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Short communication

# Promoting effects of lanthanum oxide on the NiO/CeO<sub>2</sub> catalyst for hydrogen production by autothermal reforming of ethanol



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# ABSTRACT

Promoting effects of Lanthanum oxide on the NiO/CeO<sub>2</sub> catalyst for hydrogen production by autothermal reforming of ethanol were investigated. The effects of La increased the specific surface area, stabilized the NiO phase and led to the high dispersion of Ni in active LaNiO<sub>3</sub> phase. The carrier CeO<sub>2</sub> provided big specific surface area for effective EATR reaction, promoted the H<sub>2</sub> production by accelerating the oxygen migration in the catalyst surface via the Ce<sup>4+</sup>  $\leftrightarrow$  Ce<sup>3+</sup> transformation. Consequently, the optimized Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst achieved 100% X<sub>EtOH</sub>, 69.3% S<sub>H2</sub> at 600 °C and high stability at 550 °C.

## 1. Introduction

Energy shortage and environment pollution are accelerating the evolutions of clean, high efficient and renewable energies [1]. Hydrogen energy is one of the most promising sustainable energies [2,3]. Particularly, the increasing application of fuel cells [4] requires highly-efficient and -convenient supply of H<sub>2</sub>. Catalytic reforming of organic compounds for H<sub>2</sub> production has attracted increasing attention [5,6], and the approach of autothermal reforming (ATR as abbreviation) [7] is becoming popular because it combines the advantages of steam reforming (SR) [8] and partical oxidation (PO) [9]. Therefore, developing the ATR technology is necessary for advancing the hydrogen economy.

Ethanol (EtOH) is a potential hydrogen source because of its advantages such as feasible thermodynamic decomposition, cheap, renewable, transportable and low toxicity [10,11]. Eq. (1) displays the chemical equation for ATR of EtOH (EATR). Approximate ATR process can be achieved by adjusting the molar ratio of reactants. When the value of  $\delta$  is set as 0.5, 5 mol H<sub>2</sub> could be produced from 1 mol EtOH, and  $\Delta H$  equals to - 68.06 kJ/mol. Thus, the reaction requires no extra energy from the external environment.

$$C_2H_5OH + (3 - 2\delta)H_2O + \delta O_2 \rightarrow 2CO_2 + (6 - 2\delta)H_2 \qquad \Delta H \approx 0 \frac{kJ}{mol}$$
(1)

The reforming catalyst is one of the key factors of ATR. The noble

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metal (such as Rh [12], Ru [13] and Pt [8]) catalysts are highly active and exhibit prominent anti-coke ability during reforming reactions. However, high cost of noble-metal materials inhibits their application. Herein, non-noble metals (such as Ni [10,14], Co [15,16], Cu [17]) are becoming more and more popular because of their low cost and satisfying properties. Typically, Ni and NiO possess excellent abilities for C-C, C-H and C-O bonds cleavage, and dehydrogenation [18]. However, Ni-based catalysts can be easily deactivated by coke deposition, which constrains their further application [19]. Thus, it is necessary to design new catalysts to overcome coke deposition. In our previous work, La not only increased the activity of Ni-based catalyst, but prolonged its lifetime [20]. Besides, LaNiO<sub>3</sub>, formed by the interaction between La2O3 and NiO, favored the reactions of dehydrogenation, decomposition of hydrocarbons and water gas shift (WGS) [21], which are essential for ATR reactions. Furthermore, LaNiO<sub>3</sub> promotes the dispersion of Ni, and provides more active sites than the single NiO, which is crucial for an efficient nickel-based catalyst [19]. In addition, ceria is a considerable material for reforming catalysts because of its redox ability, oxygen storage capacity (OSC) [22], and  $Ce^{3+} \leftrightarrow Ce^{4+}$ transformation [23]. CeO<sub>2</sub> can improve the activity of WGS reaction, which is a significant step of ATR [7]. Mudiyanselage et al. [13] investigated reactions of ethanol over CeO2 and Ru/CeO2. The main reactions of ethanol on CeO<sub>2</sub> were re-combinative desorption of ethanol, dehydrogenation to acetaldehyde and dehydration to ethylene. The presence of Ru considerably modified the reaction of ceria towards

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Fig. 1. The catalytic performance of the Ni<sub>a</sub>La<sub>b</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalysts. A. EtOH conversion rate of the catalysts at reaction temperature from 400 to 600 °C. B. H<sub>2</sub> selectivity of the catalysts at reaction temperature from 400 to 600 °C. (H<sub>2</sub>O/EtOH = 3:1, O<sub>2</sub>/EtOH = 0.5:1, GHSV = 20,000 h<sup>-1</sup>).

ethanol, and switched the desorption products to CO, CO<sub>2</sub>,  $CH_4$  and  $H_2$ . Active components were significant in changing selectivities of the catalyst with  $CeO_2$  as its carrier.

In this work, with the aim at enhancing the stability of Ni-based catalyst and improving its H<sub>2</sub> production, we developed a new Ni<sub>a</sub>La<sub>b</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst with La as its co-catalyst and CeO<sub>2</sub> as its carrier. The effects of lanthanum oxide on the Ni<sub>a</sub>La<sub>b</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst were investigated. The experimental section was described in the supplementary materials.

# 2. Results and discussion

#### 2.1. Catalytic performance

The study was started by evaluating the catalytic performance of Ni<sub>a</sub>La<sub>b</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalysts. As shown in Fig. 1, the X<sub>EtOH</sub> was markedly affected by Ni/La/Ce molar ratios. On the one hand, both the X<sub>EtOH</sub> and S<sub>H2</sub> went up with the increasing amount of NiLaO<sub>y</sub>. The Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst achieved the highest performance with 100% X<sub>EtOH</sub>

and 74.8% S<sub>H2</sub> at 550 °C, while X<sub>EtOH</sub> of Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst was slightly lower. The hydrogen in the ethanol and H<sub>2</sub>O was co-converted in molecular H<sub>2</sub>. However, S<sub>H2</sub> of the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst declined from 74.8% to 68.8% when increasing the temperature from 550 to 600 °C. The result indicated that undesired deactivation happened in the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst when the reaction temperature was high. Specially, S<sub>H2</sub> of Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst kept continuous growth at the entire test and reached 69.3% at 600 °C, indicating that Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> was be relatively stable during EATR. Similar tendency was concluded from the results of S<sub>CO2</sub> displayed in Fig. dramatically went up by increasing the concentration of Ni, while the addition of La also promoted the X<sub>EtOH</sub> and S<sub>H2</sub>. In addition, the H<sub>2</sub> yields of catalysts NiO/10CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>/10CeO<sub>2</sub> and Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> shown in Fig. S9 further proved the promoting effect of La. Therefore, La was an effective promoter in the reforming catalyst.

Although the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst exhibited high  $X_{EtOH}$  and S<sub>H2</sub>, the undesired deactivation might make it inapplicable. Herein, it is necessary to measure the stability of Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> and Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalysts.

The stability test was carried at 550 °C for 50 h, and the results were shown in Fig. S2. The Ni<sub>1</sub>La<sub>1</sub>O<sub>v</sub>/10CeO<sub>2</sub> catalyst exhibited high stability over the entire 50 h, whereas  $X_{EtOH}$  of the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst declined from 100% to 86% after the test. In addition, the carbon balance (the calculation method was described in Methods in supplementary materials) of the Ni1La1Ov/10CeO2 and Ni2La2Ov/10CeO2 catalysts at different reaction temperatures were calculated and shown in Table S1. At the temperature lower than 600 °C, the carbon balance of the Ni<sub>2</sub>La<sub>2</sub>O<sub>v</sub>/10CeO<sub>2</sub> catalyst was higher than that of the Ni<sub>1</sub>La<sub>1</sub>O<sub>v</sub>/ 10CeO<sub>2</sub> catalyst. However, the Ni<sub>1</sub>La<sub>1</sub>O<sub>v</sub>/10CeO<sub>2</sub> catalyst obtained the carbon balance of 85% at 600 °C, which was 10.1% higher than that of Ni<sub>2</sub>La<sub>2</sub>O<sub>v</sub>/10CeO<sub>2</sub> catalyst. The high carbon balance made the coke hardly deposited on the surface of the catalyst. The Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst was indeed deactivated during the EATR reaction, and the deactivation might be caused by the excess Ni in the catalyst. Therefore, the Ni<sub>1</sub>La<sub>1</sub>O<sub>v</sub>/10CeO<sub>2</sub> was the optimal catalyst with high activity, selectivity and stability for H<sub>2</sub> production.

The overall performance of the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst was shown in Fig. S3. The Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst exhibited relatively low selectivity towards the products of CO and CH<sub>4</sub>. As mentioned by Rupali R. Davda [24], the products of EATR reaction with very low levels of CO and CH<sub>4</sub> was directly suitable for the application of fuel cells. In addition, H<sub>2</sub> selectivity of the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst tested under different S/C and O/C feed ratios were investigated, and the data and its description were shown in Fig. S7. The result indicated that more H<sub>2</sub>O in reactants provided more hydrogen atoms, while the appropriate amount of oxygen provided the heat for the steam reforming. The highest S<sub>H2</sub> of 73.8% was obtained when S/C = 4, O/C = 0.5. Therefore, the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst was a potential catalyst for producing the fuel-cell-grade hydrogen.

## 2.2. Characterizations

#### 2.2.1. X-ray diffraction

The XRD patterns of the prepared catalysts were shown in Fig. S4. The main characteristic peaks marked by **o** at the2 $\theta$  angles of 28.3, 32.9, 41.2 and 56° were corresponding to the phase of fluorite type CeO<sub>2</sub> (PDF card 65-2975). The peaks marked by **x** with very low intensity at 2 $\theta$  angles of 37.3, 43.3 and 62.9° were corresponding to the phase of NiO. However, the La was undetectable from the XRD patterns. The result indicated that La was highly dispersed in the catalyst. Besides, the three major XRD diffraction peaks of LaNiO<sub>3</sub> phase at 2 $\theta$ angles of 32.9, 47.4 and 58.8° were overlapped by the diffraction peaks of CeO<sub>2</sub> phase, which suggested that LaNiO<sub>3</sub> might be a possible structure formed by La<sub>2</sub>O<sub>3</sub> and NiO. In addition, the 2 $\theta$  angles of CeO<sub>2</sub> phase slightly shifted towards the low angle (shown in Fig. S4-B), which might be caused by the existence of the LaNiO<sub>3</sub> phase, or the

 Table 1

 Textural property of prepared catalysts.

Sample	BET surface area/ $(m^2 g^{-1})$	Average pore diameter/(Å)	Pore volume/ $(cm^3 g^{-1})$
Ni <sub>0.5</sub> La <sub>0.5</sub> O <sub>y</sub> / 10CeO <sub>2</sub>	41	160.5	0.1599
Ni0.5La1Oy/10CeO2	43	139.1	0.1743
Ni1La0.5Oy/10CeO2	33	186.1	0.1129
Ni1La1Oy/10CeO2	47	139.1	0.1688
Ni <sub>2</sub> La <sub>2</sub> O <sub>y</sub> /10CeO <sub>2</sub>	41	139.1	0.1718

incorporation of  $La^{3+}$  (0.11 nm) and Ni<sup>2+</sup> (0.069 nm) into the lattice of CeO<sub>2</sub>[25]. The results of Raman in Fig. S8 also proved the incorporation. Both the interactions of La with NiO and CeO<sub>2</sub> were promotional for H<sub>2</sub> production via EATR [20,21,26]. Therefore, La not only highly dispersed in the catalyst but could promote the H<sub>2</sub> production.

#### 2.2.2. Texture property

The BET surface area, average pore diameter and pore volume of the prepared catalysts were shown in Table 1. All catalysts possessed relatively high specific surface area, which was contributed by the carrier CeO<sub>2</sub>. The surface area of the  $Ni_1La_1O_v/10CeO_2$  catalyst was 47 m<sup>2</sup> g<sup>-1</sup>, which was 6 m<sup>2</sup> g<sup>-1</sup> larger than both  $Ni_{0.5}La_{0.5}O_v/10CeO_2$ and  $Ni_2La_2O_v/10CeO_2$  catalysts. The trend in BET surface area when increasing the NiLaO $_{\rm v}$  loading was parabolic. In addition, the surface area of Ni<sub>0.5</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> was slightly larger than that of Ni<sub>0.5</sub>La<sub>0.5</sub>O<sub>y</sub>/ 10CeO<sub>2</sub>, whereas the surface of surface area of  $Ni_1La_{0.5}O_v/10CeO_2$  was markedly lower than that of Ni<sub>0.5</sub>La<sub>0.5</sub>O<sub>v</sub>/10CeO<sub>2</sub>. The results indicated that the addition of La could increase the specific surface area of the catalyst, whereas the addition of Ni could dramatically decrease the specific surface area. The phenomenon was mainly caused by the ionic radius of Ni and La, where Ni<sup>2+</sup> with small radius of 0.069 nm can easily enter the holes in the catalyst and La3+ with big radius of 0.11 nm can expand the structure of CeO<sub>2</sub>. Therefore, both the effects of La and CeO<sub>2</sub> led to the high specific surface area. Furthermore, the  $Ni_1La_1O_v/10CeO_2$  catalyst possessed the biggest specific surface area (similar to BET areas of  $CeO_2$  and  $Ru/CeO_2[13]$ ), which suggested that big specific surface area might enhance the stability of the catalyst.

# 2.2.3. SEM graphs of the fresh and used catalysts

As discussed above, the deactivation of the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst might be cause by the coke deposition during EATR reaction. To confirm the hypothesis, the micro-morphology of the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst after deactivation was observed by SEM. According to the SEM graph in Fig. 2, its surface was covered with cotton-shaped substances with diameter of 20–100 nm. The morphology of the substances



Fig. 3. H<sub>2</sub>-TPR results of the prepared catalysts.

suggested that the coke deposition contained multiwall carbon nanotubes. Herein, coke deposition caused the deactivation of the Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/ 10CeO<sub>2</sub> catalyst. The micro-morphology of the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst after normal EATR test (Fig. S5-A-2) showed no obvious coke deposition in the surface of the catalyst, which indicating that the catalyst possessed high anti-coke ability during EATR reaction. The high concentration of NiO in catalysts might be the cause of coke deposition, since big NiO particles could be easily deactivated [27]. As shown in Fig. S5, the surface of the fresh Ni<sub>2</sub>La<sub>2</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst had many particles with the size  $\sim 1 \mu m$ , which might be the agglomeration of NiO. Differently, there were rare particles in the surface of the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst. Consequently, an appropriate concentration of NiO in the catalyst could enhance its anti-coke ability.

#### 2.2.4. H<sub>2</sub>-TPR of catalysts

The redox properties of the prepared catalysts were investigated by H<sub>2</sub>-TPR. According to the profiles in Fig. 3, two obvious hydrogen consumption peaks were observed at 200–400 °C. The first peak was corresponding to the reduction of surface NiO, and the second peak was seemingly ascribed to the reduction of surface oxygen in Ce<sup>4+</sup>-O-Ce<sup>4+</sup>[28]. However, the variation of the second peak indicated that the concentration of La in the catalysts dramatically affected the second peak [29]. Herein, the inconspicuous peak at ~430 °C was caused by the reduction of the surface oxygen in Ce<sup>4+</sup>-O-Ce<sup>4+</sup>. Specially, the



Fig. 2. The micro-morphologies of the used  $Ni_1La_1O_y/10CeO_2$  catalyst (left) and the used  $Ni_2La_2O_y/10CeO_2$  catalyst (right).



Fig. 4. The XPS spectra of the fresh and used  $\rm Ni_1La_1O_y/10CeO_2$  catalyst: A, the XPS spectra in Ce 3d region; B, the XPS spectra in Ni 2p and La 3d region.

Ni<sub>0.5</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst exhibited only one H<sub>2</sub> consumption peak at 200–400 °C, which indicated that the small amount of Ni could easily dope and disperse into La<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub>, and formed new structures with relatively high stability. Therefore, the reduction of Ni<sup>2+</sup> became difficult at the low temperature (~250 °C), which leads to the only one H<sub>2</sub> consumption peak at 200–400 °C. In addition, the peak at ~730 °C was ascribed to the reduction of bulk CeO<sub>2</sub>[29]. Therefore, La and CeO<sub>2</sub> made the catalyst possess high OSC and redox property, which were essential for ATR reactions. Furthermore, the addition of La stabilized the NiO by the formation of the LaNiO<sub>3</sub> phase.

# 2.2.5. XPS analysis of the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub>

The surface atomic chemical states of the Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalyst before and after stability test were analyzed by X-ray photoelectron spectroscopy (XPS). The curves were fitted using the software 'XPS PEAK' to obtain characteristic peaks of certain atoms. The XPS spectra in Ce 3d region were displayed in Fig. 4A. The XPS peaks at BE of 902.5 and 883.7 eV were ascribed to Ce<sup>3+</sup>, while other peaks were referred to Ce<sup>4+</sup>[30]. Comparatively, slightly declined of Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) molar ratio from 6.6% and 4.6% after the stability test, which indicated that CeO<sub>2</sub> phase was relatively stable in the reducing atmosphere during the EATR reaction where CO and H<sub>2</sub> generated. Besides, the Raman result in Fig. S8 also proved the high stability of CeO<sub>2</sub> during the ATR reaction [31]. The variation of the Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) value indicated that the Ce<sup>4+</sup>  $\leftrightarrow$  Ce<sup>3+</sup> transformation in the catalyst was active, which could promote the oxygen migration in the surface of the catalyst and further improve the H<sub>2</sub> production via EATR.

Fig. 4B showed the XPS spectra in Ni 2p and La 3d region. The most intense Ni  $2p_{3/2}$  peak of fresh catalyst appeared at BE around 854.7 eV, while Ni  $2p_{1/2}$  peak appeared at 871.9 eV. the two peaks were characteristics of Ni<sup>2+</sup> and Ni<sup>3+</sup> ions in an oxidic environment, respectively [32]. A satellite peak appeared at BE of 863.7 eV was caused by the rise of Ni<sup>3+</sup> ions, which suggested the formation of perovskite-type LaNiO<sub>3</sub>[33] and the existence of Ni<sup>3+</sup>  $\leftrightarrow$  Ni<sup>2+</sup> transformation. The existence of Ni<sup>3+</sup>  $\leftrightarrow$  Ni<sup>2+</sup> transformation revealed that the NiO phase was relatively stable in the catalyst. In La 3d region, the peak of La  $3d_{3/2}$  located at BE of 850.1 eV, while peaks of La  $3d_{5/2}$  located at BE of 838 and 833.1 eV. These peaks were corresponding to La<sup>3+</sup> ions in an oxidic environment [34]. Additionally, the difference of the XPS spectra in O 1s region (Fig. S6) between the fresh and used Ni<sub>1</sub>La<sub>1</sub>O<sub>y</sub>/10CeO<sub>2</sub> catalysts demonstrated the La–O bond was stable in the catalyst [35].

#### 3. Conclusions

The technological evolutions for H<sub>2</sub> production are emergent in our society for solving the global energy and environment problems. With the aim at enhancing the stability of Ni-based reforming catalyst and improving its H<sub>2</sub> production, a series of Ni<sub>a</sub>La<sub>b</sub>O<sub>v</sub>/10CeO<sub>2</sub> catalysts were designed and investigated in this work. The results indicated that the mass amount of Ni<sub>a</sub>La<sub>b</sub>O<sub>v</sub> and the amount of Ni and La in the catalysts markedly affected the catalytic performance. Among the prepared catalysts, the Ni1La1Ov/10CeO2 achieved the optimized performance with 100%  $X_{EtOH},\,69.3\%$   $S_{H2}$  and high stability at 550  $^\circ C.$  The effects of La increased the specific surface area, stabilized the NiO phase and led to the formation of active LaNiO<sub>3</sub> phase by the strong interaction between La and NiO. The carrier CeO<sub>2</sub> provided big specific surface area for effective EATR reaction, promoted the H<sub>2</sub> production by accelerating the oxygen migration in the catalyst surface via the  $Ce^{4+} \leftrightarrow Ce^{3+}$  transformation. Furthermore, the NiO itself in the Ni1La1Ov/10CeO2 catalyst was active and stable, and an appropriate concentration of NiO in the catalyst could enhance its anti-coke ability. This work paves the way towards new reforming catalysts for H<sub>2</sub> production.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2018.01.024.

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