sub>2</sub> [23]. For the used L2NF and LNF, an ABO<sub>3</sub> type LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> perovskite phase (marked as P) is identified in addition to Ni and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phases, indicating the Fe<sup>3+</sup> in LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> stabilizes the perovskite structure in reducing atmosphere. Although Ni is observed in all the four samples, a close examination on the diffraction peak of Ni (111) reveals that the peak shifts to lower angle after Fe partial substitution (Figure 1(C)), which is attributed to the formation of a Ni-Fe alloy phase. The peak shift in LNF is larger than that in L2NF, demonstrating the Ni-Fe alloy in LNF possesses a higher Fe/Ni ratio [37].

Since the perovskite phase plays an important role during DRM test, the composition of the LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> phase is estimated by a close examination of the perovskite diffraction peak at around 32.8° in Figure 1 (A) and (B). Figure 1 (D) shows the 2 $\theta$  versus x values of the LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> phase. The data points marked by crosses (+) are abstracted from the standard ISCD patterns of the LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> phase (PDF-66-0633 to PDF-66-0641). The x values for our samples are obtained by fitting the 2 $\theta$  data abstracted from Figure 1(A) and (B) into the standard 2 $\theta$  - x curve (dash line in Figure 1(D)), and the results are listed in Table 2. Notice that although Fe<sup>3+</sup> stabilizes the perovskite structure of L2NF and LNF, the x values of LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> is still reducible. These Ni atoms are known to migrate to the surface of the perovskite and aggregated as small Ni particles [38]. In the fresh L2NF and LNF samples, the x

values are almost the same; but in the used samples the x value in L2NF is much smaller. This suggests that the stability of Ni in LNF is higher than that in L2NF.

#### 3.2 TPR tests

Figure 2 shows the H<sub>2</sub> consumption of DRM catalyst precursors as a function of the reduction temperature. Two H<sub>2</sub> consumption peaks locate at around 420 and 550 °C are observed in L2N and LN. Considering that both LaNiO<sub>3</sub> and La<sub>2</sub>NiO<sub>4</sub> are identified by XRD patterns in these two samples, the peak at low temperature is assigned to the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup> of LaNiO<sub>3</sub> (LaNiO<sub>3</sub>→La<sub>2</sub>Ni<sub>2</sub>O<sub>5</sub>) and a small amount of extra NiO, while the peak at high temperature is related to the reduction of Ni<sup>2+</sup> to Ni<sup>0</sup> of La<sub>2</sub>NiO<sub>4</sub> or La<sub>2</sub>Ni<sub>2</sub>O<sub>5</sub> [23] [39]. Notice that the high temperature peak is dominant in L2N, indicating the main perovskite phase is La<sub>2</sub>NiO<sub>4</sub>. However in LN, the low temperature peaks is close to the theoretic value of 2:1 for LaNiO<sub>3</sub>, suggesting LaNiO<sub>3</sub> is predominant. The reducibility of L2N and LN is in agreement with the XRD analysis that no perovskite phase remains after the DRM test at 750 °C.

The TPR curves of L2NF and LNF show three peaks. The low temperature peak (~380 °C, in both samples) comes from the reduction of extra NiO, the middle temperature peak (~ 420 °C in L2NF and ~480 °C in LNF) refers to the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup> in LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub>, and the high temperature peak (~ 680 °C in L2NF and ~700 °C in LNF) corresponds to the reduction of Ni<sup>2+</sup> and a small amount of Fe<sup>3+</sup> in the perovskite [35]. Compared to L2N and LN, the reduction peaks belonging to Ni<sup>3+</sup> and Ni<sup>2+</sup> all shift to higher temperatures in L2NF and LNF, which suggests the stability of the perovskite is improved by Fe partial substitution. The even higher reduction temperatures of the Ni<sup>3+</sup> and Ni<sup>2+</sup> in LNF indicate the perovskite in LNF is

more stable than that in L2NF, which is in consist with the XRD analysis (see Table 2). Considering the x values of LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> in L2NF and LNF are quite close, the different stability of these Fe partially substituted samples is related to the extra La species in the multiphase precursors. Based on the XRD and TPR analyses, the stability of the perovskite in these four samples should be in the order of: LNF > L2NF > L2N ≈ LN.

#### 3.3 XPS analysis

To better understand the role of Fe<sup>3+</sup> in the perovskite, we performed an XPS analysis for the LN and LNF precursors. The samples were pretreated in the XPS setup by heating at 700 °C for 1 h in vacuum to minimize the influences from the adsorbed species, such as water and CO<sub>2</sub>. The XPS profiles of O 1s are shown in Figure 3. Both the samples show two peaks. The low binding energy peak at around 528.0-529.0 eV is assigned to lattice oxygen (O<sup>2-</sup>, O<sub>β</sub>) in the perovskite, and the high binding energy one to adsorbed oxygen species (O<sub>α</sub>) [40-43]. The peaks of O<sub>α</sub> remain almost the same in the two samples, but after Fe partial substitution, the O<sub>β</sub> peak shifts to higher binding energy. Sutthiumporn et al. reported that the binding energy of O<sup>2-</sup> in La<sub>0.8</sub>Sr<sub>0.2</sub>NiO<sub>3</sub> shifts to a higher value by Fe partial substitution and the authors attributed it to the presence of Fe promoting the charge transfer from O atom to Ni [27]. This increase of the binding energy of O<sup>2-</sup> improves the stability of LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> in the reducing atmosphere.

#### 3.4 Catalytic activity for the DRM reaction

Figure 4 (A) and (B) shows the CH<sub>4</sub> and CO<sub>2</sub> conversions as a function of reaction time during DRM test of all the reduced catalyst precursors. L2N and LN exhibit high

CH<sub>4</sub> conversions (~92% for both samples) but relative low CO<sub>2</sub> conversions (~ 80% for L2N and ~83% for LN). On the other hand, lower CH<sub>4</sub> and CO<sub>2</sub> conversions are observed for the Fe partially substituted L2NF and LNF at the beginning, but they increase gradually with the reaction time. For L2NF, both the CH<sub>4</sub> and CO<sub>2</sub> conversions reach ~85% after 6 h test and close to those for L2N and LN.

It is known that the CH<sub>4</sub> conversion directly depends on the amount of active Ni in the catalyst. As discussed above that the reducibility of Ni<sup>2+</sup> to Ni<sup>0</sup> in the four samples is L2N≈LN>L2NF>LNF, thus the amount of Ni after the initial H<sub>2</sub> reduction should be in the same sequence, resulting in the difference of CH<sub>4</sub> conversion at the beginning. During the DRM test, the slow rise of CH<sub>4</sub> conversions over L2NF and LNF are due to the incomplete reduction of the perovskite after the initial H<sub>2</sub> reduction. More Ni will be reduced out as the reaction proceeds. Thus, the CH<sub>4</sub> conversions over L2NF and LNF increase. The CO<sub>2</sub> conversions show the same changing trend with CH<sub>4</sub> conversions.

Figure 4 (C) shows the H<sub>2</sub>/CO ratio in the tail gas during the DRM reaction. It is known that the value of H<sub>2</sub>/CO ratio equals to 1 theoretically (Eq. (1)) but the side reactions have great influence on its actual value (Eq. (2)-(4)). The values of H<sub>2</sub>/CO ratio for L2N and LN are above 1. This, together with the fact that the CH<sub>4</sub> conversions are higher than the CO<sub>2</sub> conversions, suggests that the CH<sub>4</sub> decomposition reaction (Eq. (3)) and the Boudouard reaction (Eq. (4)) predominates the side reactions of L2N and LN. On the contrast, the H<sub>2</sub>/CO ratio for LNF is smaller than 1 and the CH<sub>4</sub> conversion is lower than the CO<sub>2</sub> conversion, suggesting the RWGS reaction (Eq. (2)) is predominant in the side reactions. The H<sub>2</sub>/CO ratio for L2NF is below 1 at the beginning but keeps rising to above 1 after 3 h, while its CH<sub>4</sub> conversion becomes higher than the CO<sub>2</sub> conversion after 5 h, which indicates that the

main side reaction switches from the RWGS to the CH<sub>4</sub> decomposition and Boudouard reaction with the extended reaction time.

#### 3.5 Carbon deposition analysis

Fig. 5 shows the carbon formation over used catalysts measured by TG tests. Carbon forms in all the samples. Although L2N and LN possess similar  $CH_4$  and  $CO_2$  conversions, LN suffers a much more severe carbon deposition. The carbon formations of L2NF and LNF after 4 h tests are smaller than those of L2N and LN, indicating the carbon resistance is improved by the Fe partial substitution of perovskites. As the reaction time extends to 8 h, much more carbon forms in L2NF while the carbon formation in LNF is almost the same with the 4 h test result. This indicates LNF possesses the best carbon resistance, which is in good agreement with the discussions in the last section.

Figure 6 shows the SEM images of used samples. After 4 h test, fiber carbon is observed in L2N and LN, but hardly seen in L2NF and LNF. However after 8 h test, fiber carbon is evidenced in L2NF but still not in LNF. The amount of fiber carbon observed in the SEM images is consistent with the TG analysis (see Figure 5).

A probable impact to the carbon resistance is the formation of the LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> perovskite in L2NF and LNF. In order to better understand the effect of perovskite on the carbon resistance, we further performed TEM examinations of used catalysts as shown in Figure 7. The distribution of Ni particles is determined by scaling the lateral size of Ni particles (~150 particles are investigated for each sample) from the TEM images and the results are shown as the insets of Figure 7. For the 4 h used L2N and LN samples, two distinct regions can be found: (1) agglomerated Ni particles accompanied with fiber carbon (Figure 7 (A)), and (2) Ni particles distributing on the

support surface without fiber carbon. On the other hand, for the 4 h used L2NF and LNF samples, Ni particles are well dispersed on the support surface, and no fiber carbon is observed (Figure 7 (A)). The sizes of Ni particles spread from ~5-100 nm in L2N and LN, but ~ 5-50 nm in L2NF and LNF.

After 8 h test, a large amount of fiber carbon appears in L2NF, even though regions without fiber carbon coverage (Figure 7 (B)) still exist. Meanwhile, the distribution of Ni particles in L2NF spreads to bigger sizes as compared with that in the 4 h tested one. By contrast, the morphology and the size distribution of Ni particles in LNF (Figure 7 (B)) remain almost the same as those in the 4 h tested one. The fiber carbon is barely seen in LNF within the scope of the testing.

According to our discussions on TPR and XRD results, the stability of the perovskite structure is improved by the Fe partial substitution, and the stability of LNF is higher than that of L2NF. It turns out that the changing trend of the carbon resistance of these samples is the same as that of the stability. Thus the TEM observations suggest that the interaction between Ni and the perovskite can effectively suppress the sintering and agglomeration of Ni particles, and enhances the carbon resistance of catalysts for DRM.

#### 4. Conclusions

Ni-based perovskite precursors with the nominal compositions of  $La_2NiO_4$  and  $LaNiO_3$ , as well as their Fe partially substituted counterparts ( $La_2Ni_{0.5}Fe_{0.5}O_4$  and  $LaNi_{0.5}Fe_{0.5}O_3$ ), were prepared by a wet impregnation method. The main phase in L2N is  $La_2NiO_4$  while in LN is  $LaNiO_3$ . These perovskite structures are unstable and completely reduced during the DRM test, forming catalysts of Ni as the active

component and La<sub>2</sub>O<sub>3</sub> as the support.

The stability of the perovskite structure is significantly enhanced by the partial substitution of Fe. Improved carbon resistance are observed in the Fe partial substituted catalysts, which is attributed to the smaller particle size and better dispersion of Ni resulted from the stronger metal-support interaction. The LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> perovskite plays an important role in the structural stability of mixed perovskite catalysts in reducing atmosphere and the enhancement of metal-support interaction. Our results indicate that the LaNi<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> precursor synthesized by wet impregnation method is feasible to obtain stable Ni-based catalysts with high carbon resistance for DRM.

Acknowledgement: This work is supported by the National Natural Science Foundation of China (Grant No.: 21427804)

#### References

[1] Y. Vafaeian, M. Haghighi, S. Aghamohammadi, Energ Convers Manage, 76 (2013) 1093-1103.

[2] J.H. Bitter, K. Seshan, J.A. Lercher, Top Catal, 10 (2000) 295-305.

[3] J. Galuszka, R.N. Pandey, S. Ahmed, Catal Today, 46 (1998) 83-89.

[4] T. Wurzel, S. Malcus, L. Mleczko, Chem Eng Sci, 55 (2000) 3955-3966.

[5] S.T. Oyama, P. Hacarlioglu, Y.F. Gu, D. Lee, International Journal Of Hydrogen Energy, 37 (2012) 10444-10450.

[6] V.Y. Bychkov, Y.P. Tyulenin, A.A. Firsova, E.A. Shafranovsky, A.Y. Gorenberg, V.N. Korchak, Applied Catalysis A: General, 453 (2013) 71-79.

[7] J.G. Zhang, H. Wang, A.K. Dalai, J Catal, 249 (2007) 300-310.

[8] D.S. Jose-Alonso, M.J. Illan-Gomez, M.C. Roman-Martinez, International Journal Of Hydrogen Energy, 38 (2013) 2230-2239.

[9] Z.Y. Hou, P. Chen, H.L. Fang, X.M. Zheng, T. Yashima, International Journal Of Hydrogen Energy, 31 (2006) 555-561.

[10] J. Kehres, J.G. Jakobsen, J.W. Andreasen, J.B. Wagner, H.H. Liu, A. Molenbroek, J. Sehested, I. Chorkendorff, T. Vegge, J Phys Chem C, 116 (2012) 21407-21415.

[11] A.I. Tsyganok, M. Inaba, T. Tsunoda, S. Hamakawa, K. Suzuki, T. Hayakawa, Catal Commun, 4 (2003) 493-498.

[12] J.R. Rostrupnielsen, J.H.B. Hansen, J Catal, 144 (1993) 38-49.

[13] H. Arbag, S. Yasyerli, N. Yasyerli, T. Dogu, G. Dogu, Top Catal, 56 (2013) 1695-1707.

[14] J. Huang, R.X. Ma, T. Huang, A.R. Zhang, W. Huang, J Nat Gas Chem, 20 (2011) 465-470.

[15] P. Frontera, A. Macario, A. Aloise, P.L. Antonucci, G. Giordano, J.B. Nagy, Catal Today, 218 (2013) 18-29.

[16] R. Zanganeh, M. Rezaei, A. Zamaniyan, H.R. Bozorgzadeh, J Ind Eng Chem, 19 (2013) 234-239.

[17] H.G. Zhang, H. Wang, A.K. Dalai, Appl Catal a-Gen, 339 (2008) 121-129.

[18] S.M. Sajjadi, M. Haghighi, F. Rahmani, J Sol-Gel Sci Techn, 70 (2014) 111-124.

[19] Y.G. Chen, J. Ren, Catal Lett, 29 (1994) 39-48.

[20] S.M. de Lima, A.M. da Silva, L.O.O. da Costa, J.M. Assaf, G. Jacobs, B.H. Davis, L.V. Mattos, F.B. Noronha, Applied Catalysis A: General, 377 (2010) 181-190.

[21] R. Pereñíguez, V.M. González-DelaCruz, J.P. Holgado, A. Caballero, Applied Catalysis B: Environmental, 93 (2010) 346-353.

[22] Z.L. Zhang, X.E. Verykios, Catal Lett, 38 (1996) 175-179.

[23] G. Valderrama, A. Kiennemann, M.R. Goldwasser, Catal Today, 133 (2008) 142-148.

[24] G.S. Gallego, F. Mondragón, J. Barrault, J.-M. Tatibouët, C. Batiot-Dupeyrat, Applied Catalysis A: General, 311 (2006) 164-171.

[25] G. Sierra Gallego, F. Mondragón, J.-M. Tatibouët, J. Barrault, C. Batiot-Dupeyrat, Catal Today, 133-135 (2008) 200-209.

[26] C.L. Guo, J.L. Zhang, X.L. Zhang, React Kinet Catal L, 95 (2008) 89-97.

[27] K. Sutthiumporn, T. Maneerung, Y. Kathiraser, S. Kawi, International Journal Of Hydrogen Energy, 37 (2012) 11195-11207.

[28] A. Jahangiri, H. Aghabozorg, H. Pahlauanzadeh, International Journal Of Hydrogen Energy, 38 (2013) 10407-10416.

[29] G.R. Moradi, M. Rahmanzadeh, F. Khosravian, J Co2 Util, 6 (2014) 7-11.

[30] M.A. Pena, J.L.G. Fierro, Chem Rev, 101 (2001) 1981-2017.

[31] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, Nature, 418 (2002) 164-167.

[32] I. Hamada, A. Uozumi, Y. Morikawa, A. Yanase, H. Katayama-Yoshida, J Am Chem Soc, 133 (2011) 18506-18509.

[33] S. Yanagisawa, A. Uozumi, I. Hamada, Y. Morikawa, J Phys Chem C, 117 (2013) 1278-1286.

[34] He'le`ne Provendier, Corinne Petit, A. Kiennemann, Chimie : Chemistry, 4 (2000) 57–66.

[35] H. Arandiyan, J.H. Li, L. Ma, S.M. Hashemnejad, M.Z. Mirzaei, J.H. Chen, H.Z. Chang, C.X. Liu, C.Z. Wang, L. Chen, J Ind Eng Chem, 18 (2012) 2103-2114.

[36] E. Ruckenstein, Y.H. Hu, J Catal, 161 (1996) 55-61.

[37] L. Wang, D.L. Li, M. Koike, S. Koso, Y. Nakagawa, Y. Xu, K. Tomishige, Appl Catal a-Gen, 392 (2011) 248-255.

[38] J. Deng, M.D. Cai, W.J. Sun, X.M. Liao, W. Chu, X.S. Zhao, Chemsuschem, 6 (2013) 2061-2065.

[39] G.S. Gallego, F. Mondragon, J.M. Tatibouet, J. Barrault, C. Batiot-Dupeyrat, Catal Today, 133 (2008) 200-209.

[40] R.Q. Tan, Y.F. Zhu, Appl Catal B-Environ, 58 (2005) 61-68.

[41] L.G. Tejuca, J.L.G. Fierro, J.M.D. Tascon, Adv Catal, 36 (1989) 237-328.

[42] S. Kaliaguine, A.V. Neste, V. Szabo, J.E. Gallot, M. Bassir, R. Muzychuk, Applied Catalysis A: General,
345–358.

[43] J.N. Kuhn, U.S. Ozkan, J Catal, 253 (2008) 200-211.

#### **Figure captions**

**Figure 1.** XRD patterns of (A) fresh catalyst precursors, (B) used catalysts for DRM test at 750 °C (P/P'-perovskite, N-NiO,  $\bullet$ -La(OH)<sub>3</sub> and  $\bullet$ -La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>), (C) magnified diffraction peaks of Ni (111) and (D) the 2 $\theta$ -x curve of the diffraction peak of LaNi<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> at ~32.8°.



Figure 2. H<sub>2</sub>-TPR profiles of L2N, LN, L2NF and LNF catalyst precursors.



Figure 3. XPS profiles of O 1s of LN and LNF catalyst precursors.



Figure 4. Catalytic performance for DRM reaction over reduced L2N, LN, L2NF, and LNF catalyst precursors at 750  $^{\circ}$ C: (A) CH<sub>4</sub> conversion, (B) CO<sub>2</sub> conversion and (C) H<sub>2</sub>/CO ratio.



**Figure 5.** Carbon formation over used L2N, LN, L2NF and LNF after 4 h and 8 h DRM reaction.



Figure 6. SEM images of used L2N, LN, L2NF and LNF after 4 h and 8 h DRM reaction.



**Figure 7.** TEM images of (A) used L2N, LN, L2NF and LNF after 4 h DRM reaction, and (B) L2NF and LNF after 8 h DRM reaction. The insets are the Ni particle size distributions of the corresponding samples.



#### Tables

Samples	L2N	LN	L2NF	LNF
Nominal	La <sub>2</sub> NiO <sub>4</sub>	LaNiO <sub>3</sub>	La <sub>2</sub> (Ni <sub>0.5</sub> Fe <sub>0.5</sub> )O <sub>4</sub>	LaNi <sub>0.5</sub> Fe <sub>0.5</sub> O <sub>3</sub>
composition				
Actual	LaNiO <sub>3</sub>	LaNiO <sub>3</sub>	LaNi <sub>x</sub> Fe <sub>1-x</sub> O <sub>3</sub>	LaNi <sub>x</sub> Fe <sub>1-x</sub> O <sub>3</sub>
composition	La <sub>2</sub> NiO <sub>4</sub>	La <sub>2</sub> NiO <sub>4</sub>		
(fresh)	La(OH) <sub>3</sub>	La(OH) <sub>3</sub>	La(OH) <sub>3</sub>	La(OH) <sub>3</sub>
		NiO	NiO	NiO
Actual	Ni	Ni	Ni	Ni
composition			LaNi <sub>x</sub> Fe <sub>1-x</sub> O <sub>3</sub>	LaNi <sub>x</sub> Fe <sub>1-x</sub> O <sub>3</sub>
(used)	La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	$La_2O_2CO_3$	$La_2O_2CO_3$	$La_2O_2CO_3$

Table 1. The composition of samples.

Note 1: the nominal composition is a theoretical stoichiometric composition based on

the initial molar ratio of the source materials.

Note 2: the actual composition is obtained from XRD analysis.

Table 2. The x value in the  $LaNi_xFe_{1-x}O_3$  perovskite of fresh and used samples determined from Figure 1 (D).

Samples	x (fresh)	x (4 h used)	x (8 h used)
L2NF	0.60	0.19	0.14
LNF	0.59	0.29	0.18