

Microwave-assisted LaNiO_3 Perovskite catalyst on Steam Reforming of Ethanol for Hydrogen Production: Effect of Pretreatment Temperature

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Abstract

LaNiO_3 perovskite catalyst was prepared by co-precipitation-oxidation process using microwave-assisted hydrothermal method, followed by calcination in air flow at 600 °C for 2 h. Evaluation of catalytic activity of SRE reaction and selectivity of hydrogen production was carried out in a fixed-bed reactor at temperature between 200 and 400 °C. Catalyst was in-situ activated in hydrogen flow at various temperatures before SRE reaction. Nearly 100 % ethanol conversion with 72.5 % hydrogen selectivity was achieved at 300 °C over the catalyst reduced at 400 °C. Fresh and used catalysts were examined by XRD, TG, TEM, TPR and EA. The well dispersion of Ni particles on the surface was responsible for the high activity of SRE reaction. Based on TGA analysis, the amount of coke was 0.08 % on perovskite catalyst after the SRE reaction. Low coke deposition was mainly due to the formation of $\text{La}_2\text{O}_2\text{CO}_3$ that may act as a carbon reservoir to eliminate the deposited carbon and stabilize the Ni particles on the surface of La_2O_3 .

Keywords: LaNiO_3 , Perovskite, Steam reforming of ethanol, Hydrogen production.

1 Introduction

Perovskite-type oxides, ABO_3 (A cation possesses larger size than B), become an important material in recent years due to their outstanding properties. The magnetic, electrical, optical, and catalytic properties, these materials

find numerous technological uses. These oxides have been widely used in heterogeneous catalysis, such as photocatalysis, electrocatalysis, pollution abatement, chemical sensors, oxidation, hydrogenation and dehydrogenation reaction [1]. Also, perovskite oxides are considered to be good catalysts for fuel cells and metal-air batteries for their special oxygen-reduction activities [2].

Nickel-based catalysts have been used for hydrogenation and dehydrogenation reaction, for the high C-C rupture activity and low cost [3]. Among various supports, Ni dispersed on La_2O_3 exhibits high selectivity, activity, and stability towards SRE reaction for hydrogen production [4]. Recently, the LaNiO_3 perovskite catalyst has been studied in the steam reforming of ethanol (SRE). The advantage is the formation of well distribution Ni on La_2O_3 under H_2 reduction. Sun et al. [5] reported that the Ni/ La_2O_3 catalyst prepared from LaNiO_3 has high activity and selectivity toward hydrogen production and long term stability for steam reforming of ethanol. This attributed to the scavenging of coke on nickel periphery by lanthanum oxycarbonate species ($\text{La}_2\text{O}_2\text{CO}_3$) that developed on the top of Ni particle or at the Ni-La interface under the reaction [6]. The properties of perovskite catalyst are strongly depended on the preparation method which affects its performance. Co-precipitation method produces smaller metallic nickel particles and more active than impregnation and sol-gel methods [7].

As a quick, simple, uniform and energy efficient heating method, microwave irradiation has been considered as a “green” synthesis methodology for inorganic materials [8]. It has been widely applied in

chemical reactions and material synthesis due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rates.

This work focuses on the catalytic performance of LaNiO_3 perovskite, which was prepared through the precipitation-oxidation and assisted with microwave hydrothermal method. By compared with in-situ activation in hydrogen flow at various temperatures, the catalytic activity on the SRE reaction is expected to be approached to low temperature and quite stable against coke deposition.

2 Experimental

2.1 Preparation of catalyst

Lanthanum-nickel composite oxide, LaNiO_x , was prepared via co-precipitation-oxidation and assisted with microwave hydrothermal method. Initially, an aqueous solution of nickel nitrate and lanthanum nitrate was mixed in 1:1 molar ratio then stirred for 1 h after a 30 mL 3.2 M NaOH solution was added. Subsequently, a 30 mL 12% NaOCl solution was added drop-by-drop for oxidization and still stirred for 1 h. The obtained suspension was sealed in an autoclave then was irradiated by 400 W microwave at 130 °C for 4 h. The obtained suspension was then washed and filtered with 2 L DI water, and finally dried at 110 °C overnight.

2.2 Characterization of catalysts

X-ray diffraction (XRD) measurements were performed using a Philips X'Pert diffractometer with $\text{Cu K}_{\alpha 1}$ radiation ($\lambda = 1.5405 \text{ nm}$) at 40 kV and 30 mA. Thermogravimetry analysis (TG) was tested using a Perkin Elmer Pyris 1 TGA in N_2 or O_2 gas ($20 \text{ ml}\cdot\text{min}^{-1}$) at heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to 900 °C. The temperature programmed reduction (TPR) studied the reduction behavior of the fresh and used catalysts. About 50 mg sample was heated in a flowing 10% H_2/N_2 gas ($10 \text{ ml}\cdot\text{min}^{-1}$) with a heating rate of $7 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to 900 °C. Hydrogen consumption was detected through a thermal conductivity detector (TCD). Elemental analysis (EA) was performed using Thermo Flash 2000. Transmission electron microscopy (TEM) was conducted on a HITACHI (H-7100) microscope, and high

resolution transmission electron microscopy (HR-TEM) was performed on a Philips/FEI Tecnai 20 G2 S-Twin Transmission Electron Microscope, both at an accelerated voltage of 200 kV.

2.3 Evaluation of catalysts

The catalytic activities of LaNiO_3 perovskites on the SRE reaction proceeded at atmospheric pressure in a fixed-bed. The feed of the reactants comprised a gaseous mixture of H_2O , ethanol (EtOH), and Ar. The composition of reactants ($\text{H}_2\text{O}/\text{EtOH}/\text{Ar} = 37/3/60 \text{ vol.}\%$) was controlled by the flow of Ar stream ($22 \text{ ml}\cdot\text{min}^{-1}$). The gas hourly space velocity (GHSV) was maintained at $22,000 \text{ h}^{-1}$. Prior to the reaction, the catalyst was activated in-situ by reduction with hydrogen at different temperature about 300, 400, 500 and 600 °C for 2 h (denoted as H3、H4、H5 and H6). The evaluation of the catalytic activity depended on the conversion and products distribution, using the following equations:

$$X_{\text{EtOH}} = (n_{\text{EtOH-in}} - n_{\text{EtOH-out}}) / n_{\text{EtOH-in}} \times 100\% \quad (1)$$

$$S_i = nP_i / n \sum P_i \times 100\% \quad (2)$$

Where X_{EtOH} is the conversion of ethanol, S_i is the distribution of different component in the products, P_i is the different component in the reaction products, and n is the amounts of moles.

3 Results and discussions

The XRD diffraction patterns of the as-prepared and the calcined catalysts were shown in Figure 1. The as-prepared sample [Figure 1a] exhibits XRD patterns with mixed of $\text{La}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ phases. The main diffraction patterns [(100), (110), (101), (201), (211)] matched the JCPDS file 83-2034 of lanthanum hydroxide, $\text{La}(\text{OH})_3$, with a hexagonal structure. In addition, the other weak diffraction patterns [(001), (100), (011), (002)] matched the JCPDS file 74-2075 of nickel hydroxide, $\text{Ni}(\text{OH})_2$, with a hexagonal structure. After 600 °C calcination in O_2 [Figure 1b], both $\text{La}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ phases transformed to LaNiO_3 perovskite [JCPDS 88-0633]. Therefore, the heating treatment of $\text{La}(\text{OH})_3$ phase can be transferred into LaNiO_3 perovskite around 600 °C.

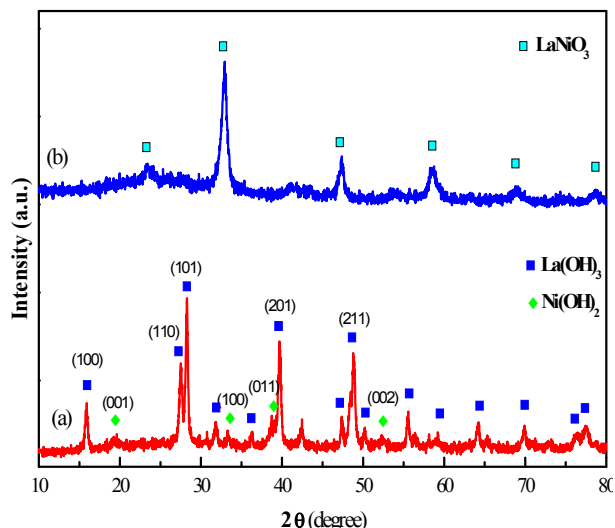


Figure 1: XRD patterns of samples: (a) as-prepared (b) calcined.

The TEM micrographs of the as-prepared and the calcined catalysts were shown in Figure 2. The as-prepared samples [Figure 2a] show the nanorods morphology of $\text{La}(\text{OH})_3$. Apparently, the peripheral dispersed nickel oxide acts as a catalyst to promote the $\text{La}(\text{OH})_3$ formation of nanorods and/or nanotubes under microwave hydrothermal condition. The nanostructures break and transform into cubic shape of LaNiO_3 after calcination at 600 °C [Figure 2b].

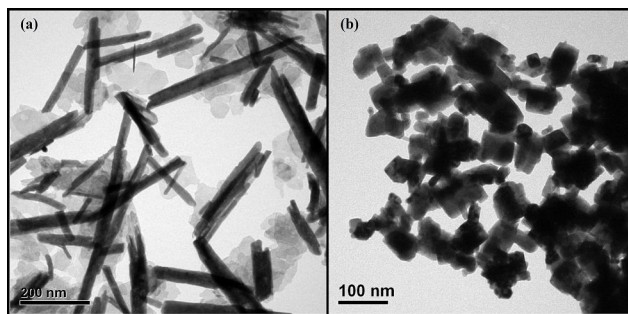


Figure 2: TEM micrographs of samples: (a) as-prepared (b) calcined

The TG/DTG profiles of as-prepared sample in N_2 flow was shown in Figure 3. The weight loss before 250 °C comes from the adsorb water. The TG/DTG profiles show three weight losses (D_1 , D_2 and D_3) at 300, 400 and 750 °C, respectively. The first weight loss (6.2 %) in D_1 comes from the decomposition of $\text{Ni}(\text{OH})_2$, the second weight loss (6.3 %) in D_2 step is related to the transformation of $\text{La}(\text{OH})_3$ into the lanthanum oxide hydroxide (LaOOH), an intermediate phase that can be obtained during the

dehydration of lanthanum hydroxide. Furthermore, the third weight loss (3.1%) in D_3 step should be the transformation of LaOOH into lanthanum oxide through dehydration. These phases transformation are shown as below:

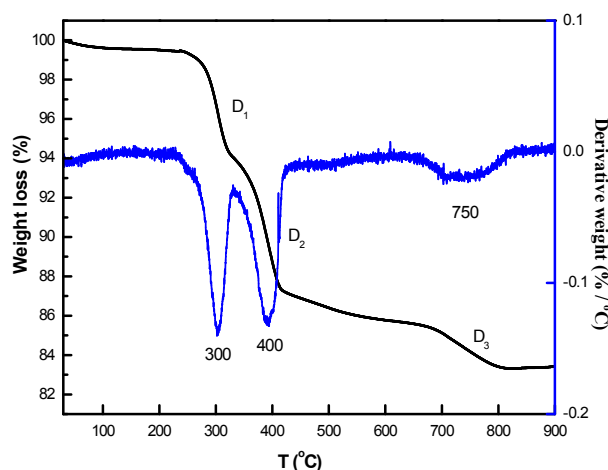
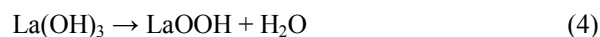
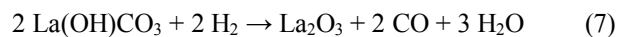
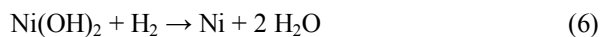


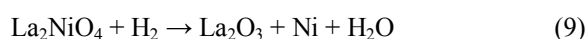
Figure 3: TG/DTG profiles of as-prepared sample.

Figure 4 shows the TPR profiles of as-prepared and the calcined samples. The as-prepared sample present four reduction peaks: Tr_1 (281 °C), Tr_2 (339 °C), Tr_3 (394 °C) and Tr_4 (580 °C). According to literature reported [9], these peaks are assigned to the reduction of: $\alpha\text{-Ni}(\text{OH})_2$ (Tr_1), $\beta\text{-Ni}(\text{OH})_2$ (Tr_2), and $\text{La}(\text{OH})\text{CO}_3$ (Tr_3 , an amorphous species did not show in XRD pattern), as shown in the following equations:



Other broad hydrogen consumption between 480 and 630 °C (Tr_4) is attributed to the difficult reduction of the $\text{Ni}^{2+}\text{-La}^{3+}$ oxidic phase.

The calcined sample presents two reduction peaks around 379 °C (Tr_5) and 528 °C (Tr_6). Based on the previous literatures reported [10], a successive reduction of LaNiO_3 can be demonstrated as following equations.



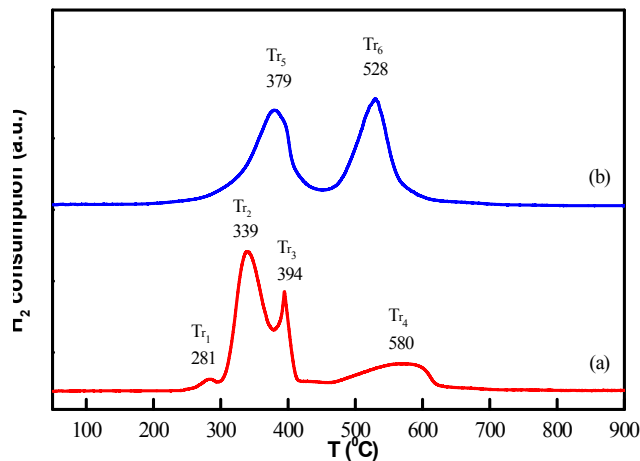
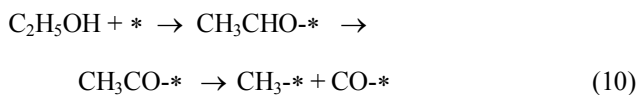


Figure 4: TPR profiles of samples: (a) as-prepared (b) calcined.

Figure 5 shows the catalytic performance of SRE over LaNiO_3 perovskite catalyst under various temperature pretreatment. The ethanol conversion approaches completion at low temperature around 300 °C for H4 catalyst in Figure 5b. The order of ethanol conversion ability is $\text{H4} > \text{H5} > \text{H6} > \text{H3}$. Comparison with the TPR profile, reduction under 300 °C obtained the A La_2NiO_4 species that possesses worse activity on the SRE reaction. As the reduction temperature arriving 400 °C can obtain well dispersed Ni on the La_2O_3 that promotes the activity. According to the products distribution with the reaction temperature in Figure 5b-d, the current experiment found that the initial reaction was the consecutive dehydrogenation of ethanol to acetaldehyde and acetyl intermediate at 225 °C. The nickel-component possesses a good capacity to crack the C–C bond in the ethanol reforming. The decomposition of acetyl into the methyl group and CO becomes significant as the temperature increase.



Where * is the active site of catalyst. Comparing the temperature on the acetyl decomposition, easy cracking of acetyl can promote the production of hydrogen. H4 catalyst possesses the best ability of acetyl decomposition compared with other catalysts, which is responsible for good ethanol conversion. Further comparing the molar ratio of CH_4 and CO, the ratio did not approach 1, and the selectivity of CO was minor (< 0.5%). This indicates that

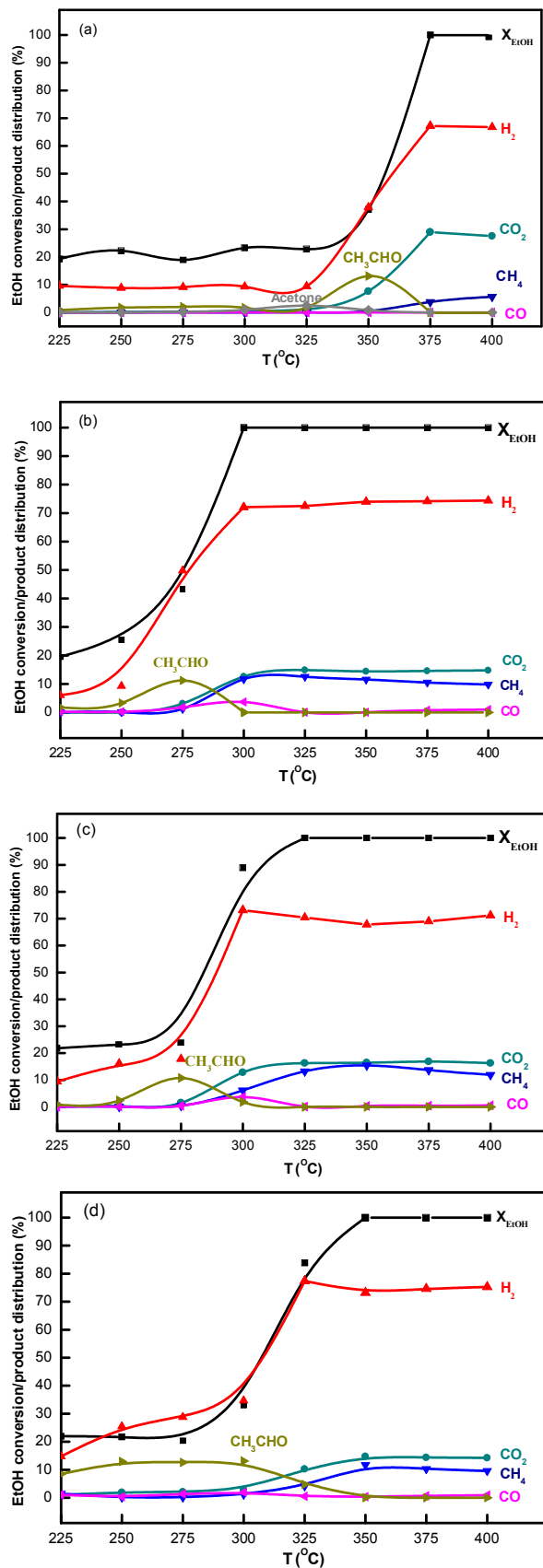
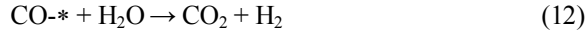


Figure 5: Catalytic performance of catalysts on SRE reaction at various pretreatment temperatures: (a) H3 (b) H4 (c) H5 (d) H6.

the adsorbed methyl group easily couples with hydrogen to form methane. The adsorbed CO easily responds the water gas shift (WGS) reaction to produce CO₂ and H₂.



The CH₄ selectivity slightly decreased, whereas the H₂ and CO selectivities gradually increased as the temperature exceeded 350 °C. This tendency may be attributed to the competing consecutive rupture of C–H bond to form coke and the steam reforming of methyl to produce CO and H₂.

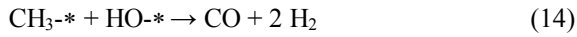
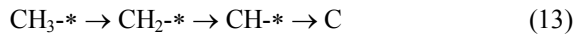


Figure 6 shows the TEM micrographs of the used catalysts (after the SRE reaction from 225 to 400 °C for 8 h). Compared with the cubic shaped nanoparticle of LaNiO₃ [Fig. 2 (b)], nano-sized metallic nickel particles migrate outward from the perovskite structure for the used catalyst. In Figure 6a, carbon depositions and carbon filaments are clearly observed on the H3 catalyst surface after the SRE reaction. No apparent carbon deposition was found on the H4 catalyst surface (Figure 6b), and the nickel nano-particles are uniformly dispersed on the support. Several new diffraction peaks on the used catalyst (no shown in this manuscript) observed that identified as La₂O₂CO₃, which is formed by the adsorption of CO₂ on

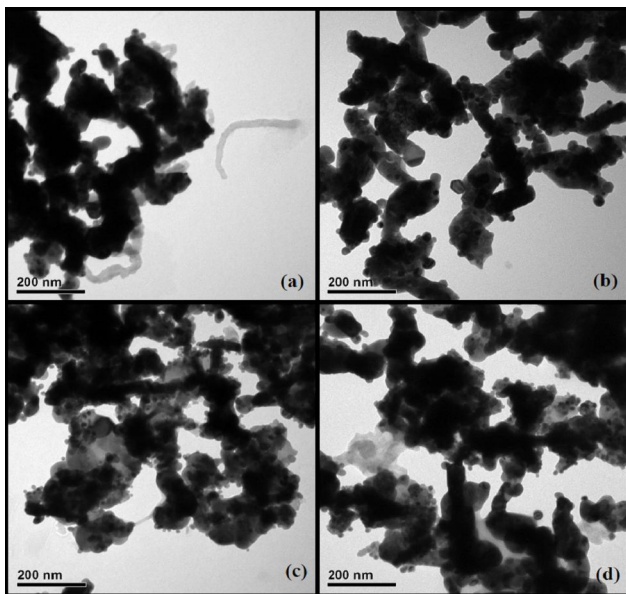


Figure 6: TEM micrographs of used catalysts: (a) H3 (b) H4 (c) H5 (d) H6.

La₂O₃. The formation of La₂O₂CO₃ may act as a carbon reservoir to remove the coke. In Figure 6c-d, carbon depositions are easily observed on catalysts.

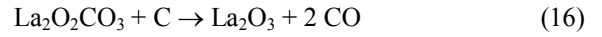
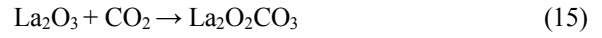


Fig. 7 shows the TG profile of the calcined sample after the SRE reaction under O₂ flow. Three fluctuations of weight (assigned as D₄, D₅, and D₆) appear around 300 – 400 °C, 400 – 650 °C, and 650 – 800 °C, respectively. Based on the previous literatures reported [11], the weight gain of D₄ should be the oxidation of Ni metal to nickel oxide, the weight loss of D₅ should be caused by the oxidation of amorphous carbon and/or oxygenated carbon to carbon dioxide and the final step of D₆ should be caused by the oxidation of graphite to carbon dioxide and/or decomposition of La₂O₂CO₃ into La₂O₃ and CO₂. The EA analysis of carbon content is 2.13% on the used H4 catalyst, which is less than other catalysts (2.26%, 2.56% and 2.39% on the H3, H5 and H6, respectively).

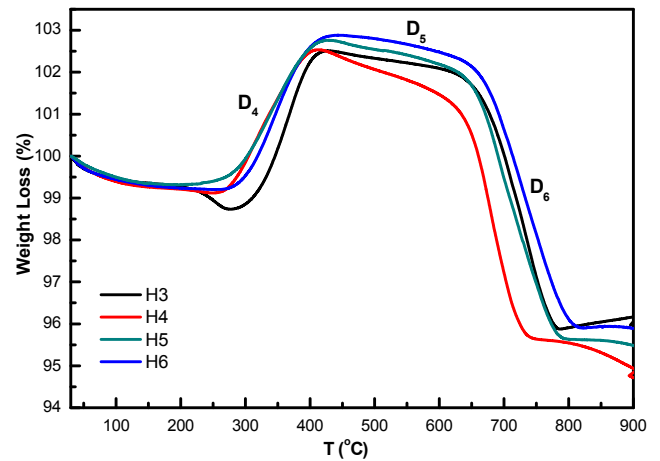


Figure 7: TG profiles of used catalysts.

4 Conclusion

This study provides an effective and novel method to prepare high performance, selectivity, and stability catalyst for low temperature SRE reaction. The reduction pretreatment of LaNiO₃ perovskite is significantly affected to the catalytic activity and product selectivity. The ethanol conversion approaches completion at 300 °C on the H4 catalyst and the H₂ selectivity is over 70%. The well

dispersion of Ni particles on the LaNiO_3 perovskite catalyst surface is the main reason for high activity at low temperature. The less deposited carbon can be further distinguished into the graphite and oxygenated-type coke.

Acknowledgments

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References

- [1] Pena MA, Fierro JLG. “Chemical Structure and Performance of Perovskite Oxides”, *Chem. Rev*, **101**, pp. 1981–2017, 2001.
- [2] Suntivich J, Gasteiger HA, Yabuuchi N, Nakanish H, Goodenough JB. “Design principle for oxygen-reduction activity on perovskite oxide catalysts for fuel cell and metal-air batteries”, *Nature Chemistry*, **107**, pp. 3952–91, 2007.
- [3] Navarro RM, Pena MA, Fierro JLG. “Hydrogen Production Reactions from Carbon Feedstocks: Fossil Fuel and Biomass”, *Chem. Rev*, **3**, pp. 546–50, 2011.
- [4] Fatsikostas AN, Kondarides DI, Verykios XE. “Production of hydrogen for fuel cells by reformation of biomass-derived ethanol”, *Catal Today*, **75**, pp. 145–55, 2002.
- [5] Sun J, Qiu X, Wu F, Zhu W. “ H_2 from steam reforming of ethanol at low temperature over $\text{Ni}/\text{Y}_2\text{O}_3$, $\text{Ni}/\text{La}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts for fuel-cell application”, *Int J Hydrogen Energy*, **30**, pp. 437–45, 2005.
- [6] Pompeo F, Nichio NN, Ferretti OA, Resasco D. “Study of Ni catalysts on different supports to obtain synthesis gas”, *Int J Hydrogen Energy*, **30**, pp. 1399–405, 2005.
- [7] Rivas ME, Fierro JLG, Goldwasser MR, Pietri E, Perez-Zurita MJ, Griboval-Constant A, et al. “Structural features and performance of $\text{LaNi}_{1-x}\text{Rh}_x\text{O}_3$ system for the dry reforming of methane”, *Appl Catal A: Gen*, **344**, pp. 10–9, 2008.
- [8] Bilecka I, Niederberger M. “Microwave chemistry for inorganic nanomaterials synthesis”, *Nanoscale*, **2**, pp. 1358–74, 2010.
- [9] Germá SG, Fanor M, Tatibouët JM, Joël B, Catherine BD. “Carbon dioxide reforming of methane over La_2NiO_4 as catalyst precursor – characterization of carbon deposition”, *Catal Today*, **133/135**, pp. 200–9, 2008.
- [10] Batiot-Dupeyrat C, Valderrama G, Meneses A, Martinez F, Barrault J, Tatibouët JM. “Pulse study of CO_2 reforming of methane over LaNiO_3 ”, *Appl Catal A Gen*, **248**, pp. 143–51, 2003.
- [11] Wang W, Chao S, Ran R, Hee JP, Chan K, Shao ZP. “Physically mixed $\text{LiLaNiAl}_2\text{O}_3$ and copper as conductive anode catalysts in a solid oxide fuel cell for methane internal reforming and partial oxidation”, *Int J Hydrogen Energy*, **36**: pp. 5632–43, 2011.