

Hydrogen Production from Sorption Enhanced Chemical Looping Ethanol Steam Reforming Using NiO-CuO-CaO-Ca₁₂A₁₄O₃₃ Multifunctional Catalyst

Talita Nimmas^a, Suwimol Wongsakulphasat^{b,*} and Suttichai assaumrungrat^a.

^a *Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand 10330*

^b *Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand 10800, E-mail: Talita.nimmas@gmail.com*

Abstract

In this work the effect of addition Cu metal in Ni/Al₂O₃-CaO catalyst investigate. The Ni-Cu/Al₂O₃-CaO multifunctional catalysts (O₂ carrier and CO₂ sorbent) prepared by sol-gel methods were investigated for H₂ production from sorption-enhanced steam ethanol reforming chemical looping. The crystalline and phase of catalyst will be characterized by X-ray diffraction (XRD). The shape of a particle was examined by scanning electron microscope technique (SEM). Surface area, pore-volume and pore size were determined by N₂ adsorption-desorption. The result found that Ni-Cu/Al₂O₃-CaO produced hydrogen purity (91%) higher than Ni/Al₂O₃-CaO catalyst (88%).

Keywords: sorption-enhanced steam ethanol reforming chemical looping, multifunctional catalysts, O₂ carrier, CO₂ sorbent

1. Introduction

Sorption enhanced chemical looping ethanol steam reforming (SECLSR) is a combined process between sorption enhanced ethanol steam reforming and chemical looping reforming. The SECLSR composes of three reactors, including reforming reactor, air reactor, calcination reactor. The process has potential to carry out under self-sufficient condition, WGS reactor and separation units at downstream process can be omitted, and the process is environmentally friendly, where the release of CO₂ into the atmosphere can be diminished. The challenge for sorption enhanced chemical looping steam ethanol reforming process for operation in fixed bed reactor is using material such as catalyst or oxygen carrier, sorbent, and support. Oxygen carriers should provide good oxygen carrying capacity, high reaction rate, great mechanism strength and long-term stability. Wang et al. [1] studied the CeNi/SBA-15 oxygen carrier via chemical looping steam reforming of ethanol at the temperature of 650 °C with a steam to carbon ratio of 3 in a fixed-bed reactor. NiO in the 12CeNi/SBA-15 showed high activity and stability in chemical looping ethanol steam reforming reaction and exhibited to be ease for reducibility (30s). Hydrogen selectivity is 84.7% after 14 cycles stability test. Furthermore, CuO as oxygen carrier both oxidation and

reduction reactions are exothermic [2]. As a consequence, heat requirement for the process can be supplied from the exothermic oxidation/reduction of CuO/Cu. Calcium oxide sorbent for CO₂ capture was widely used in process because sorption and desorption kinetics are fast, high CO₂ sorption capacity and low cost. So, in this work investigated the effect of addition Cu metal in Ni/Al₂O₃-CaO multifunction catalyst.

2. Experiment

2.1. Material

Calcium acetate monohydrate (C₄H₈CaO₅, POCH) was used as calcium oxide precursors. Aluminum nitrate anhydrate (Al(NO₃)₃.9H₂O, Ajax Finechem), Nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O, Sigma Aldrich) and copper nitrate (Cu(NO₃)₂.H₂O, KemAus) were used as nickel, copper and aluminum precursors. Citric acid (C₆H₈O₇), AJAX as a metal complex agent.

2.2. Multifunctional Catalyst Preparation

The multifunctional catalyst, containing NiO and CuO as an oxygen carrier, CaO as sorbent and Al₂O₃ as support was synthesized by sol-gel method. To prepare the catalyst, nickel nitrate hexahydrate, aluminum nitrate nanohydrate and calcium acetate monohydrate were dissolved in deionized water. After that, the citric acid was added to the solution. After stirring at 105 °C for 6 h, the obtained gel was dried at 110 °C for 12 h, followed by calcination at 850 °C for 2 h. In the case of Ni-Cu/Al₂O₃-CaO was prepared the same the cases mentioned above. But the last step, the addition Cu into Ni-/Al₂O₃-CaO was prepared by incipient impregnation. Copper nitrate trihydrate was dissolved in deionized water and dropped into Ni/Al₂O₃-CaO. The last step aqueous was dried at 110 °C for 12 h followed by calcination at 850 °C for 2 h. The sample composed by adding Cu into Ni/Al₂O₃-CaO is denoted Cu/(Ni-AC) and Ni-/Al₂O₃-CaO is named as Ni/AC.

2.3. Characterization

X-ray power diffraction measurements (XRD) Use a D8 Advance, Bruker equipped with a long fine focus Cu K α X-ray source. The XRD patterns were recorded at 10° < 2 θ < 80° with a step of 0.04, wavelength of 1.54056 nm and scan speed of 0.5 sec/step. Specific surface areas of multifunctional catalysts were determined with the Barret-Joyner-Halender (BJH) method. by N₂ adsorption desorption Micromeritics Chemisorp 2750. Scanning electron microscopy (SEM) (Hitachi S-3400N) was obtained by using AMETEK EDAX, APOLLO X.

2.4. Multifunctional Catalyst Performance Test

Sorption enhance chemical looping ethanol steam reforming tests were performed in a quartz tubular fixed bed reactor in I.D. of 13 mm. The catalyst 3 g was pretreated with 30 ml/min N₂ at 850 C for 1 h. The reaction test divided into 3 steps including hydrogen production step, oxidation step, and calcination step. The first step, a 30 ml/min N₂ and inlet steam was also added flow rate of 20 ml/min, which steam/ethanol ratio of 3 at 500 C. After that, N₂ was fed for gas sweeping to prepare for the next step. In the oxidation step, the O₂ carrier was oxidized at 500 C with an airflow rate of 30 ml/min for O₂ carrier regeneration. The reactor was heated from 500 C to 825 C with a rate of 10° C/min. The last step is the regeneration of sorbent at the temperature of 825 C with a steam flow rate of 10 ml/min. The ethanol conversion and product selectivity were calculated using the following equations 1, 2 respectively.

$$\text{Conversion (ethanol):}x (\%) = \frac{F_{\text{ethanol,in}} - F_{\text{ethanol,out}}}{F_{\text{ethanol,in}}} \times 100 \quad (1)$$

where $F_{\text{ethanol,in}}$ is molar flow rate of ethanol at the inlet steam and $F_{\text{ethanol,out}}$ is molar flow rate of ethanol at the outlet steam.

$$\text{Selectivity of products:}S (\%) = \frac{n_i}{\sum n_i} \times 100 \quad (2)$$

where n_i is the number of moles of each product, and $\sum n_i$ is the sum of the number of moles of all gaseous products.

3. Result and discussion

3.1. Catalyst Characterization

The crystalline and phase of Ni/AC and Cu/(Ni-AC) multifunctional catalysts were analysed by X-ray diffraction technique (XRD). The result shows in figure 1. The XRD pattern found the phase of NiO, CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ in both multifunctional catalysts. The diffraction of CaO at $2\theta = 32.2, 37.4, 53.9,$ and 64.2 [3] and the peaks assigned to NiO at $2\theta = 43.1, 62.65$ [4] are detected in all samples. In the case of Cu/(Ni-AC) found the phase of CuO at $2\theta = 35.50, 38.69, 51$ [4]. The morphology of a particle from scanning electron microscopy (SEM) as shown in figure 2. The morphology of Ni/AC exhibit small particle network. while after impregnation of Cu present smaller particle network than Ni/AC. Furthermore, the textural properties of catalysts were determined by N_2 adsorption-desorption as shown in table 1. Compared with Ni/AC, a significant reduction of the surface area could be observed after copper adding within Ni/AC. In summary, the Cu particle was added into the Ni/AC successfully.

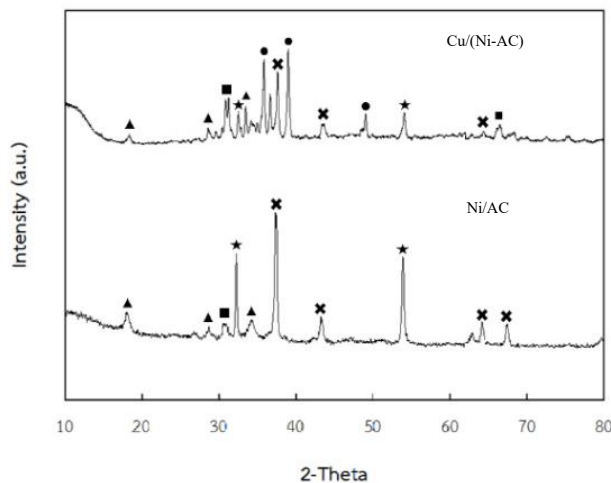


Fig.1 XRD pattern for multifunctional catalysts: \times NiO, \bullet CuO, \star CaO, \blacktriangle $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and \blacksquare Al_2O_3

Table 1 The textural properties of multifunctional catalysts.

Sample	Surface area (m^2/g)	Pore volume	Pore size diameter
Ni-AC	24.23	0.08	7

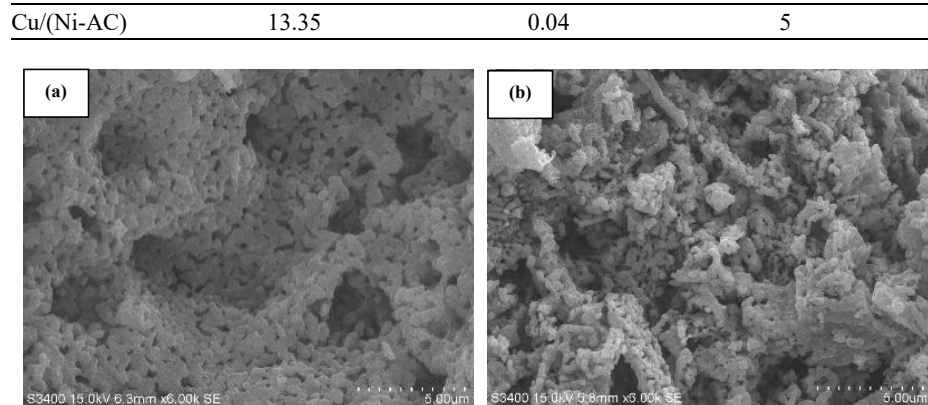
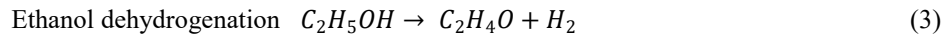


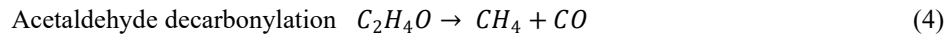
Fig.2 SEM Images: (a) Ni/AC (b) Cu/(Ni-AC)

3.2. H₂ Production

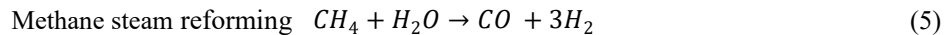
The performance of the multifunctional catalyst Ni/AC and Cu/(Ni-AC) were studied for hydrogen production from sorption enhanced chemical looping steam ethanol steam reforming process. The Cu/(Ni-AC) (Figure 3) provides the highest hydrogen purity approximately 84% for 45 min. while the Ni/AC showed hydrogen purity in pre-breakthrough period ca. 79 %. The addition of Cu metal shows low CO selectivity and high H₂ selectivity, which indicated the present of Cu metal enhanced the activation of water gas shift reaction (WGS). The Cu metal could increase the capability for water dissociative adsorption and CO oxidation [5]. Furthermore Kubacka et al [6]. explain that Cu metal can promote ethanol dehydrogenation (ED) and a water gas shift reaction (WGS). The possible reaction could be:



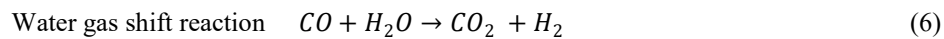
When ethanol molecules are adsorbed on the catalyst surface, ethanol dehydrogenation to acetaldehyde and hydrogen take place at the initial reaction and mainly through a Cu metal. Acetaldehyde can be proceeded by decarboxylation reaction to produce methane and carbon monoxide on a Ni metal.



After that, methane can be conducted via steam reforming to produce hydrogen and carbon monoxide through a Ni metal at high temperature.



Lastly, carbon monoxide is transformed into carbon dioxide and hydrogen through the water-gas shift reaction by Cu metal.



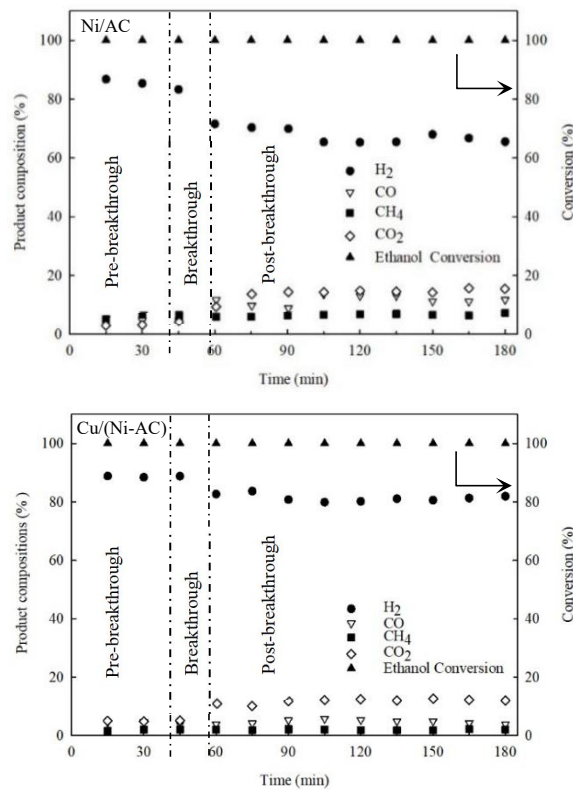


Fig. 3 Gas product compositions of Ni/AC and Cu/(Ni-AC).

Therefore, the performance of Cu/(Ni-AC) bi-metallic multifunctional catalyst greater than the solely Ni/AC multifunctional catalyst at the temperature of 500 °C and steam/ethanol ratio of 3. The Cu/(Ni-AC) multifunctional the catalyst was investigated in a single cycle to clarify performances of each a multifunctional catalyst in each step of sorption enhanced chemical looping steam ethanol steam reforming process as shown in Figure 4. The first step, metal oxide (NiO and CuO) were reduced to metal (Ni and Cu), During the initial stage of process produce H₂ about 15 min, which confirms that the NiO and CuO reduction takes place as shown in equation 7-8. The second step, as the reaction time progressed, the reduced nickel and copper is increased and hydrogen production appear to increase. After that, Ni and Cu are oxidized by air at the temperature of 500 °C according to equation 9-10. The time to complete oxidation of Ni and Cu for Cu/(Ni-AC) about 5 min. Last step, the spent sorbent (CaCO₃) is calcined to CaO and CO₂ at the temperature of 800 °C. It is also clear in sorption enhanced chemical looping steam ethanol steam reforming process of Cu/(Ni-AC) bi-metallic multifunctional catalyst that four deference step including reduction step, sorption enhanced ethanol steam reforming step, oxidation step, and calcination step.



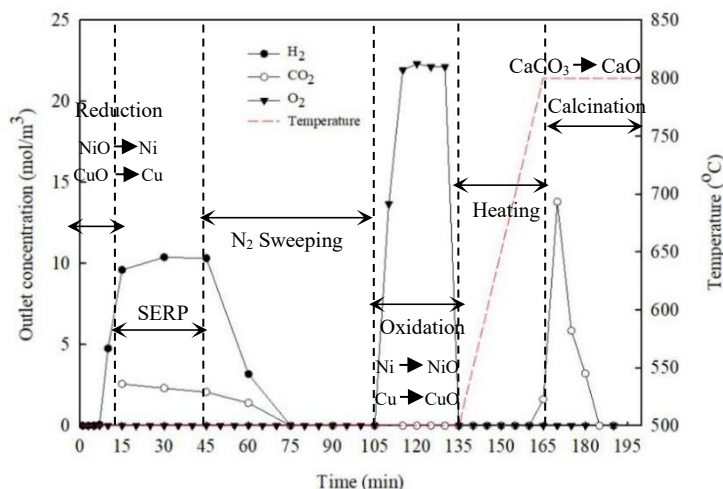


Fig.4 The single cycle of Cu/(Ni-AC)

4. Conclusion

In the present work, the performance of Ni/AC and Cu/(Ni-AC) multifunctional catalyst was studied in fixed-bed reactor. The Cu/(Ni-AC) provides the advantage of Cu addition, compared with conventional monometallic Ni multifunctional catalyst during the sorption enhanced chemical looping steam ethanol reforming reaction to H₂ production. The presence of Cu promotes the WGS reaction, which enhanced the H₂ selectivity. Moreover, the performances of each, a Cu/(Ni-AC) multifunctional catalyst in each step is four difference step including reduction step, sorption enhanced ethanol steam reforming step, oxidation step, and calcination step.

5. References

- Wang, K., Dou, B., Jiang, B., Song, Y., Zhang, C., Zhang, Q., Chen, H., and Xu, Y. (2016). 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* 41(30): 12899-12909.
- Dou, B., Zhang, H., Cui, G., Wang, Z., Jiang, B., Wang, K., Chen, H., and Xu, Y. (2017). Hydrogen production and reduction of Ni-based oxygen carriers during chemical looping steam reforming of ethanol in a fixed-bed reactor. *International Journal of Hydrogen Energy* 42(42): 26217-26230.
- Sayyah, M., Ito, B.R., Rostam-Abadi, M., Lu, Y., and Suslick, K.S. (2013). CaO-based sorbents for CO₂ capture prepared by ultrasonic spray pyrolysis. *RSC Advances* 3(43): 19872-19875.
- Papageridis, K.N., Siakavelas, G., Charisiou, N.D., Avraam, D.G., Tzounis, L., Kousi, K., and Goula, M.A. (2016). Comparative study of Ni, Co, Cu supported on γ -alumina catalysts for hydrogen production via the glycerol steam reforming reaction. *Fuel Processing Technology* 152: 156-175.
- Jeong, D.-W., Na, H.-S., Shim, J.-O., Jang, W.-J., Roh, H.-S., Jung, U.H., and Yoon, W.L. (2014). Hydrogen production from low temperature WGS reaction on co-precipitated Cu-CeO₂ catalysts: An optimization of Cu loading. *International Journal of Hydrogen Energy* 39(17): 9135-9142.

Kubacka, A., Fernández-García, M., and Martínez-Arias, A. (2016). Catalytic hydrogen production through WGS or steam reforming of alcohols over Cu, Ni and Co catalysts. *Applied Catalysis A: General* 518: 2-17.