



Short communication

Promoting effects of lanthanum oxide on the NiO/CeO₂ catalyst for hydrogen production by autothermal reforming of ethanolZhiwei Xue^{a,b,c,d}, Yuesong Shen^{a,b,c,*}, Peiwen Li^d, Youchun Pan^{a,b,c}, Junjie Li^a, Zhiliang Feng^a, Yu Zhang^{a,b,c}, Yanwei Zeng^a, Youlin Liu^{a,b,c}, Shemin Zhu^{a,b,c}^a College of Materials Science and Engineering, The University of Arizona, Tucson, AZ 85721-0119, USA^b Jiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites, The University of Arizona, Tucson, AZ 85721-0119, USA^c Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 210009, China^d Department of Aerospace and Mechanical Engineering, The University of Arizona, Tucson, AZ 85721-0119, USA

ARTICLE INFO

Keywords:

Promoting effects

Lanthanum

CeO₂

Hydrogen production

Ni-based catalyst

Autothermal reforming

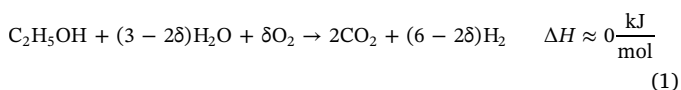
ABSTRACT

Promoting effects of Lanthanum oxide on the NiO/CeO₂ 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 LaNiO₃ phase. The carrier CeO₂ provided big specific surface area for effective EATR reaction, promoted the H₂ production by accelerating the oxygen migration in the catalyst surface via the Ce⁴⁺ ↔ Ce³⁺ transformation. Consequently, the optimized Ni₁La₁O₇/10CeO₂ catalyst achieved 100% X_{EtOH}, 69.3% S_{H₂} 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 H₂. Catalytic reforming of organic compounds for H₂ 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 partial 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 δ is set as 0.5, 5 mol H₂ could be produced from 1 mol EtOH, and ΔH equals to −68.06 kJ/mol. Thus, the reaction requires no extra energy from the external environment.



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

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, LaNiO₃, 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, LaNiO₃ 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 Ce³⁺ ↔ Ce⁴⁺ transformation [23]. CeO₂ can improve the activity of WGS reaction, which is a significant step of ATR [7]. Mudiyansele et al. [13] investigated reactions of ethanol over CeO₂ and Ru/CeO₂. The main reactions of ethanol on CeO₂ were re-combinative desorption of ethanol, dehydrogenation to acetaldehyde and dehydration to ethylene. The presence of Ru considerably modified the reaction of ceria towards

* Corresponding author at: No.5 Xinmofan Road, College of Materials Science and Engineering, Nanjing Tech University, 210009 Nanjing, China.
E-mail address: shenyuesong@njtech.edu.cn (Y. Shen).

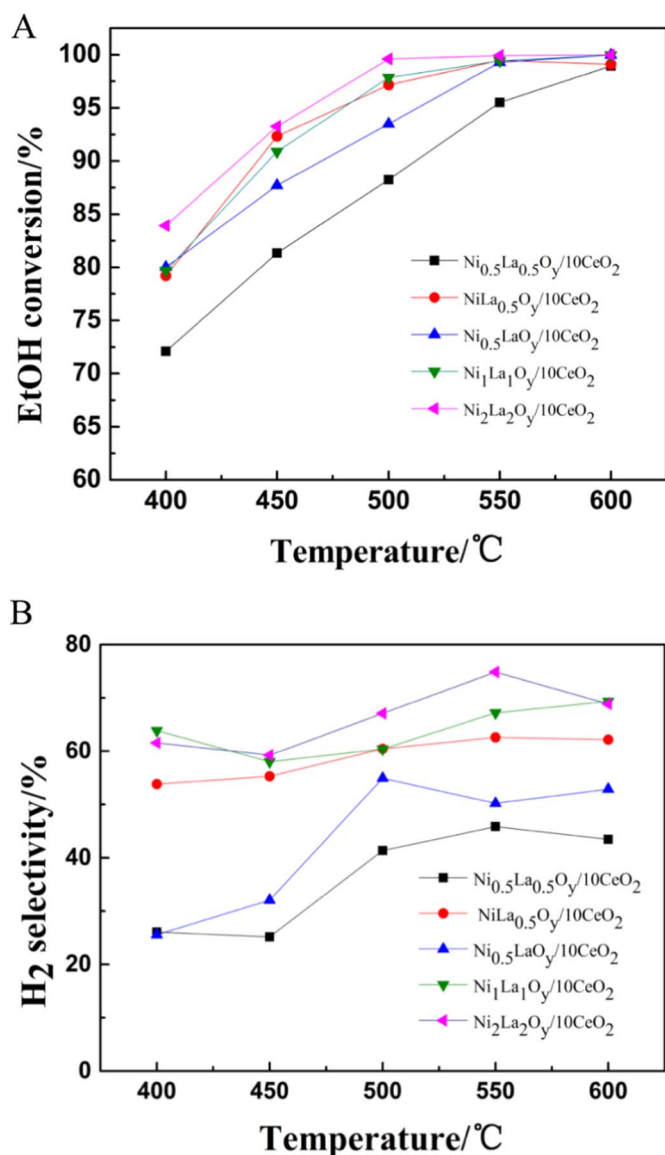


Fig. 1. The catalytic performance of the Ni_aLa_bO_y/10CeO₂ catalysts. A. EtOH conversion rate of the catalysts at reaction temperature from 400 to 600 °C. B. H₂ selectivity of the catalysts at reaction temperature from 400 to 600 °C. (H₂O/EtOH = 3:1, O₂/EtOH = 0.5:1, GHSV = 20,000 h⁻¹).

ethanol, and switched the desorption products to CO, CO₂, CH₄ and H₂. Active components were significant in changing selectivities of the catalyst with CeO₂ as its carrier.

In this work, with the aim at enhancing the stability of Ni-based catalyst and improving its H₂ production, we developed a new Ni_aLa_bO_y/10CeO₂ catalyst with La as its co-catalyst and CeO₂ as its carrier. The effects of lanthanum oxide on the Ni_aLa_bO_y/10CeO₂ 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_aLa_bO_y/10CeO₂ catalysts. As shown in Fig. 1, the X_{EtOH} was markedly affected by Ni/La/Ce molar ratios. On the one hand, both the X_{EtOH} and S_{H₂} went up with the increasing amount of NiLaO_y. The Ni₂La₂O_y/10CeO₂ catalyst achieved the highest performance with 100% X_{EtOH}

and 74.8% S_{H₂} at 550 °C, while X_{EtOH} of Ni₁La₁O_y/10CeO₂ catalyst was slightly lower. The hydrogen in the ethanol and H₂O was co-converted in molecular H₂. However, S_{H₂} of the Ni₂La₂O_y/10CeO₂ 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 Ni₂La₂O_y/10CeO₂ catalyst when the reaction temperature was high. Specially, S_{H₂} of Ni₁La₁O_y/10CeO₂ catalyst kept continuous growth at the entire test and reached 69.3% at 600 °C, indicating that Ni₁La₁O_y/10CeO₂ was be relatively stable during EATR. Similar tendency was concluded from the results of S_{CO₂} displayed in Fig. dramatically went up by increasing the concentration of Ni, while the addition of La also promoted the X_{EtOH} and S_{H₂}. In addition, the H₂ yields of catalysts NiO/10CeO₂, La₂O₃/10CeO₂ and Ni₁La₁O_y/10CeO₂ shown in Fig. S9 further proved the promoting effect of La. Therefore, La was an effective promoter in the reforming catalyst.

Although the Ni₂La₂O_y/10CeO₂ catalyst exhibited high X_{EtOH} and S_{H₂}, the undesired deactivation might make it inapplicable. Herein, it is necessary to measure the stability of Ni₁La₁O_y/10CeO₂ and Ni₂La₂O_y/10CeO₂ catalysts.

The stability test was carried at 550 °C for 50 h, and the results were shown in Fig. S2. The Ni₁La₁O_y/10CeO₂ catalyst exhibited high stability over the entire 50 h, whereas X_{EtOH} of the Ni₂La₂O_y/10CeO₂ 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 Ni₁La₁O_y/10CeO₂ and Ni₂La₂O_y/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 Ni₂La₂O_y/10CeO₂ catalyst was higher than that of the Ni₁La₁O_y/10CeO₂ catalyst. However, the Ni₁La₁O_y/10CeO₂ catalyst obtained the carbon balance of 85% at 600 °C, which was 10.1% higher than that of Ni₂La₂O_y/10CeO₂ catalyst. The high carbon balance made the coke hardly deposited on the surface of the catalyst. The Ni₂La₂O_y/10CeO₂ catalyst was indeed deactivated during the EATR reaction, and the deactivation might be caused by the excess Ni in the catalyst. Therefore, the Ni₁La₁O_y/10CeO₂ was the optimal catalyst with high activity, selectivity and stability for H₂ production.

The overall performance of the Ni₁La₁O_y/10CeO₂ catalyst was shown in Fig. S3. The Ni₁La₁O_y/10CeO₂ catalyst exhibited relatively low selectivity towards the products of CO and CH₄. As mentioned by Rupali R. Davda [24], the products of EATR reaction with very low levels of CO and CH₄ was directly suitable for the application of fuel cells. In addition, H₂ selectivity of the Ni₁La₁O_y/10CeO₂ 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 H₂O in reactants provided more hydrogen atoms, while the appropriate amount of oxygen provided the heat for the steam reforming. The highest S_{H₂} of 73.8% was obtained when S/C = 4, O/C = 0.5. Therefore, the Ni₁La₁O_y/10CeO₂ 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 the 2θ angles of 28.3, 32.9, 41.2 and 56° were corresponding to the phase of fluorite type CeO₂ (PDF card 65-2975). The peaks marked by x with very low intensity at 2θ 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 LaNiO₃ phase at 2θ angles of 32.9, 47.4 and 58.8° were overlapped by the diffraction peaks of CeO₂ phase, which suggested that LaNiO₃ might be a possible structure formed by La₂O₃ and NiO. In addition, the 2θ angles of CeO₂ phase slightly shifted towards the low angle (shown in Fig. S4-B), which might be caused by the existence of the LaNiO₃ phase, or the

Download English Version:

<https://daneshyari.com/en/article/6503056>

Download Persian Version:

<https://daneshyari.com/article/6503056>

[Daneshyari.com](https://daneshyari.com)