Hydrogen Production via Chemical Looping Steam Reforming of Ethanol: Effect of Ce and La on Ni-based Oxygen Carrier Performance

S Isarapakdeetham¹, P Kim-Lohsoontorn¹, S Wongsakulphasatch², W Kiatkittipong³ and S Assabumrungrat ¹,a

¹ Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand
² Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand
³ Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000, Thailand

a Corresponding author: suttichai.a@chula.ac.th

Abstract. Chemical looping steam reforming of ethanol for hydrogen production has been studied. In this process, the high hydrogen content compound, ethanol, was reacted with steam and oxygen carriers (OCs) through the redox reaction cycle to produce the clean fuel H₂. The effects of the different promoters, CeO₂ and La₂O₃, in Al₂O₃-supported Ni-based OCs were investigated. The mixed promoters Ni-Al₂O₃ OCs were synthesized by wet impregnation method. The fresh OCs were characterized by X-ray powder diffraction (XRD), N₂ adsorption-desorption, H₂-temperature programmed reduction (H₂-TPR) and Scanning electron microscope/Energy dispersive x-ray spectroscopy (SEM/EDX) technique. The redox activity test was performed in a fixed bed reactor by alternating between fuel and air feeds at isothermal condition of 500°C. The fuel feed was composed of ethanol and steam with steam to ethanol (S/E) mole ratio of 3. It was found that addition of CeO₂ and La₂O₃ on Ni/Al₂O₃ improved the metal dispersion, reduced the crystallite size and enhanced reducibility of NiO. The La₂O₃ promoted (Ni/La₂O₃-Al₂O₃) and CeO₂ and La₂O₃ co-promoted (Ni/La₂O₃-CeO₂-Al₂O₃) OCs showed high performance and stability in chemical looping steam reforming of ethanol with the maximum ethanol conversion of 98.3 and 92.5 %, respectively, with maximum H₂ yield of 2.9 and 3.2 mol/mol ethanol, respectively. In addition, forming of La₂O₃-CeO₂ solid solution phase in Ni/La₂O₃-CeO₂-Al₂O₃ oxygen carriers enhanced the oxygen storage capacity (OSC) and high oxygen mobility (OM) of OCs, resulting in a lower carbon deposition.

1. Introduction
Nowadays, global warming is one of the world’s major problems which have drawn great attention from many countries. Greenhouse gases (e.g. CO₂, CH₄ and O₃) generated from human activities especially fossil fuel burning are the main cause of global warming. Since 2006, CO₂ concentration level has been increased from 380 ppm to 408 ppm (https://climate.nasa.gov/). So, all sectors are cooperating to reduce energy consumption and to use more alternative energy such as solar power, wind power, biomass, tidal power, geothermal, etc.
Hydrogen has recently been given attention and proposed as one of the most desirable and efficient energy carriers instead of fossil fuels. It is often used as a clean fuel in fuel cells because only water is produced with very high energy release, and combustion of hydrogen to produce the energy is not releases the CO\textsubscript{2} [1]. Moreover, hydrogen is used for the conversion of heavy petroleum fractions into lighter by hydrocracking process, for the production of ammonia by Haber process, for the reduction of carbon monoxide to produce methanol. Hydrogen can be produced through different methods. The dominant route to produce hydrogen on a large scale from hydrocarbons or biomass is steam reforming [2-4] while other technologies such as sorption enhanced steam reforming [5, 6] with or without chemical looping process [7-11] from methane [7-9], methanol [12, 13], ethanol [3, 10, 11, 14, 15], glycerol [16, 17], acetic acid [2, 18] have been proposed. Among the hydrocarbons and oxygenated compounds, ethanol is considered as an important candidate because of high hydrogen content, less hazard, safe transport and high heating value, and it can be produced economically and sustainably in large amounts from biomass such as agricultural wastes [19, 20].

There are two groups of metal which are often used as catalysts for steam reforming of ethanol, consisting of noble metals (Rh, Pt, Pd, Ru, Ir) and transition metals (Ni, Co, Cu, Fe). In case of noble metals, there are many advantages for steam reforming comprising of good catalytic activity and resistance to carbon formation except their high cost and low availability [21]. Among the transition metals, Ni is the best catalyst for hydrogen production by steam reforming which shows more than 90% hydrogen selectivity [22]. However, Ni-based catalysts generally suffer rapid deactivation caused by sintering of active nickel species and carbon deposition, which remains a major challenge for developing Ni-based catalysts [23, 24]. An effective way of improving Ni dispersion and suppressing the aggregation of Ni nanoparticles is spreading them on porous supports [25]. Alumina is often used as support because of its high surface area but the Lewis acid sites of the alumina cause carbon deposition due to ethylene production [22, 26]. To adjust the stability of alumina supported Ni, alkali earth metals are promoted on the catalysts to reduce acidity, reduce Ni particle size and improve Ni dispersion [27].

Chemical looping steam reforming refers to the reduction and oxidation of oxygen carriers (OCs) which are circulated between a fuel reactor (FR) and an air reactor (AR). An oxygen carrier, often metal oxide, is used to transfer the oxygen from the air to the fuel between two reactors. The reduced oxygen carrier is then recycled by using air to oxidize the oxygen carrier to its original state. It should be noted that reduced oxygen carrier also acts as a reforming catalyst. The oxidation reaction of OCs is very exothermic and the reduction reaction is endothermic so this process acts as autothermal condition which reduces the external energy consumption [10]. Moreover, carbon deposition on catalyst can be eliminated during the process of OCs regeneration, this process utilizes air rather than pure oxygen from costly air separation process and achieves heat balance in autothermal condition [19].

Metal oxides of Fe, Ni, Co, Cu, Mn, and Cd have been studied, mostly for chemical looping of gaseous fuels such as natural gas or methane [9, 28, 29]. Chemical looping of liquid fuels such as ethanol has also been reported [10, 11, 30]. Metal oxide of Ni is relatively low cost and was found to provide a high oxidation/reduction rate which is suitable for chemical looping process [19, 31]. Zafar et al., (2006) [28] have studied Ni, Cu, Fe and Mn supported on SiO\textsubscript{2} or MgAl\textsubscript{2}O\textsubscript{4} as OCs and the results showed that Ni-based OCs are the most feasible for chemical looping process. However, Ni is still susceptible to agglomeration and carbon deposition during the reforming process. For the agglomeration problem, the impregnation of OCs onto substrates was found to reduce agglomeration and increase the reactivity of the OCs [19]. The different types of alumina support were reported to affect the reactivity of the OCs and on the gas product distribution. De Diego et al., (2008) [32] reported that the reduction reactivity of the NiO/α-Al\textsubscript{2}O\textsubscript{3} was higher than NiO/γ-Al\textsubscript{2}O\textsubscript{3} because of the limited solid-state reaction between NiO and α-Al\textsubscript{2}O\textsubscript{3}. The usage of proper OCs with high oxygen storage capacity (OSC) and high oxygen mobility (OM) was found to reduce carbon deposition on the OCs. Jiang et al., (2018) [33] studied the effect of Ce loading on nickel-phylllosilicate nanotube OCs and found that OCs with high OSC and OM could reduce carbon deposition during hydrogen production process due to the oxygen lattice diffusion to oxidize the carbon formation. Therefore, the
excellent OCs should perform as high reactivity, high OSC, high OM, high resistance to sintering and high stability [34]. Rare earth has been widely used as a promoter doped on catalysts in reforming process to improve the metal dispersion and metal-support interaction [26, 35, 36]. Ceria (CeO$_2$) is the interesting rare earth metal due to the existing in a fluorite structure, which is favorable for the diffusion of the oxygen lattice and oxygen vacancy formation. Therefore, ceria exhibits high OSC and OM since it easily releases, stores and transports oxygen [37]. Moreover, in reforming process, CeO$_2$ can promote the water gas shift (WGS) reaction and also prevent the sintering of metallic species. In Ni-ceria/NiO-ceria chemical looping, ceria can also act as an oxygen carrier due to its high OSC and OM properties [38]. La$^{3+}$ aliovalent dopant (La$_2$O$_3$) has been used to enhance OSC and OM of ceria. The addition of La$_2$O$_3$ is expected to reduce the surface acidity of Al$_2$O$_3$ support [39]. Although doped ceria has been employed extensively as a reforming catalyst, up to date the effect of ceria doping as an oxygen carrier on the redox property and stability has not been of much attention in the chemical looping process. The aim of this study is to study the effect of addition CeO$_2$ and/or La$_2$O$_3$ as a promoter on Ni-based OCs performance for chemical looping steam reforming of ethanol. It is expected that CeO$_2$ and/or La$_2$O$_3$ incorporation ought to improve the Ni dispersion, enhance reducibility of NiO which shortened the dead time in the fuel feed step, improve the efficiency of hydrogen production and reduce carbon deposition during the fuel feed step.

2. Experimental

2.1. Oxygen carrier preparation

The oxygen carriers were prepared by wet impregnation method with an aqueous solution of cerium nitrate hexahydrate (Ce(NO$_3$)$_3$∙6H$_2$O) and Al$_2$O$_3$ supports under stirring at the temperature of 70°C until the solution transforms to the slurry. The mixture was then dried at 110°C overnight and calcined at 650°C for 6 hours under static air to obtain CeO$_2$-Al$_2$O$_3$. After that, La$_2$O$_3$ was introduced into CeO$_2$-Al$_2$O$_3$ and Al$_2$O$_3$ using an aqueous solution of lanthanum nitrate hexahydrate (La(NO$_3$)$_3$∙6H$_2$O) as precursor using a similar procedure as mentioned above obtained La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ and La$_2$O$_3$-Al$_2$O$_3$.

Supported Ni oxygen carriers were prepared by wet impregnation method using an aqueous solution of nickel nitrate hexahydrate (Ni(NO$_3$)$_3$∙6H$_2$O) stirring with each support (Al$_2$O$_3$, CeO$_2$-Al$_2$O$_3$, La$_2$O$_3$-Al$_2$O$_3$ and La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$) using a similar procedure as mentioned above and calcined at 500°C for 4 hours. The Ni, CeO$_2$ and La$_2$O$_3$ content were fixed at 12.5 wt.%, 10 wt.% and 15 wt.%, respectively. These samples were labeled as N/A, N/CA, N/IA and N/LCA where N=Ni, C=CeO$_2$, L=La$_2$O$_3$ and A=Al$_2$O$_3$.

2.2. Oxygen carrier characterization

X-ray powder diffraction (XRD) patterns were analyzed, using a Cu Ka radiation as x-ray source at a wavelength of 0.1540 nm (Bruker D8 Advance). The crystallite size of the metal was calculated from the Scherrer’s equation. The surface area, pore size and pore volume of the oxygen carrier were calculated according to the Brunauer-Emmet-Teller (BET) method by N$_2$ adsorption-desorption technique (Micromeritics ASAP 2020 instrument). H$_2$-TPR experiments (Micromeritics ChemiSorb 2750 instrument) were carried out to determine the strength of the metal-support interaction of the OCs. 0.1 g of each OCs were packed into a quartz tube reactor and heated from room temperature to 800°C at a rate of 10°C/min in 10 % H$_2$ in Ar. The elemental distribution on a surface and morphology of the catalysts was investigated using Scanning electron microscope/Energy dispersive x-ray spectroscopy (SEM/EDX, Hitachi S-3400N/EDAX Apollo X).

2.3. Activity test

0.5 g OCs supported by quartz wool were loaded into a quartz fixed bed reactor (Ø 16 x 500 mm) to perform chemical looping steam reforming of ethanol. The reactor was equipped with a coaxial thermocouple for temperature monitoring and controlling, and was heated electrically by a tubular
furnace to set temperature of 500°C. The schematic diagram of the laboratory system is shown in figure 1.

![Figure 1. Experimental equipment for hydrogen production.](image)

The test was divided into two steps, fuel (ethanol and steam) feed step and air feed step. In the fuel feed step, the mixture of water and ethanol with steam to ethanol (S/E) mole ratio of 3 was fed from a liquid phase by a syringe pump (KD Scientific Inc.) with a flow rate of 3.4 ml/h and then it was vaporized and mixed with N\textsubscript{2} carrier gas with a total flow rate of 130 ml/min under a WHSV = 6.12 h\textsuperscript{-1}. The outlet stream was trapped by an ice bath and was analyzed by gas chromatography (Shimadzu Inc.). After the fuel feed step, the gas products were removed by N\textsubscript{2} purge until no residue gas was measured. The air feed step was then performed by flowing air at a flow rate of 100 ml/min to oxidize metal into metal oxide. The exit gas in the air feed step was collected and analyzed by gas chromatography. The activity of OCs was calculated in terms of ethanol conversion (X\textsubscript{ethanol}), hydrogen yield (Y\textsubscript{H2}) and selectivity of products (Sel. i) as follow:

\[
X_{\text{ethanol}} = \frac{n_{\text{ethanol(out)}} - n_{\text{ethanol(in)}}}{n_{\text{ethanol(in)}}} \times 100
\]

\[
Y_{H2} = \frac{n_{H2\text{out}}}{n_{\text{ethanol(in)}}}
\]

\[
\text{Sel. } i = \frac{n_{i\text{out}}}{\sum n_{i\text{out}}}
\]

where \(n\) is the relevant molar flows (mol/min), \(i\) represents CO, CO\textsubscript{2}, CH\textsubscript{4} and CH\textsubscript{3}CHO

3. Results and discussion

3.1. Characterization of oxygen carrier

Table 1 shows surface area, pore volume, pore size and NiO crystallite size of four OCs. When compared with Al\textsubscript{2}O\textsubscript{3}, Ni/Al\textsubscript{2}O\textsubscript{3} showed higher surface area, larger pore volume and smaller pore size due to the pore blocking occurring from a large NiO crystallite size. For the modified OCs, CeO\textsubscript{2} and/or La\textsubscript{2}O\textsubscript{3} was found to improve the physical properties of Ni/Al\textsubscript{2}O\textsubscript{3}, leading to higher surface area, pore volume and pore size. The crystallite size of NiO are shown in the following order: Ni/Al\textsubscript{2}O\textsubscript{3} > Ni/CoO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} > Ni/La\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} > Ni/La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}. The pore size of Ni/CoO\textsubscript{2}-
\( \text{Al}_2\text{O}_3, \text{Ni/La}_2\text{O}_3-\text{Al}_2\text{O}_3 \) and \( \text{Ni/La}_2\text{O}_3-\text{CeO}_2-\text{Al}_2\text{O}_3 \) were larger than \( \text{Ni/Al}_2\text{O}_3 \) due to a smaller NiO crystallite size, resulting in a less pore blocking.

The \( \text{H}_2 \)-TPR technique was used to identify the type of reducible species formed in the OCs after the calcination process. The three main reduction peaks obtained from \( \text{H}_2 \)-TPR profiles (Figure 2) in the range of 230 – 350, 350 – 450 and 450 – 550°C which represented the reduction of bulk NiO; NiO species having weak to medium interaction with support; and, NiO species having strong interaction with support, respectively [26]. The modified Ni/Al\(_2\)O\(_3\) showed the lower temperature of the first and second reduction peak, indicating more Ni species content with weaker metal-support interaction (MSI) [19]. The third peak of Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) and Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) shifted to the higher temperature compared to Ni/Al\(_2\)O\(_3\), indicating the stronger MSI due to relatively smaller NiO crystallite size and larger specific surface area, as shown in table 1. The addition of CeO\(_2\) and/or La\(_2\)O\(_3\) on Ni/Al\(_2\)O\(_3\) reduced the NiO crystallite size dispersed on the surface and reduced MSI obtained more bulk NiO which was easier to reduce NiO species to formed Ni species in the fuel feed step.

XRD patterns of the OCs after the calcination process are shown in figure 3. For all OCs, the reflections of NiO and Al\(_2\)O\(_3\) are present at 2\( \Theta \) = 37.3, 43.3, 62.9, 75.4, 79.32 (JCPDS 73-1523) and 25.6, 35.2, 37.8, 52.5, 57.5, 61.3, 66.5, 68.2, 76.9, respectively [19]. The peaks observed at 2\( \Theta \) of 28.6, 33.2, 47.6 and 56.4 were indexed as (111), (200), (220) and (311) planed of fluorite structure of CeO\(_2\) (JCPDS 81-0792) [36]. The small peaks of La\(_2\)O\(_3\) were located on 2\( \Theta \) of 26.8, 40.6 and 53.7, indicating the high dispersion on the surface of Al\(_2\)O\(_3\) [40, 41].

For the La\(_2\)O\(_3\)-CeO\(_2\) doping (figure 2(d)), the peaks of CeO\(_2\) on the location of 2\( \Theta \) = 28.6, 33.2, 47.6 and 56.4 were shifted to lower angle due to the formation of La\(_2\)O\(_3\)-CeO\(_2\) solid-solution, corresponding to the work of Pramila et al. (2016) [42] which reported that the partial substitution of La\(^{3+}\) (0.11nm) and Ce\(^{4+}\) (0.09 nm) leads to solid solution formation and the lattice shape distortion. In order to maintain electrical neutrality in the La\(_2\)O\(_3\)-CeO\(_2\) solid-solution crystal structure, oxygen ion vacancies will be created, in turn increasing OSC and OM [43]. The SEM micrographs and EDX mapping of Ni of fresh OCs are shown in figure 4. The morphology of fresh OCs showed the uniform dispersion of metal on the surface. Particle size from SEM micrographs could be related to the crystallite size reported in table 1.

### 3.2. Activity test

The activity test of OCs was evaluated by the ethanol conversion and hydrogen yield (figure 5-6). For ethanol conversion, all OCs presented the same trend. Ethanol conversion and hydrogen yield were initially increased since NiO was reduced by ethanol to formed metallic Ni which acts as catalyst for steam reforming. After that ethanol conversion and hydrogen yield decreased, likely due to deactivation of metallic Ni through carbon deposition. The overall ethanol conversion was shown in the following order of Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) = Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) > Ni/CeO\(_2\)-Al\(_2\)O\(_3\) > Ni/Al\(_2\)O\(_3\). The Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) and Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) exhibited relatively smaller NiO crystallite size and larger surface area which facilitated the breakage of C-C and C-H bonds [19].

| Oxygen carriers (OCs) | Surface area (m\(^2\)/g) | Pore volume (cm\(^3\)/g) | Pore size (nm) | NiO crystallite size (nm) |
|-----------------------|---------------------------|----------------------------|----------------|---------------------------|
| A                     | 1.618                     | 0.000325                   | 37.33          | -                         |
| N/A                   | 3.078                     | 0.006961                   | 9.44           | 39.40                     |
| N/CA                  | 6.407                     | 0.023791                   | 14.20          | 34.35                     |
| N/LA                  | 6.069                     | 0.025811                   | 21.90          | 21.77                     |
| N/LCA                 | 7.315                     | 0.033301                   | 21.20          | 27.97                     |

Table 1. Physical properties of oxygen carriers.
Figure 2. H$_2$-TPR profiles of the OCs.

Figure 3. XRD patterns of (a) N/A (b) N/CA (c) N/LA and (d) N/LCA OCs.
Figure 4. SEM profiles (left) and EDX mapping of Ni (right) of (a) N/A (b) N/CA (c) N/LA and (d) N/LCA OCs.
During the initial fuel feed step, there was no \( \text{H}_2 \) generation which was called ‘dead time’. Unless NiO was sufficiently reduced to Ni, steam reforming of ethanol would not occur. The dead time was considered as a significant indicator for the redox performance of OCs. Figure 6(a) showed \( \text{H}_2 \) yield of the initial 5 minutes of the fuel feed step. The results showed that Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) and Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) were easily reduced, corresponding to the \( \text{H}_2 \)-TPR results (Figure 2). The overall \( \text{H}_2 \) yield (Figure 6(b)) within 3 hours showed in the following order of Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) > Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) > Ni/CeO\(_2\)-Al\(_2\)O\(_3\) > Ni/Al\(_2\)O\(_3\). For the air feed step, air was fed into the reactor, oxygen in air would oxidize carbon deposition on OCs to form CO\(_2\) as shown in figure 7. In the initial of air feed step, the results showed that there was the same level of CO\(_2\) in the gas outlet before the amount of CO\(_2\) from Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) and Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) OCs decreased within around 40 minutes. On the other hand, Ni/Al\(_2\)O\(_3\) OCs showed a higher amount of CO\(_2\) and remained for 50 minutes. Ni/La\(_2\)O\(_3\)-Al\(_2\)O\(_3\) and Ni/La\(_2\)O\(_3\)-CeO\(_2\)-Al\(_2\)O\(_3\) showed relatively lowest carbon deposition and faster regeneration process. Addition of CeO\(_2\) and/or La\(_2\)O\(_3\) on Ni/Al\(_2\)O\(_3\) helped decrease carbon deposition and also decrease OCs regeneration duration. This was likely due to an increased OSC and OM which facilitated oxygen lattice diffuse through the structure of OCs and oxidized carbon formed on OCs during the fuel feed step.
4. Conclusion

The addition of rare earth oxide (CeO$_2$, La$_2$O$_3$) on 12.5 wt.% Ni/Al$_2$O$_3$ improved the metal dispersion with a small crystallite size of NiO and enhanced reducibility of bulk NiO. The smallest NiO crystallite size and large surface area were obtained by Ni/La$_2$O$_3$-Al$_2$O$_3$ and Ni/La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$, respectively. The La$_2$O$_3$-CeO$_2$ solid solution was formed in Ni/La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ OCs enhancing the OSC and OM. The high OSC and OM influenced to lower carbon deposition on OCs. The best performance of OCs for chemical looping steam reforming of ethanol were Ni/La$_2$O$_3$-Al$_2$O$_3$ and Ni/La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ which obtained high ethanol conversion, high H$_2$ yield and low carbon deposition.

5. References

[1] Nguyen VN, Deja R, Peters R, Blum L, Stolten D. Study of the catalytic combustion of lean hydrogen-air mixtures in a monolith reactor. International Journal of Hydrogen Energy. 2018;43(36):17520-30.

[2] Zhang C, Hu X, Zhang Z, Zhang L, Dong D, Gao G, et al. Steam reforming of acetic acid over Ni/Al2O3 catalyst: Correlation of calcination temperature with the interaction of nickel and alumina. Fuel. 2018;227:307-24.

[3] Dobosz J, Malecka M, Zawadzki M. Hydrogen generation via ethanol steam reforming over Co/HAp catalysts. Journal of the Energy Institute. 2018;91(3):411-23.

[4] Parlett CMA, Aydin A, Durndell LJ, Frattini L, Isaacs MA, Lee AF, et al. Tailored mesoporous silica supports for Ni catalysed hydrogen production from ethanol steam reforming. Catalysis Communications. 2017;91:76-9.

[5] Shokrollahi Yancheshmeh M,Radfarnia HR, Lluiita MC. High temperature CO2 sorbents and their application for hydrogen production by sorption enhanced steam reforming process. Chemical Engineering Journal. 2016;283:420-44.

[6] Xie H, Yu Q, Zuo Z, Han Z, Yao X, Qin Q. Hydrogen production via sorption-enhanced catalytic steam reforming of bio-oil. International Journal of Hydrogen Energy. 2016;41(4):2345-53.

[7] Shen Y, Zhao K, He F, Li H. The structure-reactivity relationships of using three-dimensionally ordered macroporous LaFe$_{1-x}$Ni$_x$O$_3$ perovskites for chemical-looping steam methane reforming. Journal of the Energy Institute. 2018.

[8] Ding H, Xu Y, Luo C, Wang Q, Shen C, Xu J, et al. A novel composite perovskite-based material for chemical-looping steam methane reforming to hydrogen and syngas. Energy Conversion and Management. 2018;171:12-9.
[9] Meshkars M, Daneshmand-Jahromi S, Rahimpour MR. Synthesis and characterization of cerium promoted Ni/SBA-16 oxygen carrier in cyclic chemical looping steam methane reforming. *Journal of the Taiwan Institute of Chemical Engineers*. 2017;76:73-82.

[10] Wang W, Fan L, Wang G. Study on chemical looping reforming of ethanol (CLRE) for hydrogen production using NiMn 2 O 4 spinel as oxygen carrier. *Journal of the Energy Institute*. 2017;90(6):884-92.

[11] Zhang Q, Li L, Jiang B, Tang D, Dou B. Hydrogen by chemical looping reforming of ethanol: The effect of promoters on La2-xMxNiO4-λ (M = Ca, Sr and Ce) oxygen carriers. *Chemical Engineering Science*. 2017;174:259-67.

[12] Lei Y, Luo Y, Li X, Lu J, Mei Z, Peng W, et al. The role of samarium on Cu/Al2O3 catalyst in the methanol steam reforming for hydrogen production. *Catalysis Today*. 2018;307:162-8.

[13] González-Gil R, Herrera C, Larrubia MA, Kowalik P, Pieta IS, Alemany LJ. Hydrogen production by steam reforming of DME over Ni-based catalysts modified with vanadium. *International Journal of Hydrogen Energy*. 2016;41(43):19781-8.

[14] Santander JA, Tonetto GM, Pedernera MN, López E. Ni/Co2-MgO catalysts supported on stainless steel plates for ethanol steam reforming. *International Journal of Hydrogen Energy*. 2017;42(15):9482-92.

[15] Li L, Song Y, Jiang B, Wang K, Zhang Q. A novel oxygen carrier for chemical looping reforming: LaNiO3 perovskite supported on montmorillonite. *Energy*. 2017;131:58-66.

[16] Aman D, Radwan D, Ebaid M, Mikhail S, van Steen E. Comparing nickel and cobalt perovskites for steam reforming of glycerol. *Molecular Catalysis*. 2018;452:60-7.

[17] Bepari S, Pradhan NC, Dalai AK. Selective production of hydrogen by steam reforming of glycerol over Ni/Al2O3 catalysts. *Catalysis Today*. 2017;291:36-46.

[18] Li L, Jiang B, Tang D, Zhang Q, Zheng Z. Hydrogen generation by acetic acid steam reforming over Ni-based catalysts derived from La1-λCeNiO3 perovskite. *International Journal of Hydrogen Energy*. 2018;43(14):6795-803.

[19] Wang K, Dou B, Jiang B, Zhang Q, Li M, Chen H, et al. Effect of support on hydrogen production from chemical looping steam reforming of ethanol over Ni-based oxygen carriers. *International Journal of Hydrogen Energy*. 2016;41(39):17334-47.

[20] Wang K, Dou B, Jiang B, Song Y, Zhang C, Zhang Q, et al. Renewable hydrogen production from chemical looping steam reforming of ethanol using xCeNi/SBA-15 oxygen carriers in a fixed-bed reactor. *International Journal of Hydrogen Energy*. 2016;41(30):12899-909.

[21] Sharma YC, Kumar A, Prasad R, Upadhyay SN. Ethanol steam reforming for hydrogen production: Latest and effective catalyst modification strategies to minimize carbonaceous deactivation. *Renewable and Sustainable Energy Reviews*. 2017;74:89-103.

[22] Contreras JL, Salones J, Colín-Luna JA, Nuño L, Quintana B, Córdova I, et al. Catalysts for H2 production using the ethanol steam reforming (a review). *International Journal of Hydrogen Energy*. 2014;39(33):18835-53.

[23] Zhang C, Li S, Wu G, Gong J. Synthesis of stable Ni-Co2 catalysts via ball-milling for ethanol steam reforming. *Catalysis Today*. 2014;233:53-60.

[24] Sehested J. Four challenges for nickel steam-reforming catalysts. *Catalysis Today*. 2006;111(1-2):103-10.

[25] Cao A, Lu R, Veser G. Stabilizing metal nanoparticles for heterogeneous catalysis. *Phys Chem Chem Phys*. 2010;12(41):13499-510.

[26] Osorio-Vargas P, Flores-González NA, Navarro RM, Fierro JLG, Campos CH, Reyes P. Improved stability of Ni/Al2O3 catalysts by effect of promoters (La2O3, CeO2) for ethanol steam-reforming reaction. *Catalysis Today*. 2016;259:27-38.

[27] Song JH, Han SJ, Yoo J, Park S, Kim DH, Song IK. Hydrogen production by steam reforming of ethanol over Ni–X/Al2O3–ZrO2 (X = Mg, Ca, Sr, and Ba) xerogel catalysts: Effect of alkaline earth metal addition. *Journal of Molecular Catalysis A: Chemical*. 2016;415:151-9.

[28] Zafar Q, Mattisson T, Gevert B. Redox Investigation of Some Oxides of Transition-State Metals Ni, Cu, Fe, and Mn Supported on SiO2 and MgAl2O4. *Energy & Fuels*. 2006;20:34-44.
[29] Karimi E, Forutan HR, Saidi M, Rahimpour MR, Shariati A. Experimental Study of Chemical-Looping Reforming in a Fixed-Bed Reactor: Performance Investigation of Different Oxygen Carriers on Al2O3 and TiO2 Support. *Energy & Fuels*. 2014;28(4):2811-20.

[30] Trevisan C, Vozniuk O, Mari M, Urrea SYA, Lorentz C, Millet J-MM, et al. The Chemical-Loop Reforming of Alcohols on Spinel-Type Mixed Oxides: Comparing Ni, Co, and Fe Ferrite vs Magnetite Performances. *Topics in Catalysis*. 2016;59(17-18):1600-13.

[31] Rubel A, Liu K, Neathery J, Taulbee D. Oxygen carriers for chemical looping combustion of solid fuels. *Fuel*. 2009;88(5):876-84.

[32] de Diego LF, Ortiz M, Adáne J, García-Labiano F, Abad A, Gayán P. Synthesis gas generation by chemical-looping reforming in a batch fluidized bed reactor using Ni-based oxygen carriers. *Chemical Engineering Journal*. 2008;144(2):289-98.

[33] Jiang B, Li L, Bian Z, Li Z, Othman M, Sun Z, et al. Hydrogen generation from chemical looping reforming of glycerol by Ce-doped nickel phyllosilicate nanotube oxygen carriers. *Fuel*. 2018;222:185-92.

[34] Adanexporto J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF. Progress in Chemical-Looping Combustion and Reforming technologies. *Progress in Energy and Combustion Science*. 2012;38(2):215-82.

[35] Li D, Zeng L, Li X, Wang X, Ma H, Assaubumrungrat S, et al. Ceria-promoted Ni/SBA-15 catalysts for ethanol steam reforming with enhanced activity and resistance to deactivation. *Applied Catalysis B: Environmental*. 2015;176-177:532-41.

[36] Dan M, Mihet M, Tasnadi-Asztalos Z, Imre-Lucaci A, Katona G, Lazar MD. Hydrogen production by ethanol steam reforming on nickel catalysts: Effect of support modification by CeO2 and La2O3. *Fuel*. 2015;147:260-8.

[37] Cheng Z, Qin L, Fan JA, Fan L-S. New Insight into the Development of Oxygen Carrier Materials for Chemical Looping Systems. *Engineering*. 2018;4(3):343-51.

[38] Löffberg A, Guerrero-Caballero J, Kane T, Rubbens A, Jalowiecki-Duhamel L. Ni/Co2 based catalysts as oxygen vectors for the chemical looping dry reforming of methane for syngas production. *Applied Catalysis B: Environmental*. 2017;212:159-74.

[39] Charisiou ND, Tzounis L, Sebastian V, Hinder SJ, Baker MA, Polychronopoulou K, et al. Investigating the correlation between deactivation and the carbon deposited on the surface of Ni/Al2O3 and Ni/La2O3-Al2O3 catalysts during the biogas reforming reaction. *Applied Surface Science*. 2018.

[40] Sanchez Sanchez M, Navarro R, Fierro J. Ethanol steam reforming over Ni/La–Al2O3 catalysts: Influence of lanthanum loading. *Catalysis Today*. 2007;129(3-4):336-45.

[41] Xu J, Zhou W, Wang J, Li Z, Ma J. Characterization and Analysis of Carbon Deposited during the Dry Reforming of Methane over Ni/La2O3/Al2O3 Catalysts. *Chinese Journal of Catalysis*. 2009;30(11):1076-84.

[42] Patil P, Selvakumar D, Kumar NS. Size Controlled Preparation and Effect of Sintering Temperature on the Structural Properties of Nanocrystalline Ceria-Lanthana Solid Solution. *Materials Today: Proceedings*. 2016;3(6):1712-7.

[43] Li F, Sun Z, Luo S, Fan L-S. Ionic diffusion in the oxidation of iron—effect of support and its implications to chemical looping applications. *Energy & Environmental Science*. 2011;4(3):876.

Acknowledgements
The authors would like to acknowledge the joint project “The National Research Council of Thailand (NRCT) and The National Natural Science Foundation of China (NSFC)” for funding support.