Catalytic Non-oxidative Dehydrogenation of Ethanol into Acetaldehyde and Hydrogen using Monometallic Cu, Ag and Bimetallic Cu-Ag Catalysts Supported by SiO₂

Pornlada Daorattanachai^{*}, Sansanee Totong and Navadol Laosiripojana

The Joint Graduate School of Energy and Environment, Center of Excellence on Energy Technology and Environment, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd., Bang Mod, Thung Khru, Bangkok 10140, Thailand Corresponding author: pornlada@jgsee.kmutt.ac.th

Abstract: The purpose of this work was to investigate catalytic non-oxidative dehydrogenation of ethanol into acetaldehyde and hydrogen using monometallic Cu, Ag and bimetallic Cu-Ag catalysts supported on SiO₂ at metal loading variations (2.5, 5, and 10 wt.%). The experimental results revealed that Cu catalysts with low Cu loading (2.5-5 wt.%) exhibited better activity than Ag catalysts in temperature range of 250-400°C. Moreover, we found that the addition of Cu considerably promoted the catalytic dehydrogenation activity of Ag/SiO₂ catalysts. Among all prepared catalysts, the 10 wt.% Cu-Ag/SiO₂ showed the best catalytic activity for non-oxidative dehydrogenation of ethanol with ethanol conversion of 53%, acetaldehyde yield of 42%, and hydrogen yield of 49% at 400°C.

Keywords: Dehydrogenation; Ethanol; Acetaldehyde; Hydrogen; Cu; Ag; Cu-Ag.

1. Introduction

Currently, the shortage of fossil fuels has become an important global concern. Furthermore, pollutant emissions during the combustion of fossil fuels also cause a serious impact on climate change and other environmental problems. The use of renewable energy is known as one sustainable solution to minimize these problems. Among renewable feedstocks to produce intermediates and fine chemicals, ethanol is one of the most promising candidates because of its relatively high hydrogen content, possibility to generate from renewable sources, non-toxicity, and easy storage and handling [1-2]. A wide range of intermediates and fine chemicals such as acetaldehyde, hydrogen, ethylene, ethyl acetate, acetic acid, carbon monoxide, and other compounds can be produced from ethanol [3-5].

Acetaldehyde has been considered a promising intermediate platform for producing acetic acid, acetic anhydride, ethyl acetate, butyraldehyde, n-butanol, pentaerythritol, and many other products [6]. The dehydrogenation of ethanol is an important industrial step to produce acetaldehyde and hydrogen [7-8] and it is also the first step in other processes such as ethanol steam reforming and partial oxidation reaction processes [9-10]. Acetaldehyde was first synthesized from ethanol oxidation over a platinum black catalyst by Davy in 1817 [11]. Nowadays, Cu-based catalysts are widely used for dehydrogenation reaction because of their acceptably high activity and significantly lower cost in comparison with noble metal-based catalysts. However, Cu suffers from poor thermal stability at high temperatures [12-14]. Other alternatives to Cu, including Ag [15], V [16], Au [17], Pd-Zn [18], and NiCu [19] have also been proposed. Xu et al. [15] investigated Ag nanoparticles supported on a hydroxyapatite. They found that Ag nanoparticles showed high activity (1.38 s⁻¹ in turnover frequency), selectivity (~100%), and durability (~100 h) for the oxidative dehydrogenation of ethanol to acetaldehyde.

The focus of this study was on metallic Cu and Ag catalysts supported by SiO₂. Moreover, the addition of Cu in Ag as a novel catalyst for the selective non-oxidative dehydrogenation of ethanol to acetaldehyde and hydrogen has investigated. the characterization of Cu, Ag, and Cu-Ag catalysts supported by SiO₂ were evaluated using N₂ sorption, X-ray diffraction (XRD) and Temperature programmed reduction (TPR) to study the relationship between their catalytic activity and physical-chemical properties.

2. Experimental

2.1 Catalyst synthesis

The silica-supported metal catalysts were impregnated using the solution of Cu(NO₃)₂·3H₂O (Qrec, 99.5%) and AgNO₃ (BDH, AR grade) to prepare Cu/SiO₂, Ag/SiO₂, and Cu-Ag/SiO₂ catalysts. The concentrations of Cu and Ag solutions were calculated before impregnation in order to achieve 2.5, 5, and 10 wt.% of Cu, Ag, and Cu-Ag loading. The atomic ratio of Cu and Ag in bimetallic Cu-Ag catalyst was equal to 1.

A commercial fumed silica powder (SiO₂, Sigma-Aldrich) was calcined in air at 400°C for 4 hours to eliminate impurities before using as support in this work. As the next step, the metal-containing solutions were added to silica support. After that, prepared catalysts were dried overnight at 120°C and calcined at 400°C for 4 hours to obtain silica-supported monoand bimetallic catalysts in oxide form. Before the characterization and testing reaction, the prepared catalysts were reduced under 10% hydrogen in nitrogen at 300°C for 3 hours.

2.2 Catalyst characterization

Specific surface area, pore diameter, and pore volume of the prepared catalysts were measured by Brunauer-Emmett-Teller (BET) nitrogen physisorption technique using Quantachrome Nova 4200e instrument. Prior to each measurement, a fresh sample was degassed at 150°C for 3 hours. The crystalline phases of the catalysts in a reduced state were analyzed by X-ray diffraction (XRD, Bruker Model D8 Discover with GADDS) using a CuKa radiation at 40 kV and 30 mA with a scanning rate of 0.05°/s. The scanning steps were recorded in 2θ scanning range of $10-90^\circ$. Temperature programmed reduction (TPR) was used to characterize the reducibility and the strength of the metal support. A Quantachrome Chem BET Pulsar TPR/TPD instrument was used for analysis in this experiment. About 50 mg of catalyst was placed in U-quartz tube and purged with N2 for 30 min. Then, the temperature was ramped from 25 to 850°C at a rate of 10°C/min in 5 v/v.% hydrogen in argon mixture with a flow rate of 30 mm/min. A TPR profile was plotted between the reducibility temperature and the amount of hydrogen consumption.

2.3. Catalyst activity testing

The schematic diagram for the experimental system of catalytic non-oxidative dehydrogenation of ethanol is shown in



Figure 1. Schematic diagram of catalytic non-oxidative dehydrogenation of ethanol system.

Table 1.	The results	of BET	surface a	rea and	pore size	analysis

No.	Catalyst	Surface area (m²/g)	Pore volume (cm ³ /g)	Pore diameter (nm)
1	SiO ₂ (support)	302.30	0.61	3.67
2	2.5 wt.% Cu/SiO2	215.50	1.58	27.72
3	5 wt.% Cu/SiO2	257.20	1.16	16.43
4	10 wt.% Cu/SiO ₂	151.60	1.22	27.89
5	2.5 wt.% Ag/SiO2	259.00	1.53	27.87
6	5 wt.% Ag/SiO ₂	242.60	1.31	27.27
7	10 wt.% Ag/SiO ₂	159.40	1.54	27.83
8	2.5 wt.% Cu-Ag/SiO2	258.80	1.34	27.88
9	5 wt.% Cu-Ag/SiO ₂	231.90	1.15	27.53
10	10 wt.% Cu-Ag/SiO ₂	157.60	1.37	27.67

Figure 1. This system was designed with four main sections: supplied gases, ethanol feeder, reaction zone, and analysis zone. The supplied gas section consisted of nitrogen and hydrogen. At the outlet of each gas cylinder, the pressure regulator was installed in order to set the constant pressure to the mass flow controller. The mass flow controller was used to adjust the flow rate of inlet gases.

In order to study catalytic non-oxidative dehydrogenation, ethanol was introduced into the system via high performance liquid chromatography (HPLC) pump. The HPLC pump was used to feed and control the flow rate of the absolute ethanol into tubular quartz reactor. The ethanol stream was heated by cable heater for 80°C in order to evaporate the mixer and supply both ethanol and gas streams to the reactor.

The catalytic experiments were carried out in a fixed bed quartz tubular reactor (inside diameter 10 mm and length 500 mm) and operated at atmospheric pressure. 0.2 g of catalyst samples (0.18-0.5 mm size particles) were introduced into the reactor. Experiments were carried out in 250-400°C temperature range. The reactant (ethanol) and reaction products (acetaldehyde and hydrogen) were analyzed by on-line gas chromatography with thermal conductivity detector (TCD) and flame ionization detector (FID) with a CP-Pora PLOT U (0.53 mm ID x 12m) column. The oven-temperature program was initially set at 50°C with a hold of 1 minute and ramped to 150°C at 10°C/min with a hold of 4 minutes. Ethanol conversion ($X_{Ethanol}$) and yields of hydrogen ($Y_{Hydrogen}$) and acetaldehyde ($Y_{Acetaldehyde}$) were calculated from the molar flows of the reactant and products in the output of the reactor using the following equations:

$$X_{Ethanol} = \left(\frac{F_{Ethanol,in} - F_{Ethanol,out}}{F_{Ethanol,in}}\right) \times 100\% \tag{1}$$

$$Y_{Product,i} = \left(\frac{F_{Product,i}}{F_{Ethanol,in}}\right) \times 100\%$$
(2)

3. Results and Discussion

3.1 Physical properties of prepared catalysts

The specific surface area, total pore volume, and average pore diameter of all prepared catalysts in a reduced state were analyzed by the Brunauer, Emmett and Teller (BET) measurement and summarized in Table 1. The specific surface area of the catalyst was determined by multi-point technique while the total pore volume and average pore size diameter were analyzed by the Barrett, Joyner and Halenda (BJH) technique. The BET surface area of commercial silica support was 302 m²·g⁻¹. After doping silica with Cu, Ag, and mixed Cu and Ag, the specific surface area of all prepared catalysts decreased whereas pore volume and pore diameter increased. This is possible due to pore blockage which leads to further loss in surface area. Moreover, with the increase of metal loading, the surface area decreased.

XRD patterns for silica-supported Cu, Ag and Cu-Ag catalysts at different metal loadings are shown in Figure 2. The XRD pattern of the amorphous silica presented the much broader diffused peak between 20° and 30° . The Cu/SiO₂ catalyst exhibited three main diffraction peaks ($2\theta = 43.4^{\circ}$, 50.5° and 74.1°) which related to crystalline copper (Cu) metal phase, see in Figure 2(a). We also found that the peak intensity increased with increasing copper loading. Figure 2 (b) presents the XRD pattern of Ag/SiO2 at different silver loadings. At low Ag loading (2.5 wt.%), no diffraction peaks for Ag were identified in this catalyst. This indicates the amorphous and very small particle size of Ag particles. After increasing Ag loading, XRD patterns showed four diffraction peaks related to crystalline metallic Ag phase at $2\theta = 38.2^{\circ}$, 44.4° , 64.5° and 77.7° , which correspond to $(1\ 1\ 1)$, $(2\ 0\ 0)$, $(2\ 2\ 0)$ and $(3\ 1\ 1)$ planes, respectively. Thus, it can be concluded that Ag₂O can be converted to metallic Ag after reducing at 300°C with 10% v/v H₂ for 3 hours. In the case of the bimetallic Cu-Ag catalysts at different total metal loadings from 2.5 to 10 wt.%, the XRD patterns are shown in Figure 2(c). As a result, both Cu and Ag metallic crystalline peak were detected. We found that peak positions of Cu and Ag in bimetallic catalyst did not change.



Figure 2. XRD patterns of (a) Cu/SiO₂ (b) Ag/SiO₂ and (c) Cu-Ag/SiO₂ at different metal loadings after reduction in 10% v/v H_2 in N_2 at 300°C for 3 hours.

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The reducibility of all synthesized catalysts was evaluated from TPR technique. The H2-TPR profile of 2.5 wt.% Cu/SiO2 showed four overlapping peaks at 320, 340, 360, and 400°C. It is an indication that the catalyst sample possessed presence of more than one copper oxide species. At 5 wt.% Cu/SiO₂, there were three peaks at 320, 340 and 450°C. On the other hand, TPR profile of 10 wt.% Cu/SiO2 catalysts presented a single broad peak in the range of 300-450°C, indicating the presence of the large particle size of CuO. Figures 3(b) depicts the TPR profiles for Ag-based catalysts. We found that the Ag loading of 2.5 and 5 wt.% exhibited the reduction peak at 205°C whereas the reduction peak shifted into 235°C at 10 wt.% Ag loading. For the bimetallic Cu-Ag catalyst, it was found that the reduction temperature of the catalyst was the combination of the reduction temperature region between Cu and Ag. The reduction temperature signals shifted to high temperatures when the metal content increased, as shown in Figure 3 (c).

3.2 Catalytic activity toward non-oxidative dehydrogenation of ethanol

Monometallic Cu, Ag and bimetallic Cu-Ag catalysts supported by SiO₂ at 2.5, 5, 10 wt.% metal loadings were first studied for the non-oxidative dehydrogenation of ethanol at the temperature range of 250 to 400°C. The variations in the ethanol conversion as well as acetaldehyde and H₂ yields over the different catalysts and metal loadings are shown in Figures 4-6. From the experimental results, we found that acetaldehyde and H₂ were main reaction products. Therefore, it can be concluded that the reaction proceeds via the following equation.

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \tag{3}$$

The non-oxidative dehydrogenation of ethanol was carried out at 200-400°C temperature range. Different loadings of Cu, Ag, and Cu-Ag were carried out in order to elucidate the effect of metal loading on the non-oxidative dehydrogenation of ethanol. Their performance in terms of ethanol conversion, acetaldehyde yield and H₂ yield were evaluated. A series of Cu/SiO₂ catalysts with Cu loadings from 2.5 to 10 wt.% was tested, as presented in Figure 4. It can be seen that the ethanol conversion, acetaldehyde yield, and hydrogen yield increased when increasing Cu loading from 2.5 to 5 wt.% whereas they inversely decrease at Cu loading of 10 wt.%. Among Cu/SiO2 catalysts, the 5 wt.% Cu/SiO2 showed the best catalytic activity for dehydrogenation of ethanol with ethanol conversion of 48%, acetaldehyde yield of 39%, and hydrogen yield of 46 % at 400°C. However, the performance of copper catalysts is usually rapid deactivation especially at high temperature because of sintering of copper particles.

In the case of Ag/SiO₂ catalysts, as shown in Figure 5, it was found that the ethanol conversion and product yields increased when the reaction temperature increased from 250 to 400°C. The highest catalyst performance of Ag/SiO₂ catalysts was 10 wt.% Ag loading at all reaction temperatures. The highest ethanol conversion, acetaldehyde and hydrogen yields at a reaction temperature of 400°C were 57, 44, and 50%, respectively. Moreover, the result showed that the Ag/SiO₂ was more active than the Cu/SiO₂ for the dehydrogenation of ethanol to acetaldehyde and hydrogen at 10 wt.% metal loading and 400°C.



Figure 3. TPR profiles of (a) Cu/SiO₂, (b) Ag/SiO₂, and (c) Cu-Ag/SiO₂ at different total metal loadings.



Figure 4. Ethanol conversion, acetaldehyde and hydrogen yields as a function of reaction temperature for non-oxidative dehydrogenation of ethanol over (a) 2.5 wt.% Cu/SiO₂, (b) 5 wt.% Cu/SiO₂, and (c) 10 wt.% Cu/SiO₂. (\blacksquare Ethanol conversion, \square Acetaldehyde yield and \square Hydrogen yield).



Figure 5. Ethanol conversion, acetaldehyde and hydrogen yields as a function of reaction temperature for non-oxidative dehydrogenation of ethanol over at (a) 2.5 wt.% Ag/SiO₂, (b) 5 wt.% Ag/SiO₂, and (c) 10 wt.% Ag/SiO₂. (\blacksquare Ethanol conversion, \square Acetaldehyde yield and \square Hydrogen yield).



Figure 6. Ethanol conversion, acetaldehyde and hydrogen yields as a function of reaction temperature for non-oxidative dehydrogenation of ethanol over (a) 2.5 wt.% Cu-Ag/SiO₂ (b) 5 wt.% Cu-Ag/SiO₂, and (c) 10 wt.% Cu-Ag/SiO₂. (\blacksquare Ethanol conversion, \square Acetaldehyde yield and \square Hydrogen yield).

Bimetallic Cu-Ag catalysts at 2.5-10 wt.% total metal loading were also tested for comparison. It was also observed that the catalyst activity of bimetallic Cu-Ag/SiO₂ increased with increasing total metal loading and reaction temperature. Moreover, the results revealed that the multicomponent or bimetallic catalysts exhibited superior activity compared to the monometallic catalysts. The addition of Cu considerably promoted the catalytic activity of Ag/SiO₂ catalysts. At 400°C, 10 wt.% Cu-Ag/SiO₂ showed the best catalytic activity for non-oxidative dehydrogenation of ethanol with ethanol conversion of 53%, acetaldehyde yield of 42%, and hydrogen yield of 49%. This result suggests the benefit of using Cu to partially replace Ag for improving catalysts and cost reduction.

It should be noted that the monometallic Ag/SiO₂ and bimetallic Cu-Ag/SiO₂ catalysts at 10 wt.% metal loading were good candidate catalysts for non-oxidative dehydrogenation of ethanol at 250-400°C because they provided the highest ethanol conversion and product yields. Figure 7 presents stability test of 10 wt.% Ag/SiO₂ and 10 wt.% Cu-Ag/SiO₂ catalysts at 400°C. Within 12 h of operation, bimetallic Cu-Ag/SiO₂ exhibited slight deactivation. The stability of bimetallic Cu-Ag/SiO₂ was much better than monometallic Ag/SiO₂ catalyst. Therefore, this highlights the successful development of catalyst and process for ethanol conversion in this work.



Figure 7. Acetaldehyde yield as a function of time over 10 wt.% Ag/SiO_2 and 10 wt.% $Cu-Ag/SiO_2$ for non-oxidative dehydrogenation of ethanol operated at 400°C for 12 h. (\blacksquare 10 wt.% Ag/SiO_2 , \bullet 10 wt.% $Cu-Ag/SiO_2$).

4. Conclusions

In this work, the influence of types of metal catalysts and metal loadings on catalytic non-oxidative dehydrogenation of ethanol into acetaldehyde and hydrogen was investigated. Monometallic Cu, Ag and bimetallic Ag-Cu catalysts at 2.5, 5, and 10 wt.% metal loadings were investigated. It was found that catalytic activity over monometallic Cu/SiO₂ and Ag/SiO₂ catalysts increased with increasing metal loading from 2.5 to 10 wt.% and reaction temperature from 250 to 400°C except over 10 wt.% Cu/SiO₂ catalyst. The addition of Cu over Ag to form a bimetallic Cu-Ag catalyst considerably promoted the activity of monometallic Cu/SiO₂ and Ag/SiO₂ catalysts.

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