Hydrogen Production from Dehydrogenation of Ethanol over Ag-Based Catalysts

S. Totong, K. Faungnawakij, N. Laosiripojana

Abstract—The development of alternative energy is interesting in the present especially, hydrogen production because it is an important energy resource in the future. This paper studied the hydrogen production from catalytic dehydrogenation of ethanol through via low temperature (<500°C) reaction. Copper (Cu) and silver (Ag) supported on fumed silica (SiO_2) were selected in the present work; in addition, bimetallic material; Ag-Cu supported on SiO_2 was also investigated. The catalysts were prepared by the incipient wetness impregnation method and characterized via X-ray diffraction (XRD), temperature-programmed reduction (TPR)and nitrogen adsorption measurements. The catalytic dehydrogenation of ethanol was carried out in a fixed bed continuous flow reactor at atmospheric pressure. The effect of reaction temperature between 300-375°C was studied in order to maximize the hydrogen yield. It was found that Ag-Cu/SiO_2 exhibited the highest hydrogen yield compared to Ag/SiO_2 and Cu/SiO_2 at low reaction temperature (300°C) with full ethanol conversion. The highest hydrogen yield observed was 40% and will be further used as a reactant in fuel cells to generate electricity or feedstock of chemical production.

Keywords—Catalyst, dehydrogenation, ethanol, hydrogen production.

I. INTRODUCTION

ENERGY is one of the key elements in driving global activities and human's daily life so the global energy demand is increasing continuously. More than 90% of the energy supply comes from fossil fuels such as coal, crude oil and natural gas. However, the limitation amounts of conventional fuels are sharply depleted and the price is still increasing which are problems in the present. In addition, the energy usage from fossil fuels is the main cause to produce environmental pollutions, greenhouse effects, climate change and also affect to living organisms on the earth. Therefore, there is significantly effort being placed into researching alternative and/or renewable energy instead of petroleum fuels. Hydrogen is one of the most interesting alternatives energy due to it is sustainable, clean, environmentally friendly and high energy capacity. Hydrogen gas is used as a fuel instead of fossil fuels which helping in reducing carbon dioxide emission, it causes global warming. Hydrogen gas can be used as a primary chemical feedstock to produce various

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chemical products such as ammonia and methanol, direct fuels and also be fed as a reactant for fuel cells to produce electricity [1]. Hydrogen can be produced via several technologies for examples, coal gasification, steam reforming, plasma reforming, partial oxidation, thermal decomposition of water, electrolysis of water and dehydrogenation.

Nowadays, the most interesting technologies for hydrogen production is ethanol steam reforming. In general, transition metals have shown a good level of activity and selectivity for ethanol steam reforming, in the order: Co> Ni> Rh>Pt, Ru, Cu. The main problem was found when using these catalysts was deactivation by sintering and carbon deposition due to the harsh conditions of low H/C and O/C ratios in the feed stream and high temperatures used [2]-[4]. Vizcaino et al. [5] studied hydrogen production by ethanol steam reforming over Cu–Ni supported catalysts were tested in ethanol steam reforming reaction. Two commercial amorphous solids (SiO_2 and γ-Al_2O_3) and three synthesized materials (MCM-41, SBA-15 and ZSM-5 nanocrystalline) were used as supports. A series of Cu–Ni/SiO_2 catalysts with different Cu and Ni content were also prepared. It was found that aluminum containing supports favored ethanol dehydration to ethylene in the acid sites, which in vice versa, promotes the coke deactivation process. The highest hydrogen selectivity is achieved with the Cu–Ni/SBA-15 catalyst due to a smaller metallic crystallite size. Nevertheless, the Cu–Ni/SiO_2 catalyst showed the best catalytic performance, since a better equilibrium between high hydrogen selectivity and CO_2/CO_x ratio was obtained. Selectivity towards hydrogen production was favored by increasing the reaction temperature, and a value of 600 °C was chosen. It was seen that nickel is the phase responsible for hydrogen production in a greater grade, although both CO production and coke deposition were decreased when copper was added to the catalyst. Dimitris et al. [6] studied the catalytic performance of supported noble metal catalysts for the steam reforming (SR) of ethanol by investigating in the temperature range of 600–850⁰C with respect to the nature of the active metallic phase (Rh, Ru, Pt, Pd) [7-10], the nature of the support (Al_2O_3, MgO, TiO_2) and the metal loading (0–5 wt.%). It has been found that for low-loaded catalysts, Rh was significantly more active and selective toward hydrogen formation compared to Ru, Pt and Pd, which showed a similar behavior. The catalytic performance of Rh and, particularly, Ru is significantly improved with increasing metal loading, leading to higher ethanol conversion and hydrogen selectivity at given reaction temperatures. The catalytic activity and selectivity of high-loaded Ru catalyst was comparable to that of Rh and, therefore, ruthenium was further investigated as a

World Academy of Science, Engineering and Technology
International Journal of Energy and Power Engineering
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less costly alternative. It was found that under certain reaction conditions the 5% Ru/Al_2O_3 catalyst was able to completely convert ethanol with selectivity toward hydrogen above 95%, the only byproduct being methane. Long-term tests conducted under severe conditions showed that the catalyst was acceptably stable and could be a good candidate for the production of hydrogen by steam reforming of ethanol for fuel cell applications. From the previous studied that mentioned above, it was usually operated at high temperature. Therefore, hydrogen production from dehydrogenation of ethanol is the promising technique to produce hydrogen gas because the reaction can be achieved at lower temperature (<500°C) than the other techniques. In the present work, the dehydrogenation of ethanol over Cu, Ag and Cu-Ag supported on SiO_2 catalysts were carried out. The effect of the reaction temperatures were observed in different catalysts for studying H_2 yield.

II. Experiments

A. Catalyst Preparation

A fumed silica (Sigma-Aldrich, 0.007μm, 390m^2/g) sample, which calcined in air at 400℃ for 4h, was used as support. Initially, a loading of 2.28 wt% of each metal was targeted in the experiment except bimetallic sample, loading of each metal was 1.14 wt%. The catalysts were prepared by incipient wetness impregnation method using aqueous solutions of metal precursors; $Cu(NO_3)_2\cdot3H_2O$ (Qrec, 99.5%), $AgNO_3$ (BDH) and mixture of bimetallic $Cu(NO_3)_2\cdot3H_2O$ and$AgNO_3$. The impregnated samples were dried at 120℃ overnight and calcined at 400℃ for 4h in air.

B. Catalyst Characterization

X-ray diffraction (XRD) was used to identify the metal species presented on catalysts by an X-ray diffractometer (Bruker, Model D8 Discover with GADDS) using Cu Kα radiation of a wavelength of 1.54006 Å from 10 to 90° of 2θ at a rate of 0.05°/s.

The specific surface area, pore diameter and pore volume of catalysts were measured by nitrogen adsorption-desorption using Quantachrome Nova 4200e instrument. Before measurement, all samples were degassed under vacuum condition at 150℃ for 3h.Surface areas were calculated according to BET method.

Temperature Programmed Reduction (TPR) profiles were recorded using a Quantachrome Chem BET PulsarTPR/.

TPD instrument, using 20mg of catalyst, placed in U-quartz tube under 5% H_2 in Ar flow (30ml/min) with a heating rate of 10°C/min from 25 to 850°C while the TCD signal was recorded.

C. Catalytic Test

The catalyst testing was carried out in a fixed bed continuous flow reactor. The dehydrogenation of ethanol performed between 300–375℃ at atmospheric pressure. The amount of catalyst 200 mg having particle size about 0.18–0.5 mm was packed in quartz tube reactor. This procedure avoided leakage of catalyst particle into the reactor by using a layer of quartz wool packed in the bottom of the reactor tube, then

filled the catalyst bed as middle layer and placed quartz wool above the catalyst bed again. Previously, catalyst was reduced with 10% H_2 in N_2 at 300℃ for 3h. Ethanol was fed to evaporator at the flow rate 0.007ml/min and sent to the reactor with flow rate of nitrogen 20ml/min which acted as the carrier gas. The gaseous products of reaction were analyzed by on-line micro gas chromatography (Varian CP-4900 micro-GC) using a Pora PLOT Q, molecular sieve column and thermal conductivity detector (TCD).

III. Results and Discussion

A. Catalyst Characterization

One of the important properties of catalyst, that affected an activity, was the specific surface area of catalyst. The specific surface area could be determined by adsorption-desorption isotherm from the BET method. The specific surface area, pore volume and mean pore diameter of the catalysts and support are summarized in Table I. Modification of the silica support with metal oxide led to decrease in specific surface area.

TABLE I
PHYSICAL PROPERTIES OF CATALYST

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
SiO_2	284.3	1.11	3.2
Ag/SiO_2	160.3	0.85	16.4
Cu/SiO_2	168.2	0.69	16.5
$Ag-Cu/SiO_2$	166.3	0.77	16.5

[a]Calculated by the BET equation; [b] BJH desorption pore volume;
[c]BJH desorption pore diameter.

The XRD patterns of the prepared catalysts were shown in Fig. 1. The angle (2θ) between 20° and 30° presented amorphous silica. For Cu/SiO_2, the XRD diffraction peaks were presented in Fig. 1 (a). The crystalline of CuO phase with peak positions at 2θ=35.5° and 38.5° and for Ag/SiO_2, the crystalline of Ag_2O phase with peak positions at 2θ=32.3° and 37.2° (Fig. 1 (b)). No detectable phase of transition metal oxide was observed on the diffractograms of $Ag-Cu/SiO_2$ sample, which relatively small or disordered oxide particles (Fig. 1 (c)).
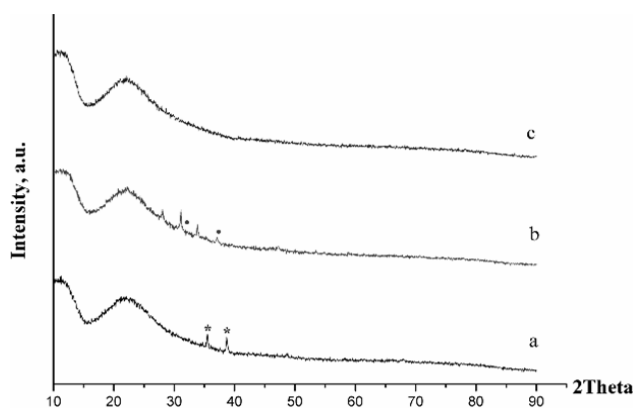

Fig.1 XRD patterns of the prepared catalysts: a-Cu/SiO_2, b-Ag/SiO_2, and c-$Ag-Cu/SiO_2$
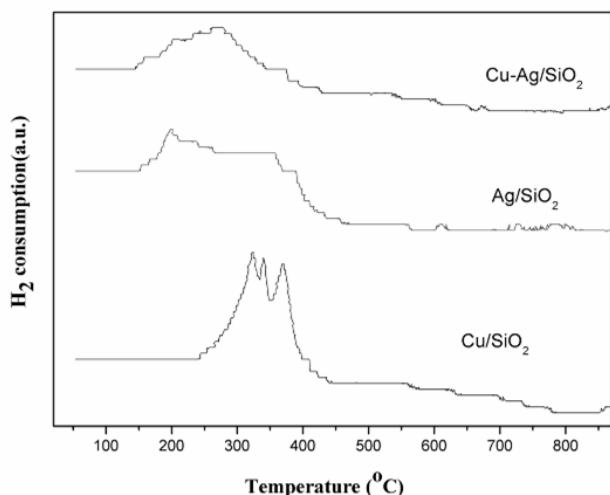
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International Journal of Energy and Power Engineering
Vol:8, No:2, 2014

Fig. 2 TPR-H$_2$ profiles for catalyst Cu-SiO$_2$, Ag/SiO$_2$, and Ag-Cu/SiO$_2$

The TPR profiles of Ag/SiO$_2$, Cu/SiO$_2$, and Ag-Cu/SiO$_2$ catalysts were exhibited in Fig. 2. Cu/SiO$_2$ exhibited peak at 325ºC and 375ºC. Ag/SiO$_2$ and Ag-Cu/SiO$_2$ exhibited peak at 300ºC and 275ºC respectively. So, the selected temperature used to reduce catalysts was 300ºC for 3h. After reduction, the metal oxide in catalyst was reduced to metallic (Cu, Ag and Ag-Cu).
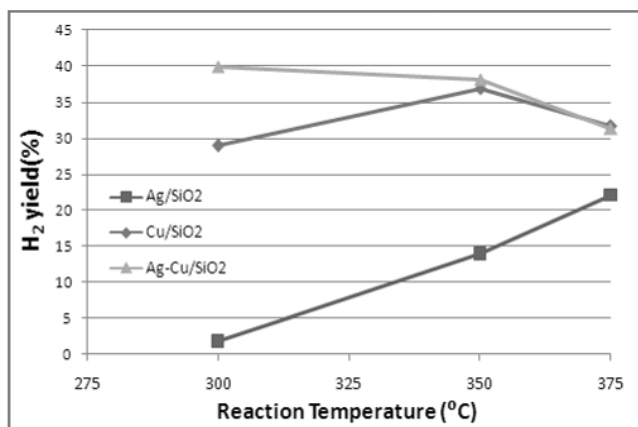
B. Catalytic Test

Fig. 3 Hydrogen yield over Ag/SiO$_2$, Cu/SiO$_2$, and Ag-Cu/SiO$_2$ catalysts in the dehydrogenation of ethanol

From Fig. 3, it could be seen that the yield of hydrogen production from ethanol dehydrogenation by using bimetallic catalysts was highest when compared to the monometallic catalysts. The use of single Ag exhibited very low H$_2$ production yield at low temperature, while Cu produced relatively higher H$_2$ production yield. This result was in good agreement with the literature, which generally indicated that Cu was the good catalyst for dehydrogenation reaction. In this work, the additional of Ag over Cu was found and it could be further promoted Cu catalytic activity toward the dehydrogenation reaction, particularly at the temperature around 300°C. It was noted that the reaction temperature

significantly affected the yield of hydrogen produced, e.g. for Cu/SiO$_2$, and Ag-Cu/SiO$_2$ as increasing temperature, the hydrogen production was decreased, which could be due to the occurring of ethanol cracking to other hydrocarbon compounds e.g. C$_2$H$_6$ and C$_2$H$_4$ at higher temperature.

IV. CONCLUSION

The dehydrogenation of ethanol over Ag/SiO$_2$, Cu/SiO$_2$, and Ag-Cu/SiO$_2$ catalysts were synthesized by an incipient wetness impregnation method. The influence of the reaction temperature was studied. The increase in hydrogen yield was in the following order: Ag-Cu/SiO$_2$ > Cu/SiO$_2$ > Ag/SiO$_2$. Ag-Cu/SiO$_2$ exhibited the best catalyst activity in term of hydrogen yield.

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