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 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 increasing which are problems 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 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 increasing which are problems 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 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.
less costly alternative. It was found that under certain reaction conditions the 5% Ru/Al₂O₃ 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 study 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 SiO₂ catalysts were carried out. The effect of the reaction temperatures were observed in different catalysts for studying H₂ yield.

II. EXPERIMENTS

A. Catalyst Preparation

A fumed silica (Sigma-Aldrich, 0.007µm, 390m²/g) sample, which calcined in air at 400°C 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(NO₃)₂·3H₂O (Qrec, 99.5%), AgNO₃ (BDH) and mixture of bimetallic Cu(NO₃)₂·3H₂O and AgNO₃. The impregnated samples were dried at 120°C overnight and calcined at 400°C 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° 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°C 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% H₂ 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 catalytic testing was carried out in a fixed bed continuous flow reactor. The dehydrogenation of ethanol performed between 300–375°C 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% H₂ in N₂ at 300°C 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>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area</th>
<th>Pore Volume</th>
<th>Pore Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>284.3</td>
<td>1.11</td>
<td>3.2</td>
</tr>
<tr>
<td>Ag/SiO₂</td>
<td>160.3</td>
<td>0.85</td>
<td>16.4</td>
</tr>
<tr>
<td>Cu/SiO₂</td>
<td>168.2</td>
<td>0.69</td>
<td>16.5</td>
</tr>
<tr>
<td>Ag-Cu/SiO₂</td>
<td>166.3</td>
<td>0.77</td>
<td>16.5</td>
</tr>
</tbody>
</table>

*Calculated by the BET equation; †BJH desorption pore volume; ‡BJH desorption pore diameter.

The XRD patterns of the prepared catalysts were shown in Fig. 1. The angle (2θ) between 20⁰ and 30⁰ presented amorphous silica. For Cu/SiO₂, the XRD diffraction peaks were presented in Fig. 1 (a). The crystalline of CuO phase with peak positions at 2θ=35.5⁰ and 38.5⁰ and for Ag/SiO₂, the crystalline of Ag₂O phase with peak positions at 2θ=32.3⁰ and 37.2⁰ (Fig. 1 (b)). No detectable phase of transition metal oxide was observed on the diffractograms of Ag-Cu/SiO₂ sample, which relatively small or disordered oxide particles (Fig. 1 (c)).
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 325°C and 375°C. Ag/SiO$_2$ and Ag-Cu/SiO$_2$ exhibited peak at 300°C and 275°C respectively. So, the selected temperature used to reduce catalysts was 300°C for 3h. After reduction, the metal oxide in catalyst was reduced to metallic (Cu, Ag and Ag-Cu).

B. Catalytic Test

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.

ACKNOWLEDGMENT

The author is very grateful to Dr. Navadol Laosiripojana, Dr. Kajornsak Faungnawakij for their suggestion. The author would like to thanks the Joint Graduate School of Energy and Environment (JGSEE) for financial support and also thanks the Nanomaterials for Energy and Catalysis Laboratory (NEC) for BET, TPR-H$_2$, XRD measurements. The author thanks the referees for useful discussion during the reviewing process.

REFERENCES