HYDROGEN AND ACETALDEHYDE PRODUCTION FROM CATALYTIC DEHYDROGENATION OF ETHANOL

MS. SANSANEE TOTONG
ID: 55300700515

A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF ENGINEERING
IN ENERGY TECHNOLOGY AND MANAGEMENT

THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT
AT KING MONGKUT'S UNIVERSITY OF TECHNOLOGY THONBURI

2ND SEMESTER 2013

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Thesis Committee

.... (Assoc. Prof. Dr. Navadol Laosiripojana)	Advisor
Kajornsak Faungnawakij (Dr. Kajornsak Faungnawakij)	Co-Advisor
.... (Asst. Prof. Dr. Worapon Kiatkittipong)	Member
Nawin V. (Dr. NawinViriya-empikul)	Member
.... (Prof. Dr. Suttichai Assabumrungrat)	External Examiner

Thesis Title: Hydrogen and Acetaldehyde Production from Catalytic Dehydrogenation of Ethanol

Student's name, organization and telephone/fax numbers/e-mail

Ms. Sansanee Totong
The Joint Graduate School of Energy and Environment (JGSEE)
King Mongkut's University of Technology Thonburi (KMUTT)
126 Pracha Uthit Rd., Bangmod, Tungkru, Bangkok 10140 Thailand
Telephone: 0-9242-00404, 0-8354-95477
E-mail: sansanee.tt@gmail.com, nn_ssn_tt@hotmail.com

Supervisor's name, organization and telephone/fax numbers/e-mail

Assoc. Prof. Dr. Navadol Laosiripojana
The Joint Graduate School of Energy and Environment (JGSEE)
King Mongkut's University of Technology Thonburi (KMUTT)
126 Pracha Uthit Rd., Bangmod, Tungkru, Bangkok 10140 Thailand
Telephone: 02-872-6736 ext 4146
E-mail: navadol_l@jgsee.kmutt.ac.th

Topic: Hydrogen and Acetaldehyde Production from Catalytic Dehydrogenation of Ethanol
Name of student: Ms. Sansanee Totong **Student ID:** 55300700515
Name of supervisor: Assoc. Prof. Dr. Navadol Laosiripojana
Name of co-supervisor: Dr. Kajornsak Faungnawakij

ABSTRACT

The aim of this research is to produce acetaldehyde and hydrogen through a catalytic dehydrogenation of ethanol. In this research, Cu, Ag, and bimetallic Cu-Ag supported by SiO_2 were prepared with the metal loading of 2.5-10% and applied as catalysts. They were synthesized by the conventional impregnation technique and the microwave-assisted technique, and tested in the ethanol dehydrogenation reaction under the temperature range of 250-400°C. Catalyst physical and chemical characterizations by BET, XRD, and TPR were carried out in order to elucidate the effect of active metal types, metal loading, and catalyst preparation methods on the ethanol dehydrogenation activity. From the studies, it is revealed that types of active metals, metal loading, and catalyst preparation methods had a significant influence on the reactivity. For all different metal loading (2.5, 5, and 10 wt.% of Cu, Ag, and mixed Cu-Ag) prepared by conventional impregnation technique, the catalyst activity increased with increasing metal loading and reaction temperature except at 10 wt.% Cu/SiO_2 catalyst. This was probably due to Cu loading increasing as a result of poor dispersion of Cu metal on support surface. In addition, bimetallic $Cu\text{-}Ag/SiO_2$ enhanced reaction activity higher than monometallic Ag. It was also found that the catalysts prepared by microwave-assisted technique were more active than the catalyst prepared by the conventional impregnation technique, which could be mainly due to the dispersion improvement of metal over support by this preparation. Among all catalysts, bimetallic $Cu\text{-}Ag/SiO_2$ prepared by microwave-assisted technique showed the highest activity and stability after 12 h of reaction.

Keywords: Acetaldehyde, Dehydrogenation, Ethanol, Hydrogen, Microwave-assisted technique

ACKNOWLEDGEMENTS

I would like to express my great appreciation to my advisor and co-advisor, Assoc. Prof. Dr. Navadol Laosiripojana and Dr. Kajornsak Faungnawakij, for their helpful ideas, valuable guidance, support and affectionate encouragement throughout my research.

Moreover, I am grateful to my thesis committee members, Dr. Nawin Viriya-empikul and Asst. Prof. Dr.Worapon Kiatkittipong, and my external examiner, Prof. Dr. Suttichai Assabumrungrat, for their time, advice and useful suggestions.

I would also like to thank the Joint Graduate School of Energy and Environment (JGSEE) for the scholarship, financial support, the affectionate lecture and the helpful staff.

Finally, I am really grateful to the Nanomaterials for Energy and Catalysis Laboratory (NEC), National Science and Technology Development Agency (NSTDA) for laboratory setup, facilities efficient laboratory, analytical techniques and instruments (i.e. BET, TPR-H_2, XRD measurements).

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CHAPTER 1

INTRODUCTION

1.1 Rationale/Problem Statement

Nowadays, energy is one of the key elements in driving global activities and daily life, so global energy demand is increasing continuously. More than 90 percent of the world's primary energy supply comes from fossil fuels i.e., coal, crude oil, natural gas and their byproducts. Normally, the primary consumer of the energy can divide to four main sectors; the first sector is industrial sector, the second sector is transportation, the third sector is residential and the finally is commercial sector. Therefore, the amounts of fossil fuels are dramatically decreasing and not enough for energy consumption in the future. In addition, the energy usage by the burning of fossil fuels will release large amount of toxic gases (i.e., carbon dioxide, carbon monoxide, nitrous oxide, methane etc.) which are the main cause to produce environment pollutions, greenhouse effects, climate change and affect to a living organisms on the earth. Therefore, there is significantly effort being placed into researching alternative and/or renewable energies to instead of petroleum fuels. The alternative and/or renewable energies are known to be clean and environmental friendly. Some important examples of renewable energy resources include wind, hydropower, solar, geothermal energy and biomass.

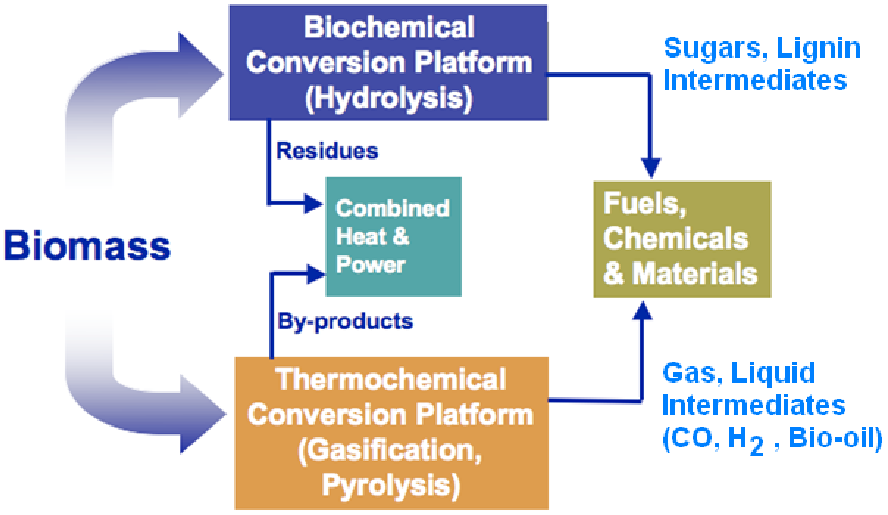

Figure 1.1 The biorefinery concept.

Among them, biomass is one of the most important renewable energy resources, because it can be re-grown, regenerated and recycled. Moreover, it has high potential to replace petroleum fuel, because it contains carbon and hydrogen compounds as the main components and can be converted to various products, such as fuels, chemicals, materials, heat and power. Currently, there are several attempts by the researchers to transform biomass to useful and high value products, as in biorefinery processes. The concept of the biorefinery process is shown in **Figure 1.1**.

In the process of biomass conversion to fuels, chemicals and several products can be generated, such as ethanol, furans, organic acids, liquid alkenes, polylactic acid, etc. Among these products, one of the most important chemicals is ethanol because it is potentially a promising platform molecule for the production of a variety of value-added chemicals. Moreover, it is easily and readily produced by fermentation of sugar, molasses and lignocellulosic biomass. Ethanol is one of the most relevant potential sources of “bio-carbon” and high hydrogen content. The pathways of ethanol conversion into various products or chemicals are presented in **Figure 1.2**. This covers hydrogen, small oxygenates (i.e., acetaldehyde, 1-buanol, etc.) and hydrocarbons ranging from light olefins to longer chain alkenes, alkanes and aromatics.

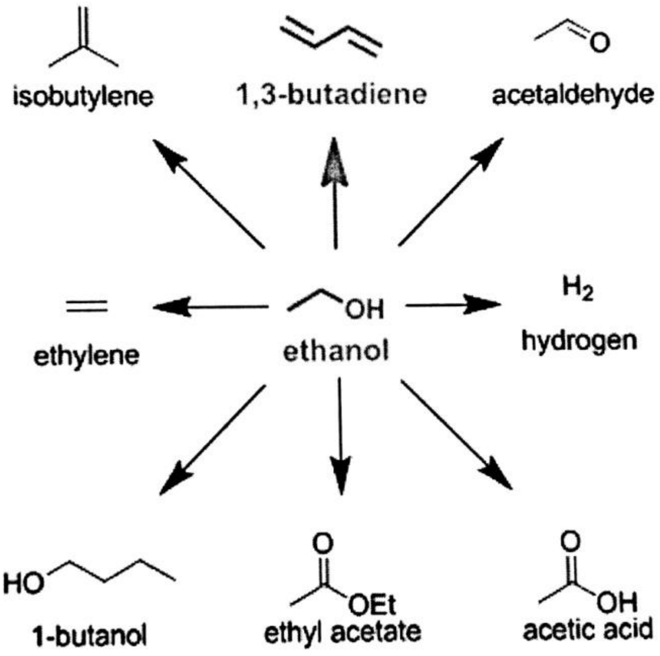

Figure 1.2 The ethanol conversion into various chemicals *(Carlo Angelici et al, 2013).*

The development of conversion of ethanol into various products or chemicals is interesting in the present, especially, acetaldehyde production, because there are an important energy resources and building blocks for the chemical industries in the future. The market price of acetaldehyde in the present is high because raw material (ethylene and acetylene; product from petrochemical process) for acetaldehyde production is increasing. So, the acetaldehyde production from ethanol is the process which can helps to reduce production cost and it is also increased the value of ethanol. An acetaldehyde is an important intermediate in the production of acetic acid, acetate esters, acetic anhydride, ethyl acetate, peracetic acid, 1,3-Butylene glycol, butanol, butadiene, 2-ethylhexanol, pentaerythritol, chlorinated acetaldehydes (chloral), glyoxal, alkyl amines, pyridines, pyridine base and other chemicals. The consumption of acetaldehyde for some other chemical production in many countries is presented in **Table 1.1**.

Table 1.1 The consumption of acetaldehyde (10^3 t) in 2003 [1].

Product	**USA**	**Mexico**	**W. Europe**	**Japan**	**Total**
Acetic acid/acetic anhydride	-	11	89	47	147
Acetate esters	35	8	54	224	321
Pentaerythritol	26	-	43	11	80
Pyridine and pyridine bases	73	-	10	*	83
Peracetic acid	23	-	-	*	23
1,3-Butylene glycol	14	-	-	*	14
Others	5	3	10	80	98
Total	176	22	206	326	766

* Included in others (glyoxal/glyoxalic acid, crotonaldehyde, lactic acid, n-butanol, 2-ethylhexanol).

Currently, an acetaldehyde can be synthesized by various methods such as partial oxidation of ethanol or ethylene that are shown in reactions (1) and (2) respectively, hydration of acetylene; reaction (3) and ethanol dehydrogenation; reaction (4).

$$CH_3CH_2OH + 1/2O_2 \rightarrow CH_3CHO+H_2O \qquad (1)$$

$$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO \qquad (2)$$

$$C_2H_2 + H_2O \rightarrow CH_3CHO \qquad (3)$$

$$CH_3CH_3OH \rightarrow CH_3CHO + H_2 \qquad (4)$$

The catalytic dehydrogenation of ethanol is an interesting alternative process to produce acetaldehyde because this method uses only one reactant. Moreover, this process also produces hydrogen as a co-product. The hydrogen formed is pure enough to be used directly for hydrogenation. Hydrogen can be used as a fuel substitute for fossil fuels, primary chemical feedstock to produce various chemical products such as ammonia and methanol, direct fuels and as a reactant fed into fuel cells to produce electricity [2]. Normally, the dehydrogenation of ethanol is usually done over Cu-catalysts activated with Zn, Co, or Cr. The temperature is regulated to 270-300°C so that the ethanol conversion is limited to 30-50%. The selectivity to acetaldehyde of 90-95% is attained. Byproducts include crotonaldehyde, ethyl acetate, higher alcohols, and ethylene.

In this research, the catalytic dehydrogenation of ethanol was selected as the process for acetaldehyde and hydrogen production. The Cu-catalyst, Ag-catalyst and modified Cu-catalyst (Cu-Ag catalyst) were used for catalyst activity testing. The suitable catalyst and optimized condition of reaction were studied to maximizing ethanol conversion and yields of acetaldehyde and hydrogen.

1.2 Literature Review

This review focuses on previous works related to the dehydrogenation of ethanol and acetaldehyde production for the dehydrogenation of ethanol. All previous research works have investigated the background information about the reaction, the suitable catalyst for the reaction and factors influencing their significance. Furthermore, a comprehensive literature review is presented the observation about technologies and development of this field.

1.2.1 Ethanol Dehydrogenation

An extensive amount of literature concerning the dehydrogenation of ethanol was investigated. Copper-based catalysts were frequently used in various reactions, such as methanol synthesis [3,4], gas shift reactions [5,6], and alcohol dehydration or dehydrogenation [7,8]. However, the performance of copper catalyst is usually confined to rapid deactivation which results from sintering due to the metal copper have a low melting point. Therefore, an adequate support is particularly necessary for distributing copper particles to avoid, or at least retard the occurrence of sintering. It has been well documented in some reacting systems that the support of a catalyst plays not only the role of an inert material for increasing the degree of metal dispersion, promoting thermal stability and modifying mechanical properties, but also the role of an active species.

Copper-on-silica catalysts have shown good activities for a variety of reactions, such as methanol and ethanol dehydrogenation, steam reforming of methanol, ester hydrogenolysis and nitrogen oxide transformation [9-14]. The dispersion of the metal over the support is an important factor. Such dispersion can be well established by the ion exchange method. This method was first reported by Kobayashi et al. [15]. Several parameters, such as the copper concentration in the preparation solution, the pH, the type of silica used, and the washing procedure, were found to influence the copper loading of the dried catalyst. This technique was most widely studied by Kohler et al. [16], Sodesawa [17], and Takesawa et al. [18]; the authors claimed that both high metal dispersions and high activities are achieved by means of this method.

Chang *et al.* [19] studied a samples of copper on rice husk ash (Cu/RHA) and other silica support that were prepared by incipient wetness impregnation and ion exchange. Such samples were tested for dehydrogenation of ethanol to acetaldehyde. The effects of metal loading, calcination temperature and reaction temperature of the catalysts have been investigated. For the samples which have been prepared by incipient wetness impregnation and tested at the reaction temperature of 250^{o}C, the effects of copper loading (vary from 1 to 15 wt.%) on the ethanol conversion or acetaldehyde yield for ethanol dehydrogenation is shown in **Figure 1.3**. The initial (at 5 min after a run of the reaction proceeds) can be found that the ethanol conversion increased with the increased copper loading from 1 to 10 wt.%, followed by a slight drop in conversion as loading increased up to 15 wt.%. The catalyst with 5 wt.% copper loading has the smallest conversion dropping from 83 to 62% within 3 hours so, it is a suitable copper loading for using as catalyst in this reaction.

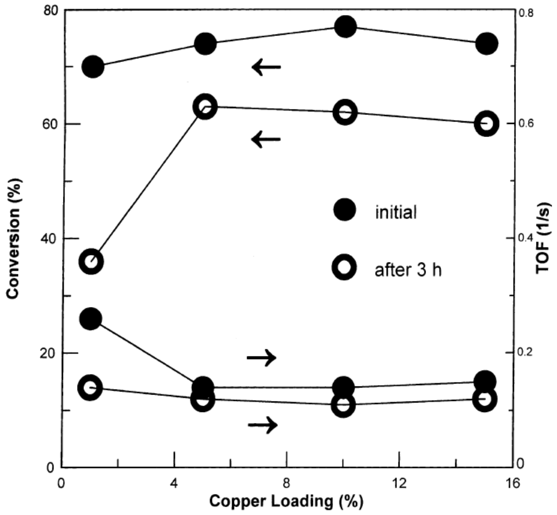

Figure 1.3 Effects of copper loading on ethanol conversion and turnover frequency (TOF) for ethanol dehydrogenation (reaction temperature, 250°C).

The effects of reaction temperature and silica support on ethanol conversion for ethanol dehydrogenation were studied. The results are shown in **Figure 1.4**. It was found that when the reaction temperature is increased from 200 to 300°C, the initial conversion increases from 68 to 81% for the reaction system catalyzed by Cu/RHA, while it increases from 62 to 74% by Cu/SiO$_2$. In conclusion, Cu/RHA catalysts have a lower deactivation rate and higher catalytic activity in comparison with Cu/SiO$_2$ catalysts with the same copper loading. Therefore, one can conclude that Cu/RHA with the same copper loading for ethanol dehydrogenation.

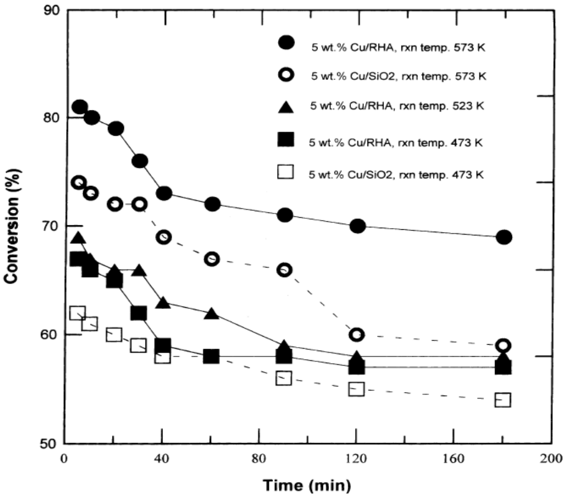

Figure 1.4 Effects of reaction temperature on ethanol conversion for ethanol dehydrogenation.

Chang *et al.* [20] studied samples prepared by ion exchange. The effect of calcined temperature (vary from 350 to 700°C) on the catalytic behavior of 5.75 wt.% Cu/RHA catalysts for dehydrogenation of ethanol at 275°C was shown **Figure 1.5**. It was found that the optimum calcined temperature for ethanol dehydrogenation is 450°C. **Figure 1.6** shows the effects of copper loading over Cu/RHA catalyst on ethanol conversion, a slight increase in ethanol conversion when increasing copper loading of Cu/RHA catalyst.

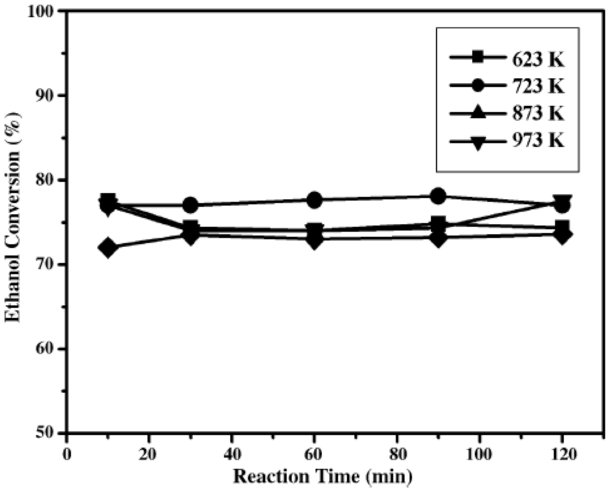

Fig. 1.5 Effects of calcined temperature on ethanol conversion for dehydrogenation of ethanol over 5.75 wt.% Cu/RHA catalysts (reaction temperature, 275°C).

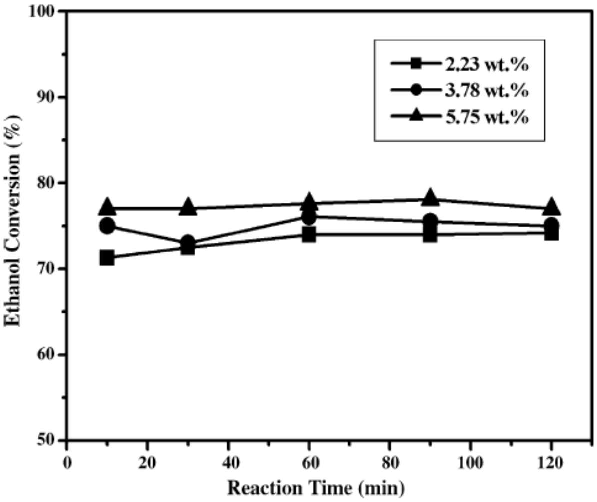

Figure 1.6 Effects of copper loading on ethanol conversion for dehydrogenation of ethanol over Cu/RHA catalysts (reaction temperature, 275°C and calcined temperature, 450°C).

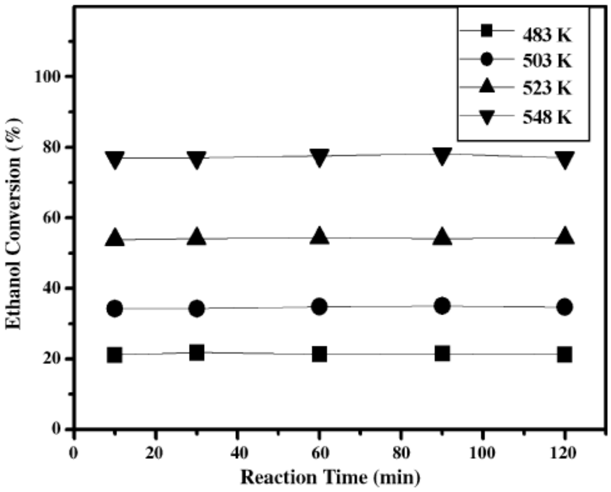

Fig. 1.7 Effects of reaction temperature on ethanol conversion for dehydrogenation of ethanol over 5.75 wt.% Cu/RHA catalysts (calcined temperature, 450°C).

In addition, the effects of reaction temperature on the ethanol conversion over Cu/RHA catalysts, were also studied as shown in **Figure 1.7**. The ethanol conversion increased from 22.1 to 77.0% with rise in reaction temperature from 210 to 275°C. The highest ethanol conversion is 77% when ethanol dehydrogenation reaction occurs at temperature of 275°C. In that research, the copper catalysts supported on rice husk ash (RAH) prepared by ion exchange technique are found to be active and stable for dehydrogenation of ethanol to produce acetaldehyde. Ethanol conversion is found to be independent of calcined temperature, reaction temperature and to have little effect on Cu loading. The Cu/RHA catalysts exhibit higher catalytic activity and lower deactivation rate in comparison with Cu/SiO_2 catalysts and Cu/RHA catalysts which have been prepared by incipient wetness impregnation, shown in the previous work.

Another interesting report, Sato *et al.* [21] investigated the origins and influences of active sites on supported copper catalysts, and their catalytic properties for ethanol conversion using Cu/SiO_2, Cu_2O/SiO_2 and Cu/ZrO_2. The changes in catalytic activity and selectivity for ZrO_2, and for Cu supported on SiO_2 or ZrO_2 are presented in **Table 1.2**. The products formed during ethanol conversion on Cu/SiO_2 and Cu/ZrO_2 were acetaldehyde (AcH), ethyl acetate (AcOEt), methyl ethyl ketone (MEK), butanol (BOL), crotonaldehyde (CROT), diethyl ether (DEE), ethylene (ETE), propanone (PrO), CO and CO_2. The action of Cu/SiO_2 was mainly in the dehydrogenation of ethanol, as shown by a selectivity for acetaldehyde (S_{AcH}=87%). The Cu_2O/SiO_2 catalyst was the highest selective for dehydrogenation of ethanol to acetaldehyde (S_{AcH}=100%). Reaction of ethanol on the ZrO_2 support formed products of the dehydration of ethanol (DEE and ETE).

Table 1.2 Products distribution in ethanol reaction over Cu/ZrO_2, Cu/SiO_2 and Cu_2O/SiO_2.

Run	T(K)	Reactant feed	Catalyst	Ethanol Conversion (%)	Selectivity (%)							AcOEt formation rate (mmol/g_{cat} h)
					AcH	AcOEt	MEK/ BOL	CROT	DEE	ETE	Others	
1	498	EtOH	Cu/SiO_2	41	87	5.3	6.3	0.7	0.4	0.3	–	0.34
2	473	EtOH	Cu/ZrO_2	45	23	13	2.0	1.3	0.4	-	0.3	5.12
3	498	EtOH	ZrO_2	0.7	30	-	-	-	46	17	7.0	-
4	498	EtOH	$(Cu/SiO_2/ZrO_2)$	41	66	11	7.8	14	0.5	0.2	0.5	0.70
5	498	EtOH	Cu/SiO_2+ZrO_2 mixed	47	51	11	18	19	0.6	0.1	0.3	0.81
6	473	EtOH +AcHc	Cu/ZrO_2	43	32	54	5.3	7.4	0.2	0.1	1.0	3.62
7	523	EtOH	Cu_2O/SiO_2	45	100	-	-	-	-	-	-	-

1.2.2 Acetaldehyde from Dehydrogenation of Ethanol

Acetaldehyde production from the dehydrogenation of ethanol were widely investigated because acetaldehyde is a high-value chemical and is used as the raw material to produce other chemicals, i.e. acetic acid, ethyl acetate, butadiene and butanol.

Iwasa *et al.* [22] studied the catalytic performances over various supported Pd catalysts for the dehydrogenation of ethanol. The various metal oxides, i.e., ZnO, Ga_2O_3, In_2O_3, MgO , SiO_2 and Al_2O_3 were selected as a support. Dehydrogenation of ethanol was carried out in a conventional flow reactor at 493K. **Figure 1.8** shows the selectivities to carbon-containing products, the conversion of ethanol and the turnover frequency for the hydrogen formation at 493 K over various supported Pd catalysts prepared. They was found that over Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3, acetaldehyde is produced with high selectivity, while over the other supported Pd catalysts and Pd black methane and carbon monoxide are produced. Over Pd/Ga_2O_3 and Pd/In_2O_3 ethyl acetate was formed along with acetaldehyde.

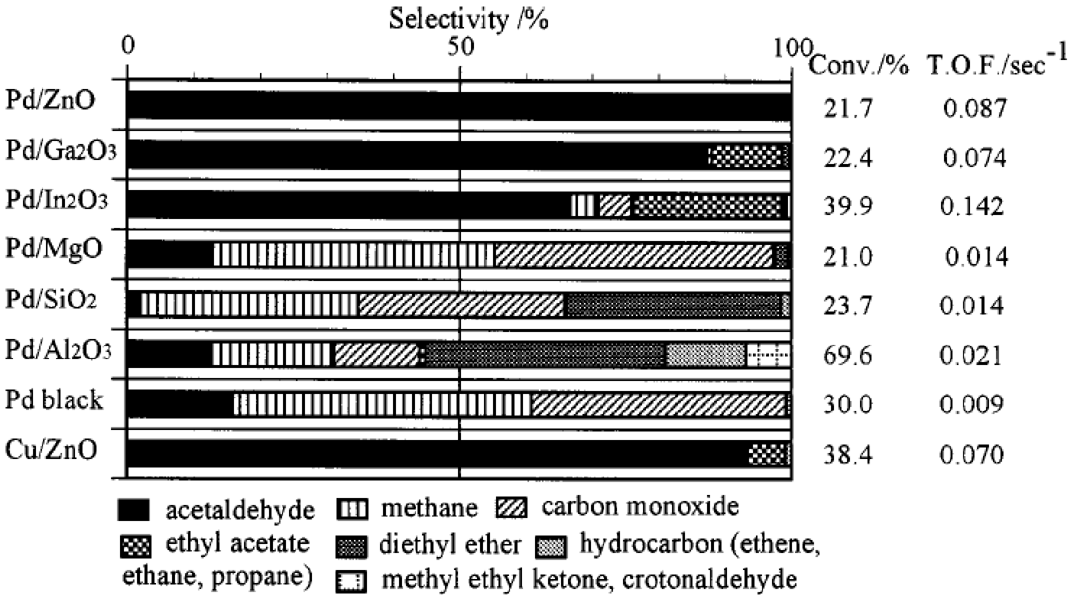

Figure 1.8 Selectivity of carbon-containing products in the dehydrogenation of ethanol at 493 K.

The effects of the reaction temperature upon the dehydrogenation of ethanol over Pd/ZnO are shown in **Figure 1.9**. From the results, hydrogen and acetaldehyde were produced nearly in 1:1 molar ratio along with a small amount of ethyl acetate and no other products were formed. The mole fraction of hydrogen and acetaldehyde were increased rapidly with the increased reaction temperature, while that of ethyl acetate increases slowly with reaction temperature.

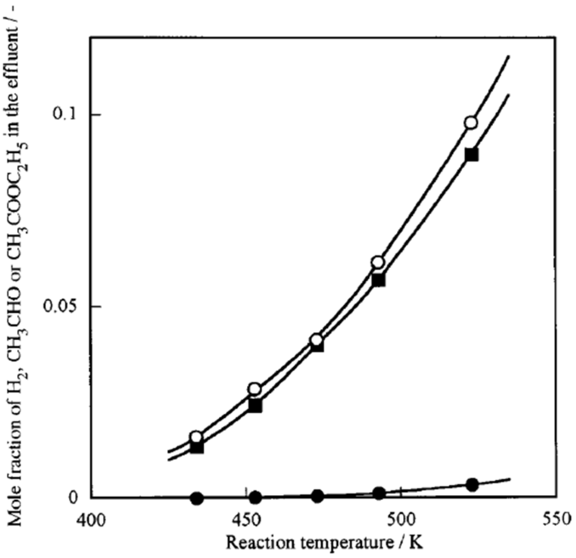

Figure 1.9 Mole fractions of hydrogen, acetaldehyde and ethyl acetate against reaction temperature over Pd/ZnO catalysts. (o) H_2, (■) CH_3CHO and (●) $CH_3COOC_2H_5$.

Figures 1.10(A) and **(B)** present the mole fraction of hydrogen, acetaldehyde, ethyl acetate, methane and carbon monoxide in the effluent against space time over Pd/ZnO prepared and over Pd black, respectively. For Pd/ZnO, the mole fraction of acetaldehyde in the effluent increases with the increased space time, passes through a maximum and decreases gradually, while that of ethyl acetate increases with space time. These results suggested that ethyl acetate is produced through acetaldehyde. For Pd black, the mole fraction of acetaldehyde increases with space time, showing a maximum, and then decreases. Methane and carbon monoxide are produced nearly in 1:1 molar ratio. They increase with increasing space time. No ethyl acetate was produced over Pd black.

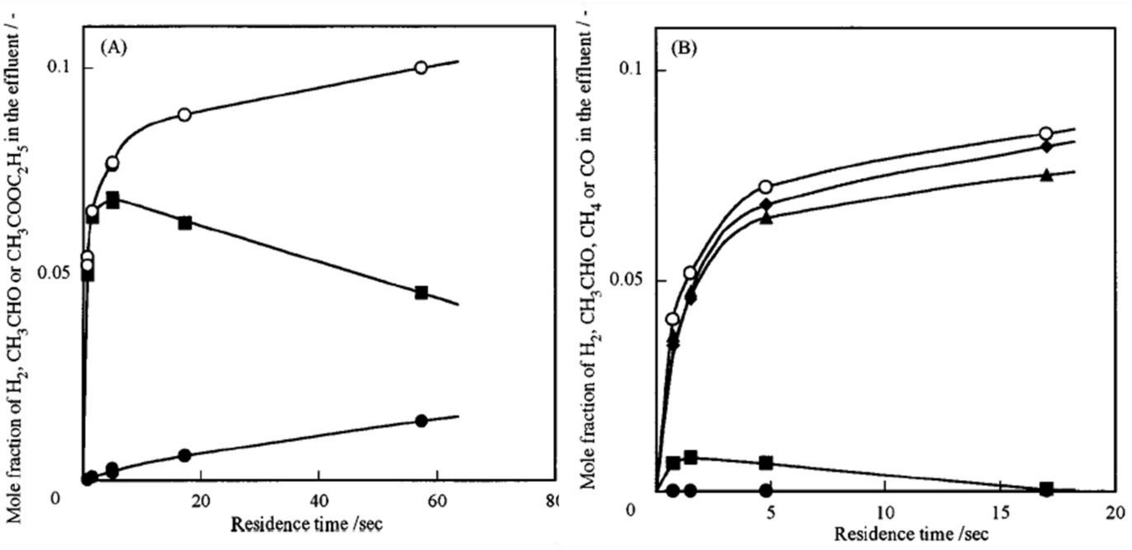

Figure 1.10 Mole fractions of hydrogen, acetaldehyde, ethyl acetate, methane and carbon monoxide in the effluent against the space time (A) Pd/ZnO and (B) Pd black; (o) H_2, (■) CH_3CHO, (●) $CH_3COOC_2H_5$, (♦) CH_4 and (▲) CO.

Arthit *et al.* [23] studied the catalytic ethanol dehydrogenation to acetaldehyde over nickel-based catalysts. SnO_2, Al_2O_3 and SiO_2 were used as supporting materials. The reactions were carried out in a catalytic flow system operated in the temperature range of 200 and 350°C under atmospheric pressure. Various parameters such as Ni loading, a kind of supporting materials, contact time on the ethanol conversion and selectivity to acetaldehyde were investigated. The main product in all cases is acetaldehyde, with secondary products such as ethyl acetate and diethyl ether.

Table 1.3 Ethanol conversion and acetaldehyde selectivity at 200–350°C over Ni-based catalyst. Conditions: total flow rate 40 ml/min (10% EtOH), catalyst weight: 1 g, 5 wt.% Ni loading.

Temp (°C)	**Conversion (%)**			**Acetaldehyde selectivity (%)**		
	Ni/SnO_2	**Ni/Al_2O_3**	**Ni/SiO_2**	**Ni/SnO_2**	**Ni/Al_2O_3**	**Ni/SiO_2**
200	1.24	0.29	0.43	100	100	100
250	9.23	1.25	1.99	98.87	77.71	97.98
300	41.48	7.55	7.45	83.73	59.47	77.13
350	33.11	24.64	0	84.07	53.78	0

First, they studied ethanol conversion and acetaldehyde selectivity at 200–350°C over Ni based catalysts useing different supporting materials. It has been found that Ni/SnO_2 showed the highest ethanol conversion with high selectivity to acetaldehyde. After that they have studied the effect of Ni loading and contact time of the catalyst activity as shown in **Figure 1.11** and **Figure 1.12** respectively. The 10 wt.% Ni/SnO_2 exhibited the highest yield of acetaldehyde at 300°C with low contact time (0.05 g min ml^{-1}). The deactivation of 10 wt.% Ni/SnO_2 was occurred after 200 minutes on stream due to the formation of Ni–Sn alloy phase.

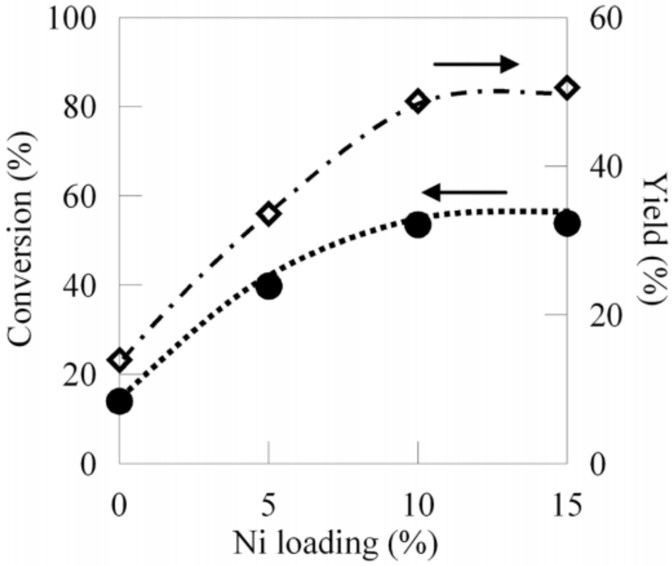

Figure 1.11 Ethanol conversion and acetaldehyde yield over Ni/SnO_2 as a function of Ni loading at 300°C; ◊ acetaldehyde yield and ● ethanol conversion.

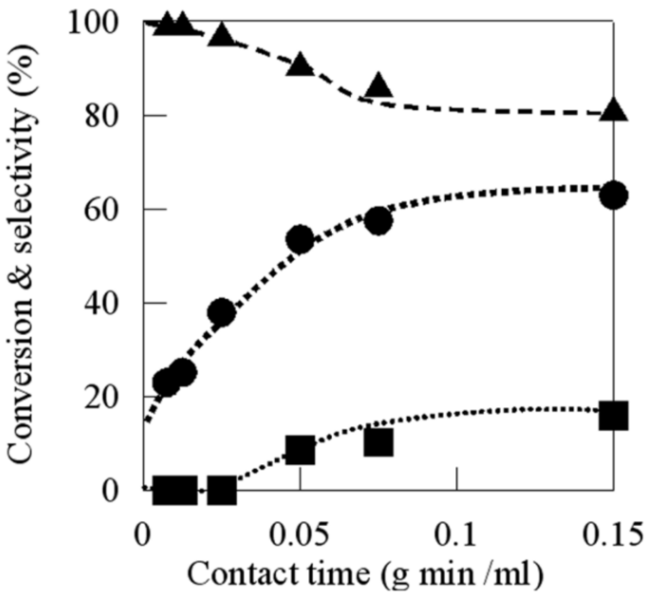

Figure 1.12 Ethanol conversion, acetaldehyde and ethyl acetate selectivity over 10 wt% Ni/ SnO_2 as a function of contact time at 300°C; ▲ acetaldehyde selectivity, ● ethanol conversion and ■ ethyl acetate selectivity.

Hayder [24] has investigated the conversion of ethanol to acetaldehyde using NiO/Al_2O_3 catalyst. They have studied the effects of the reaction temperature, ethanol feed flow rate and ethanol concentration on the conversion of ethanol and yield of acetaldehyde. The results of these effects are illustrated in **Figure 1.13, Figure 1.14** and **Figure 1.15** respectively**.**

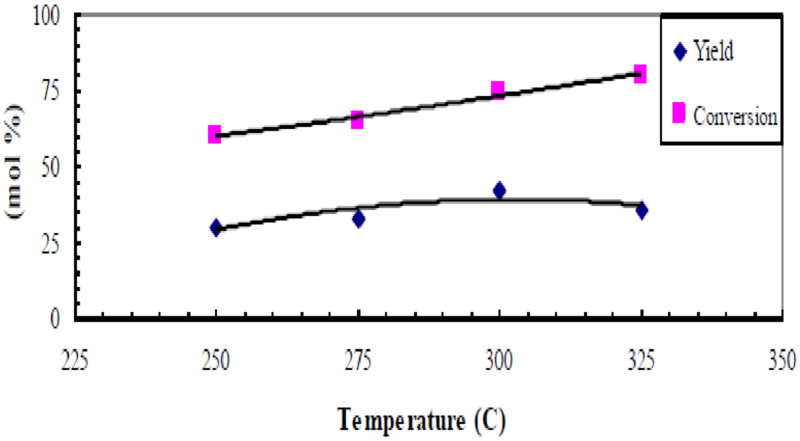

Figure 1.13 Effects of reaction temperature on ethanol conversion and acetaldehyde yield for NiO/Al_2O_3 catalyst (F =3 ml/min, 95% Mole percent concentration of ethanol).

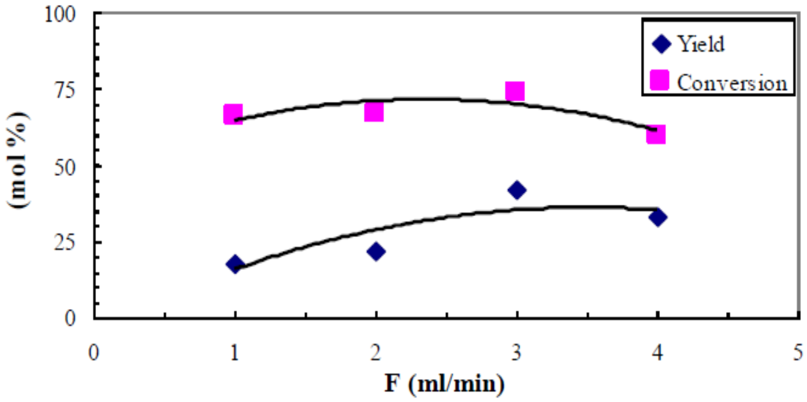

Figure 1.14 Effects of ethanol feed flow rate on ethanol conversion and acetaldehyde yield for NiO/Al_2O_3 catalyst (T= 300°C, 95% Mole percent concentration of ethanol).

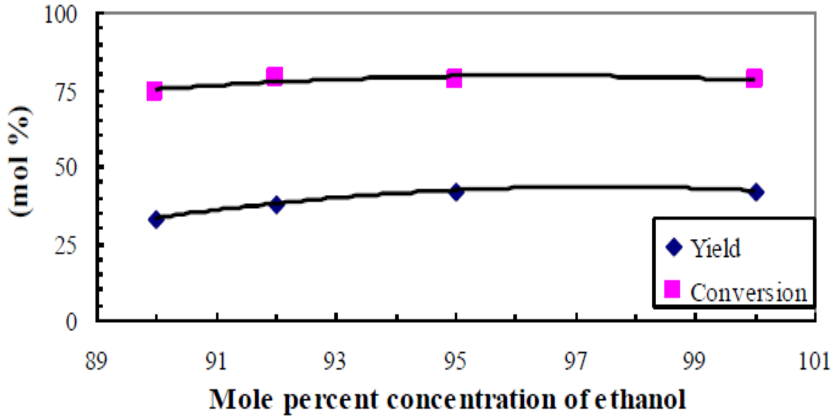

Figure 1.15 Effects of mole percent concentration on ethanol conversion and acetaldehyde yield for NiO/Al_2O_3 catalyst (T = 300°C, F =3 ml/min).

As seen in **Figure 1.13**, it was found that the conversion of ethanol and yield of acetaldehyde increased with increasing temperature. Then, the effect of ethanol flow rate was studied at different molar ratios of ethanol to water as shown in **Figure 1.14**. The ethanol conversion and acetaldehyde yield increased with increasing feed flow rate until flow rate 3 ml/min, then began to decrease. This decrease is attributed to the resulting decrease in contact time of the reactant. As the last effect, **Figure 1.15** shows the effect of water on acetaldehyde yield and ethanol conversion. From the conversion of ethanol to acetaldehyde using NiO/Al_2O_3 catalyst; the maximum yield of acetaldehyde is 43% mole and the conversion of ethanol is 74% mole at the optimum reaction conditions are reaction temperature (300°C), optimum flow rate (3 ml/min) and concentration of ethanol can be 95%.

1.3 Research Objectives

The aim of this research work is to study the potential of catalysts for the catalytic dehydrogenation of ethanol reaction to produce hydrogen and acetaldehyde. Copper (Cu) and silver (Ag) were selected as a metal and impregnated on silica support. For Cu/SiO_2, Ag/SiO_2 and Cu-Ag/SiO_2, different total metal content and preparation methods were firstly investigated to develop a novel catalyst. The synthesized catalyst were characterized by their properties, such as total surface area, pore diameter, pore volume, phase formation, etc. The suitable conditions for catalytic dehydrogenation of ethanol process were then studied. The results of catalytic performance were presented in term of percent conversion of ethanol, and hydrogen and acetaldehyde yield.

1.4 Scope of Research Work

- To determine the suitable type of catalysts and supports (i.e. Cu and Ag supported by SiO_2) for the catalytic dehydrogenation of ethanol in terms of activity.
- To study the effect of the catalyst preparation processes (i.e. typical impregnation and microwave-assisted method) for the conversion of ethanol to hydrogen and acetaldehyde.
- To study and optimize the operating conditions (i.e. temperature) for maximizing the yield of hydrogen and acetaldehyde production from the catalytic dehydrogenation of the ethanol reaction.

CHAPTER 2

THEORIES

2.1 Bioethanol

Ethanol (also called ethyl alcohol) is a hydrocarbon compound that consists of hydroxyl group (-OH) connected with hydrocarbon chain, as shown in **Figure 2.1**. The molecular formula of ethanol is C_2H_5OH. Generally, there are two main processes for the manufacture of ethanol; the chemical synthesis of ethylene and fermentation from sugar. Importantly, at the present ethanol can also be produced from renewable energy resources i.e. corn, cassava, rice husk, rice straw, biomass and lignocellulosic materials.

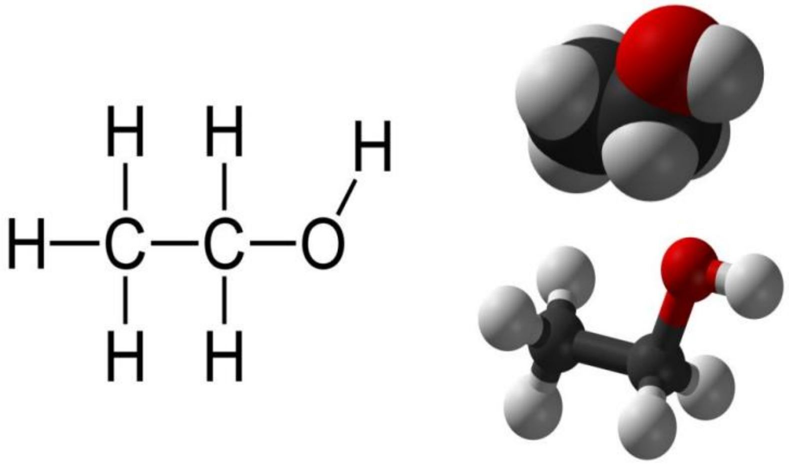

Figure 2.1 Schematic structure of ethanol.

Ethanol is an important industrial chemical. It is used as a solvent or raw materials in the synthesis of other chemicals and used as an additive to automotive gasoline (forming a mixture known as a gasohol). Ethanol also improves the combustion performance in vehicles and help to reduce the emission of carbon monoxide, unburned hydrocarbons and carcinogens.

2.2 Hydrogen

Hydrogen is the simplest, lightest, and also the most plentiful element in the universe. It is also found in many compounds such as water, gasoline, natural gas, methanol, ethanol and propane. At standard temperature and pressure, hydrogen is a colorless, odorless, highly flammable and combustible diatomic gas with the molecular formula H_2. Recently, hydrogen has become widely used as a feedstock in the petroleum and chemical industries. In the future, hydrogen will be an important energy carrier because it has high energy capacity, clean, is environmentally friendly and is sustainable. An energy carrier moves and delivers energy in a usable form to another form, for example, feed as a reactant for fuel cells to produce electricity, directly used as fuel in a fuel cell vehicle.

2.3 Acetaldehyde

2.3.1 Acetaldehyde Properties

Acetaldehyde is a saturated aldehyde with a pungent and suffocating odor, but at more dilute concentrations, the odor is fruity and pleasant. It has the chemical formula CH_3CHO and the structure of acetaldehyde is shown in **Figure 2.2**. It is a colorless liquid, volatile at room temperature, and both the liquid and the vapors are highly flammable. Acetaldehyde as a liquid is lighter than water, and the vapors are heavier than air. It is soluble in water, alcohol, ether, acetone, and benzene. The summary of physical and chemical properties of acetaldehyde is shown in **Table 2.1**.

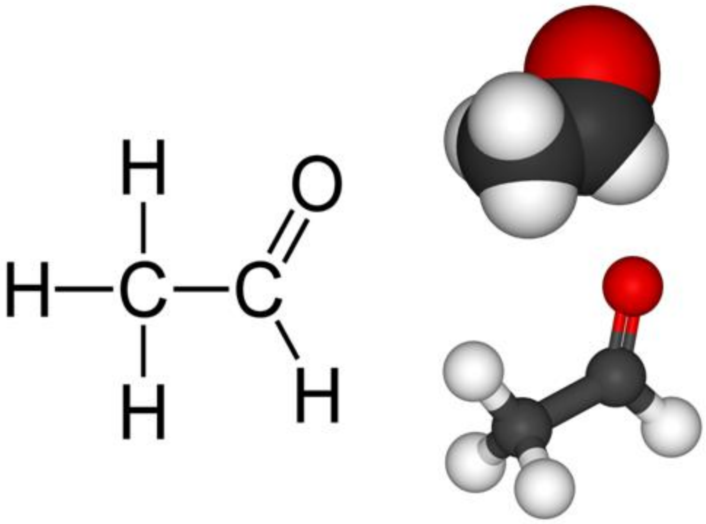

Figure 2.2 Schematic structure of acetaldehyde.

Table 2.1 The physical and chemical properties of acetaldehyde.

Property	**Characteristic**
Synonyms:	acetic aldehyde, aldehyde, ethanal, ethylaldehyde
Chemical formula:	CH_3CHO
CAS number:	75-07-0
Molecular weight:	44.05 g/mol
Color:	colorless to yellowish
Physical state:	Liquid
Melting point:	-123.5 ºC
Boiling point at 101.3 kPa (1 atm):	20.16 ºC
Density (liquid) at 20ºC:	0.7780 g/ml
Odor:	pungent and suffocating odor
Solubility:	
water at 25ºC	infinite
organic solvents	alcohol, ether, acetone, and benzene
Vapor density (air = 1):	1.52
Vapor pressure at 20ºC:	740 mmHg
Critical temperature:	181.5ºC
Critical pressure:	6400 kPa
Flash point:	
closed cup	-38ºC
open cup	-40ºC
Ignition temperature in air:	165ºC
Latent heat of vaporization:	25.71 kJ/mol
Heat of formation at 0ºC:	-165.48 kJ/mol ºC
Explosive limits:	4.5 – 60.5% by volume in air
Flammability:	extremely flammable liquid and vapor when exposed to heat and flame

2.3.2 History of Acetaldehyde

Acetaldehyde was one of the earlier organic compounds to be discovered. Acetaldehyde was first observed by the Swedish pharmacist/chemist Carl Wilhelm Scheele in 1774 in a reaction of black manganese dioxide and sulfuric acid with alcohol. Then in 1800, it was investigated by the French chemists Antoine François, comte de Fourcroy. The French chemists Louis Nicolas Vauquelin, the German chemists Johann Wolfgang Döbereiner and Justus von Liebig was investigated its properties in 1821. In 1835, Liebig was settled on the name "aldehyde" which would be changed the name to "acetaldehyde" in 1860s.

2.3.3 Acetaldehyde Applications

The largest use of acetaldehyde is as a chemical intermediate for the production of acetic acid. The production of esters, principally ethyl acetate and isobutyl acetate, is the second most significant use. It is used as an intermediate for a number of other chemicals, including pyridine and pyridine bases, pentaerythritol, peracetic acid, 1,3-butylene glycol, and chloral. Acetaldehyde is also used in silvering mirrors, hardening gelatin fibers, denaturing alcohol, and in the manufacture of disinfectants, dyes, drugs, explosives, flavorings, phenolic and urea resins, rubber accelerators and antioxidants, varnishes, and yeast.

2.3.4 Acetaldehyde Production

The economics of the various commercial processes for the manufacture of acetaldehyde are strongly dependent on the price and the ability of the feedstock. Since 1960, the liquid-phase oxidation of ethylene has been the process of choice. However, there is still commercial production by the partial oxidation of ethyl alcohol, the dehydrogenation of ethyl alcohol and the hydration of acetylene. Acetaldehyde is also formed as a co-product with ethyl alcohol and acetic acid.

2.3.4.1 Production from Ethylene

Ethylene is now the most important starting material for the production of acetaldehyde. Most of the present capacity works by the direct oxidation of ethylene (Wacker Process).

- Direct Oxidation of Ethylene

Wacker–Chemie and Farbwerke Hoechst, developed the direct liquid phase oxidation of ethylene in 1957 – 1959. The catalyst is an aqueous solution of $PdCl_2$ and $CuCl_2$. In 1894, F.C. Phillips observed the reaction of ethylene with an aqueous palladium chloride solution to form acetaldehyde.

$$C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$$

The metallic palladium is reoxidized to PdCl2 with CuCl2 and the cuprous chloride formed is reoxidized with oxygen or air.

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

$$2CuCl + 1/2\ O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

The net result is a process in which ethylene is oxidized continuously through a series of oxidation – reduction reactions.

$$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO \qquad \Delta H = -244\ kJ/mol$$

Studies of the reaction mechanism of the catalytic oxidation have suggested that a cis–hydroxyethylene–palladium π complex is formed initially, followed by an intramolecular exchange of hydrogen and palladium to give a gem–hydroxyethyl palladium species which leads to acetaldehyde and metallic palladium.

There are two variations for the production of acetaldehyde by the oxidation of ethylene: the one–stage process developed by Farbwerke Hoechst and the two–stage process developed by Wacker–Chemie.

In the one-stage process ethylene, oxygen, and recycle gas are directed to a vertical reactor for contact with the catalyst solution under slight pressure. The water evaporated during the reaction absorbs the heat evolved, and make-up water is fed as necessary to maintain the catalytic solution concentration. The gases are water-scrubbed and the resulting acetaldehyde solution is fed to a distillation column. The tail–gas from the scrubber is recycled to the reactor. Inerts are eliminated from the recycle gas in a bled-stream which flows to an auxiliary reactor for additional ethylene conversion. This oxidation process for olefins has been exploited commercially principally for the production of acetaldehyde, but the reaction can also be applied to the production of acetone from propylene and methyl ethyl ketone from butanes.

In the two–stage process, ethylene and oxygen (air) react in the liquid phase in two stages. In the first stage ethylene is almost completely converted to acetaldehyde in one pass in a tubular plug-flow reactor made of titanium. The reaction is conducted at 125-1300°C and 1.13 MPa (150 psig) palladium and cupric chloride catalysts. Acetaldehyde produced in the first reactor is removed from the reaction loop by adiabatic flashing in a tower. The flash step also removes the heat of reaction. The catalyst solution is recycled from the flash – tower base to the second stage (or oxidation) reactor where the cuprous salt is oxidized to the cupric state with air. The high pressure off – gas from the oxidation reactor, mostly nitrogen, is separated from the liquid – catalyst solution and scrubbed to remove acetaldehyde before venting. A small portion of the catalyst stream is heated in the catalyst regenerator to destroy undesirable copper oxalate. The flasher overhead is fed to a distillation system where water is removed for recycle to the reactor system and organic impurities, including chlorinated aldehydes, are separated from the purified acetaldehyde product.

2.3.4.2 Production from Ethanol

For the production of acetaldehyde, ethanol can either be dehydrogenated or oxidized in the presence of oxygen. Between 1918 and 1939, dehydrogenation took precedence over oxidation because of the simultaneous production of hydrogen. Later, however, the catalytic vapor phase oxidation of ethanol became the preferred process, probably because of the long catalyst life and the possibility of recovering energy.

- Dehydrogenation of Ethanol

In the first work on ethanol dehydrogenation, published in 1886, ethanol was passed through glass tubes at 260°C. Ethanol vapor is passed at 260–290°C over a catalyst consisting of copper sponge or copper activated with chromium oxide in a tubular reactor [25]. A conversion of 25–50% per run is obtained. By washing with alcohol and water, acetaldehyde and ethanol are separated from the exhaust gas, which is mainly hydrogen. Pure acetaldehyde is obtained by distillation. The ethanol is separated from water and higher-boiling products by distillation and flows back to the reactor. The final acetaldehyde yield is 90 %. Byproducts include butyric acid, crotonaldehyde, and ethyl acetate.

$$CH_3CH_2OH\ (l) \rightarrow CH_3CHO\ (l) \rightarrow H_2\ (g) \qquad \Delta H = +82.5\ \text{kJ/mol}$$

Improved yields are obtained in the presence of catalysts, such as platinum, copper, or oxides of zinc, nickel, or cobalt. In later patents, zinc and chromium catalysts [26], oxides of rare earth metals [27], and mixtures of copper and chromium oxides [28] have been reported. The lowest amounts of decomposition products are obtained using copper catalysts.

- Oxidation of Ethanol

Oxidation of ethanol is the oldest and the best laboratory method for preparing acetaldehyde. In the commercial process, ethanol is oxidized catalytically with oxygen (or air) in the vapor phase. Copper, silver, and their oxides or alloys are the most frequently used catalysts [29].

$$CH_3CH_2OH\ (g) + 1/2O_2\ (g) \rightarrow CH_3CHO\ (l) + H_2O\ (l) \qquad \Delta H = -242.0\ \text{kJ/mol}$$

- Veba-Chemie Process

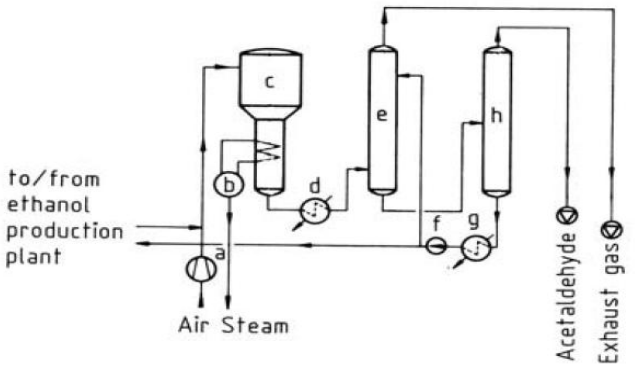

Figure 2.3 The acetaldehyde production by the Veba-Chemie process.

As shown in **Figure 2.3**, ethanol is mixed with air and passed over a silver catalyst at 500–650°C in reactor (c). The temperature depends on the ratio of alcohol to air and the flow rate of the gas through the catalyst. Alcohol conversion varies between 50% and 70% and the yield is between 97% and 99% depending on the reaction conditions. Acetaldehyde and unconverted alcohol are removed from the waste gas by washing with cold alcohol at Waste-gas scrubber (e) and separated by fractional distillation (h); after concentration the alcohol returns to the reactor. Heat formed in the reaction is utilized for steam production using a waste-heat recovery system immediately after the reaction zone. The waste gas consists mainly of nitrogen, hydrogen, methane, carbon monoxide and carbon dioxide. It is burned as lean gas with low calorific value in steam generators. Small amounts of acetic acid are obtained as a byproduct.

2.3.4.3 Production from Acetylene

Acetaldehyde has been produced commercially by the hydration of acetylene since 1916. The most important catalysts for the industrial water addition (hydration) of acetylene are mercury compounds:

$$C_2H_2\,(g) + H_2O\,(l) \rightarrow CH_3CHO\,(l) \qquad \Delta H = -138.2 \text{ kJ/mol}$$

This method only succeeds industrially when the polymerization and condensation products of acetaldehyde formed in the acid medium are eliminated. To achieve this, the Consortium für Elektrochemische Industrie in 1912 proposed a process using excess acetylene at an elevated temperature and removing the acetaldehyde product immediately from the reaction liquid. At the same time, the heat of reaction is removed by distilling an appropriate amount of water. Secondary reactions, such as the oxidation of acetaldehyde to form acetic acid and carbon dioxide, result in reduction of Hg^{2+} to metallic mercury. In Western countries, acetaldehyde production from acetylene has now been discontinued.

- Wet Oxidation Process (Hoechst)

The wet oxidation process avoided direct handling of the toxic mercury compounds. It was operated by Wacker-Chemie until the changeover to ethylene as the starting material in 1962. In this method, iron(III) sulfate is added to reoxidize the mercury metal to the mercury(II) salt, thus ensuring sufficient concentrations of active catalyst. The acetylene reacts at 90–95°C with the aqueous catalyst solution; between 30 and 50% of the injected acetylene reacts in one run. The gas emerging from the reactor is cooled; mainly water and traces of mercury are separated and returned to the reactor. Acetaldehyde and water are condensed in additional coolers and the acetaldehyde finally is washed out with water from the cycle gas which has been cooled to 25–30°C. An 8–10% aqueous acetaldehyde solution is obtained. Nitrogen is introduced with the feed gas while carbon dioxide is formed as a byproduct; to avoid excessive accumulation, these gases are removed by withdrawing a small stream of the cycle gas. Iron(II) sulfate is formed in the reaction and is oxidized in a separate reactor with 30% nitric acid at 95°C. Pure acetaldehyde is obtained by fractional distillation of the aqueous solution at about 200 kPa [30].

- Chisso Process

The Chisso process [31] also uses sulfuric acid/mercury sulfate solution as a catalyst. The acetylene reacts completely with the catalyst solution at 68–78°C and a gauge pressure of 140 kPa. A combination of pressure and vacuum process stages at low temperature and without excess acetylene is used. Pure acetaldehyde can be isolated and distilled by utilizing the heat of the reaction. As in the Hoechst process, the catalyst can be regenerated with nitric acid. Production of acetaldehyde by this method was discontinued at Chisso Corp. more than a decade ago. Acetaldehyde may also be made from methyl vinyl ether and ethylidene diacetate, both of which can be made from acetylene. Methyl vinyl ether is made by the addition of methanol to acetylene at 1.62 MPa (16 atm) in a vertical reactor containing a 20% methanolic solution of potassium hydroxide. Hydrolysis of the ether with dilute sulfuric acid yields acetaldehyde and methanol which are separated by distillation; the methanol is recycled to the reactor. Acetylene and acetic acid form ethylidene diacetate in the presence of mercuric oxide and sulfuric acid at 60-800°C and atmospheric pressure. After separation, the ethylidene diacetate is decomposed to acetaldehyde and acetic anhydride by heating to 1500°C in the presence of a zinc chloride catalyst. Acetaldehyde has been made from methyl vinyl ether and ethylidene diacetate in the past, but neither process is used today.

2.3.4.4 Production from Saturated Hydrocarbons

Acetaldehyde is formed as a co-product in the vapor phase oxidation of saturated hydrocarbons, such as butane or mixtures, containing butane with air or oxygen as operated by Celanese in the United States [32]. Oxidation of butane yields acetaldehyde, formaldehyde, methanol, acetone, and mixed solvents as major products; other aldehydes, alcohols, ketones, glycols, acetals, epoxides, and organic acids are formed in smaller concentrations. Unlike the acetylene route, it has almost no chance to be used as a major process.

2.3.4.5 Production from Synthesis Gas

From synthesis gas: A rhodium-catalyzed process capable of converting synthesis gas directly into acetaldehyde in a single step was reported in 1974.

$$CO + H_2 \rightarrow CH_3CHO + \text{other products}$$

The process comprises passing synthesis gas over 5% of rhodium on SiO_2 at 3000°C and 2.0 MPa (20 atm) [33]. The principal co products are acetaldehyde, 24% acetic acid, 20%; and ethanol, 16%. There is so far no industrial use of this process. In the years 1980 beyond, if there will be a substantial degree of coal gasification, the interest in the use of synthesis gas as a raw material for acetaldehyde production will increase.

2.4 Dehydrogenation of ethanol

The ethanol dehydrogenate to acetaldehyde is shown in the equation below.

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

The dehydrogenation of ethanol is usually done over Cu-catalysts activated with Zn, Co, or Cr. One frequently applied process originates from the Carbide & Carbon Corporation. The temperature is regulated to 270-300°C so that the ethanol conversion is limited to 30-50%, and selectivity to acetaldehyde of 90-95% is attained. Byproducts include crotonaldehyde, ethyl acetate, higher alcohols, and ethylene. The hydrogen formed is pure enough to be used directly for hydrogenation. If the dehydrogenation of ethanol is conducted in the presence of air or oxygen (e.g., the Veba process), the concomitant combustion of the hydrogen formed supplies the necessary heat of dehydrogenation (oxidative dehydrogenation or autothermal dehydrogenation).

In the industrial process, silver catalysts in the form of wire gauzes or bulk crystals are preferred. Ethanol vapors mixed with air at 3 bar and at 450-550°C are passed over the catalyst. The reaction temperature is contingent upon the amount of air used. A temperature is reached at which the heat of oxidation and heat consumption of the dehydrogenation compensate one another. Depending on the reaction temperature, 30-50% of the ethanol is converted per pass with a selectivity of 85-95%. The byproducts are acetic acid, formic acid, ethyl acetate, CO and CO_2.

In both process modifications, the acetaldehyde is separated from the unreacted alcohol and byproducts and purified in various washes and distillations. The recovered ethanol is recycled to the reaction.

Dehydrogenation is a chemical reaction that involves the removal of hydrogen from a molecule. It is the reverse process of hydrogenation. The reaction is strongly endothermic, and therefore, heat must be supplied to maintain the reaction temperature.

The primary types of dehydrogenation reactions are vapor-phase conversion of primary alcohols to aldehydes, vapor-phase conversion of secondary alcohols to ketones, dehydrogenation of a side chain, and catalytic reforming of naphthas and naphthenes in the presence of a platinum catalyst. All four of these types of dehydrogenation reactions are of major industrial importance. They account for the production of billions of pounds of organic compounds that enter into the manufacture of lubricants, explosives, plastics, plasticizers, and elastomers. Acetaldehyde can be obtained by catalytic dehydrogenation of Ethanol. This is analogous to the manufacture of formaldehyde from methanol. However, in contrast to methanol manufacture, oxidation is not used as an alternative. Instead, two modifications of the dehydrogenation are customary:

1. Dehydrogenation on silver, or preferably copper, catalysts
2. Oxidative dehydrogenation with silver catalysts in the presence of oxygen.

Hydrogenation is a chemical reaction between molecular hydrogen (H_2) and another compound or element, usually in the presence of a catalyst.

2.5 Possible Reaction of Ethanol and Acetaldehyde

2.5.1 Possible Reaction of Ethanol

Ethanol is capable of undergoing several of the general types of reaction under a variety of conditions. The possible reactions of ethanol involved can be as follows.

$CH_3CH_2OH \rightarrow CH_4 + CO + H_2$ (ethanol decomposition) (1)

$CH_3CH_2OH \rightarrow CH_3CHO + H_2$ (ethanol dehydrogenation) (2)

$CH_3CH_2OH \rightarrow C_2H_4 + H_2O$ (ethanol dehydration) (3)

$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2$ (ethanol steam reforming) (4)

$CH_3CH_2OH + H_2O \rightarrow 2CO + 4H_2$ (ethanol incomplete reforming) (5)

$2CH_3CH_2OH \rightarrow (C_2H_5)_2O + H_2O$ (ethanol dehydration coupling) (6)

$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$ (acetic acid formation) (7)

$2CH_3CH_2OH \rightarrow CH_3COOC_2H_5 + 2H_2$ (ethyl acetate formation) (8)

$CH_3CH_2OH + CO_2 \rightarrow 3H_2 + 3CO$ (CO_2 dry reforming) (9)

$CH_3CH_2OH + 0.5O_2 \rightarrow 3H_2 + 2CO$ (ethanol partial oxidation) (10)

$CH_3CH_2OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2$ (ethanol oxidation) (11)

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ (ethanol combustion) (12)

2.5.2 Possible Reaction of Acetaldehyde

An acetaldehyde is an intermediate chemical that has the ability to easily react in various reactions and lead to many different products. The possible reactions of acetaldehyde are shown as follows.

$CH_3CHO \rightarrow CH_4 + CO$ (acetaldehyde decomposition) (1)

$CH_3CHO + H_2O \rightarrow CH_3OH + CO + H_2$ (acetaldehyde reforming) (2)

$CH_3CHO + H_2O \rightarrow C_2H_6O_2$ (acetaldehyde hydration) (3)

$2CH_3CHO + O_2 \rightarrow 2CH_3COOH$ (acetaldehyde oxidation) (4)

$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$ (acetaldehyde aldol condensation) (5)

2.6 Principle of catalyst

A catalyst is a substance or material that accelerates or increases the rate of a chemical reaction. A catalyst is not consumed by the reaction and chemically unchanged at the end of the reaction. A schematic depiction of the effect of a catalyst on a reaction coordinate can be seen in the **Figure 2.4**. Catalysts allow reactions to proceed by a different reaction pathway involving a lower-energy transition state. By lowering the energy of the rate-limiting step (the transition state), catalysts reduce the required energy of activation and allow a reaction to proceed, and in the case of a reversible reaction, reach equilibrium more rapidly.

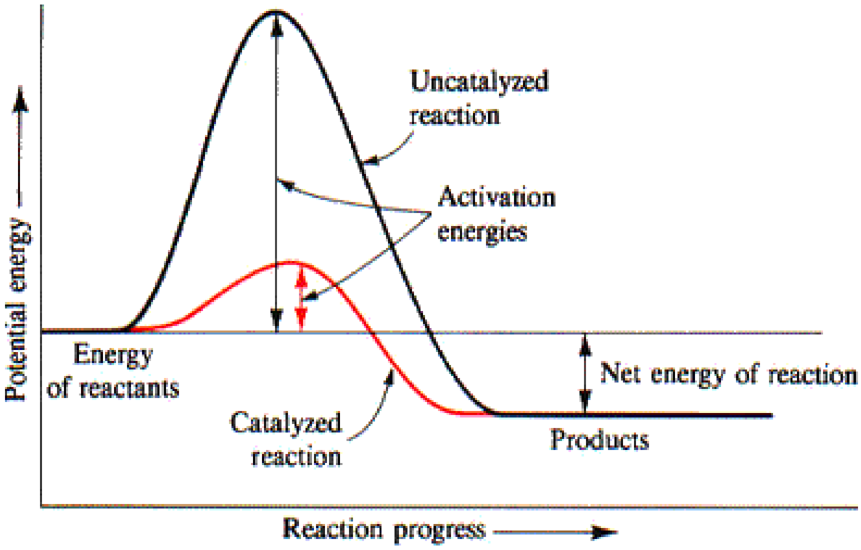

Figure 2.4 Effect of catalyst on rate of the reactions.

(http://chem.wisc.edu/deptfiles/genchem/sstutorial/Text13/Tx133/tx133.html)

2.6.1 Types of catalysts

There are many types of catalysts in the world. In a chemical reaction, a catalyst can be classified based on phase of catalyst and reactant into two main types: heterogeneous and homogeneous catalysts. A homogeneous catalyst is a catalyst which has the same phase as the reactant. A heterogeneous catalyst has a different phase from the reactants. Usually, a heterogeneous catalyst is a solid and the reactant are fluids (liquids or gaseous). The major advantages and disadvantages of heterogeneous and homogeneous catalyst are summarized in **Table 2.2**.

Table 2.2 Comparison of main advantages and disadvantages of heterogeneous and homogeneous catalysts.

Property	Homogeneous	Heterogeneous
Catalyst recovery	difficult and expensive	easy and cheap
Thermal stability	poor	good
Selectivity	excellent/good-single active site	good/poor-multiple active sites

2.6.2 Composition of catalysts

Typically, the composition of a catalyst consists of the active agent, the supporter, and the promoter.

- Active agent

The active agent causes the reduction in the free energy of the transition-complex formation. Active agents can be metals and semiconductors.

- Supporter

Since catalytic activity is normally proportional to the concentration of active sites, supporters with high surface areas are commonly employed. Porous solids provide area ranging from one to several hundred square meters per gram. The support should not be assumed to be inert in the catalytic process because it may exhibit the ability to adsorb reactants and atomic species dissociated by the deposited active agent.

- Promoter

The promoter can enhance the activity, selectivity or stability of a catalyst, even though it is added in relatively small amounts in the preparation of the catalyst. In general, a promoter is an inert substance that inhibits the sintering of microcrystal of the active catalyst. The good promoter should have smaller particle size than that of the active species and must be well dispersed. Furthermore, it should not react to form a solid solution with the active agent and have a relatively high melting point. The good catalyst has three main properties; good activity, good selectivity and long life time.

2.6.3 Catalyst Properties

The physical and chemical properties of the catalyst represent the performance of that catalyst. Excellent performance such as high surface area and high activity, are required for good catalyst. The properties of good catalysts can be determined for the following items.

- Size

Size of the catalyst is one of the most important parameters in considering the performance of the catalyst. The small size of the catalyst provides a high surface area and gives better catalytic performance.

- Surface area

High surface area is usually desirable for high activity per unit volume or unit weight. Consequently, most catalysts are made to be porous, with high internal surface area about 1000 m^2g^{-1}. The porous structure and pore size distribution of the catalyst may cause diffusion resistance that affects the access of the reactant to the catalyst sites and the removal of the product. Therefore, they also affect the rate and selectivity of the reaction. For very fast reaction, a large pore size (low surface area) catalyst may be desired.

- Stability

This includes the stability of heat, to poisons, to fluctuation in process conditions, and to such common components of the reacting mixture.

- Activity

The activity of the catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. The rate of the reaction depends on temperature, pressure and concentration of reactants and products.

- Selectivity

The selectivity of the catalyst is a measure of the extent to which the catalyst accelerates the reaction to form one or more of the desired product. The selectivity usually varies with pressure, temperature, extent of conversion, reactant composition, and the nature of the catalyst.

- Sintering

The sintering of the support metal crystallites is a complicated phenomenon. It may result in an overall loss of the area of the support material, or may cause a loss of dispersion of the metal crystallite in the support metal catalyst. The rate of sintering increases rapidly with increasing temperature. It varies with the nature of the metal and the chemical morphology of the support, as well as temperature, pressure and time.

2.6.4 Mechanism of Catalytic Reaction

The overall rate of the reaction is equal to the rate of the slowest step in the mechanism. The overall process of heterogeneous catalytic reaction can be divided into seven steps:

1. External mass transfer (diffusion) of reactants from bulk fluid phase (boundary layer) to the external surface of the catalyst
2. Internal diffusion of the reactants to active sites on the catalyst’s surface
3. Adsorption of the reactants on the catalyst’s surface
4. Reaction on the surface of the catalyst
5. Desorption of products from the catalyst’s surface
6. Internal diffusion of the desorbed products from the external surface of the catalyst
7. External diffusion of the products from the external surface to the bulk fluid phase

The diffusion steps 1, 2, 6 and 7 are very fast compared of the reaction in steps 3, 4, and 5. The concentration in the immediate vicinity of the active sites is not different from those in the bulk fluid.

CHAPTER 3

METHODOLOGY

This chapter describes the experimental procedures for preparing catalysts, apparatus used, as well as the analytical methods undertaken in the course of this study to achieve the objectives mentioned previously.

3.1 Catalyst preparation

A series of Cu, Ag, Cu-Ag catalysts were prepared using commercial silica as supports and two preparation methods, incipient wetness impregnation and microwave-assisted technique, according to the scheme outline in **Figure 3.1**.

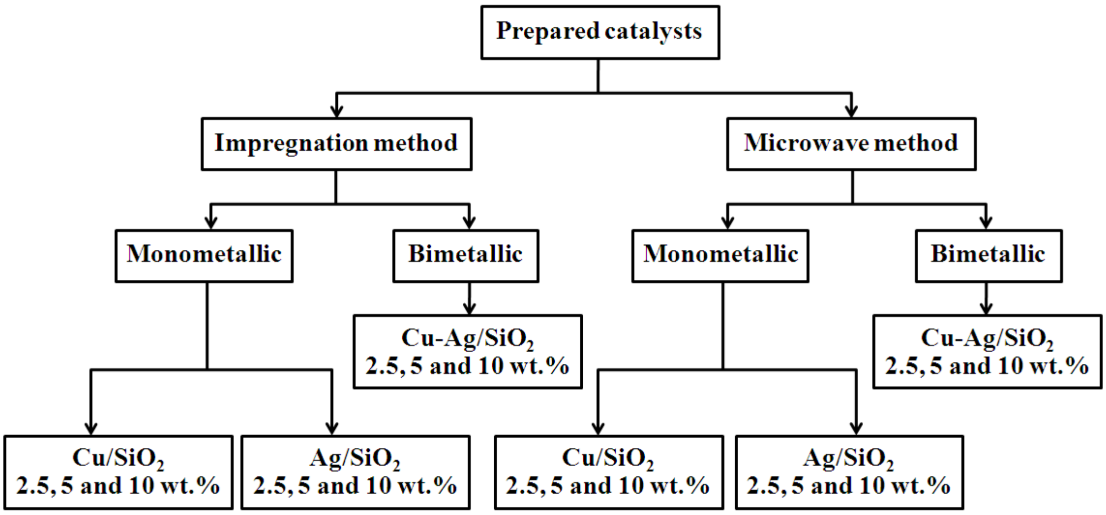

Figure 3.1 A series of prepared catalysts synthesized in this work.

First, a commercial fumed silica powder (SiO_2, Sigma-Aldrich, 0.007µm, 390 m^2/g) was calcined in air at 400^0C for 4 hours to eliminate impurities before using as support in this work. Then, an aqueous solution containing calculated amount of Cu, Ag, and mixed Cu-Ag (with atomic ratio equal to 1), which was prepared by dissolving $Cu(NO_3)_2{\cdot}3H_2O$ (Qrec, 99.5%) and/or $AgNO_3$ (BDH) (all of AR grade) in deionized water, was adding dropwise into commercial fumed silica powder support. After that, the catalysts were dried in an oven at 120ºC overnight (method (a)) or dried in microwave at 450 watt for 5 min (method (b)). Finally, all prepared catalyst samples were calcined at 400°C for 4 hours. The procedures are schematized in **Figure 3.2**.

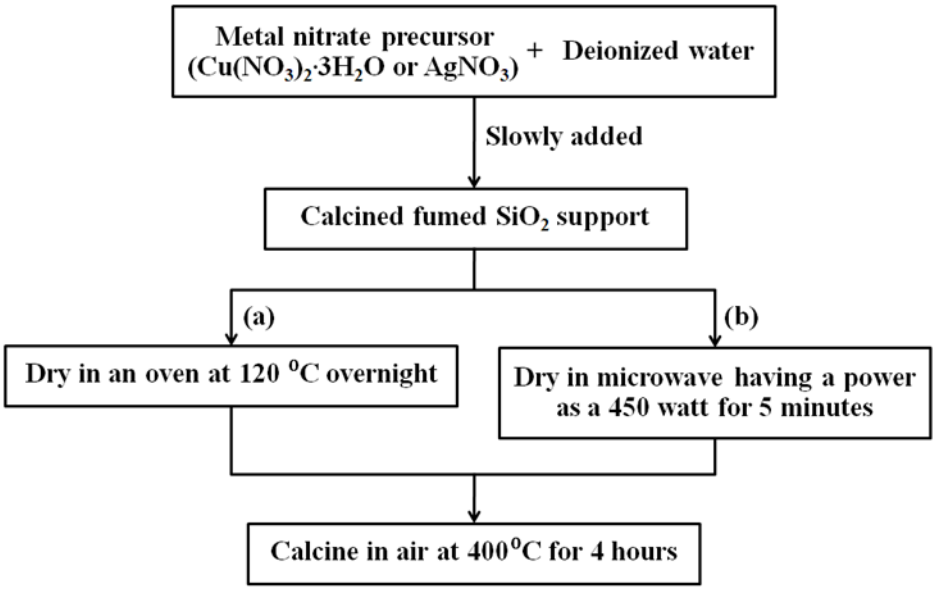

Figure 3.2 Schematic diagram of catalyst preparation by (a) impregnation technique and (b) microwave-assisted technique.

3.2 Catalyst characterization

The synthesized catalysts were carried out to identify properties of catalysts by various techniques such as XRD, BET, TPR and SEM. The properties of the catalysts in this experiment were analyzed after reduced with 10% hydrogen in nitrogen at 300^{0}C for 3 hours, except for TPR technique.

3.2.1 Surface Area and Pore Analysis

The specific surface area, pore diameter and pore volume of catalysts were measured by Brunauer-Emmett-Teller (BET) Nitrogen physicsorption technique using Quantachrome Nova 4200e instrument. This method used nitrogen (N_2) adsorption-desorption isotherm. Before measurement, all samples were degassed under vacuum conditions at 150^{0}C for 3 hours.

3.2.2 Phase Identification

X-ray diffraction (XRD) was used to identify the metal species and obtain information about the crystalline phase of catalysts. The X-ray diffractometer were carried out using a Bruker Model D8 Discover with GADDS, with Cu Kα radiation of a wavelength of 1.54006 Å from 10 to 90° of 2θ at a rate of 0.05°/s.

3.2.3 Reduction temperature of catalysts

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 to analyze in this experiment. About 50 milligram of catalyst was placed in U-quartz tube and purged with N_2 for 30 minutes. Then, the temperature was ramped from 25 to 850°C at a rate of 10°C per minute in 5v/v.% hydrogen in argon mixture with flow rate 30 millimeters per minute. The gas leaving the reactor is cooled down in a cold trap to remove water from the gas stream prior to being analyzed by a thermal conductivity detector (TCD). The rate of hydrogen consumed is measured as the temperature increases. A TPR profile was plotted between the reducibility temperature and the amount of hydrogen consumed.

3.3 Catalyst Activity Testing

3.3.1 Experimental Set up for Catalytic Dehydrogenation of Ethanol

Schematic diagram for the experimental system of catalytic dehydrogenation of ethanol was shown in **Figure 3.3**. This system was designed with four main sections: supplied gases, ethanol feeder, reaction zone and analysis zone.

The supplied gas section consisted of 99.999% nitrogen and 99.999% 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 ethanol 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 80^0C in order to evaporate the mixer and supply both ethanol and gas streams to the reactor.

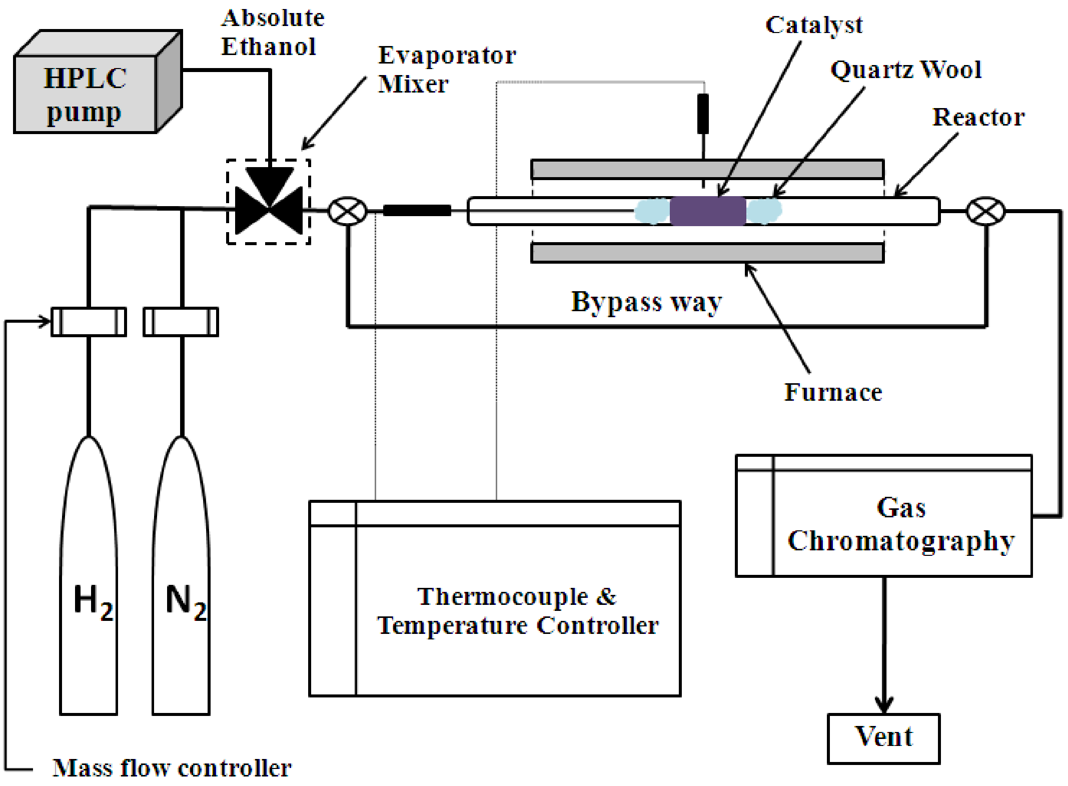

Figure 3.3 Schematic diagram of catalytic dehydrogenation of ethanol system.

The catalytic experiments were carried out in a fixed bed quartz tubular reactor (i.d. 10 mm, length 500 mm), working at atmospheric pressure. 0.2 g of catalyst samples (0.18-0.5 mm particle size) were introduced in the reactor. Experiments were carried out in the 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. Photograph of a reforming bench-scale apparatus is shown in **Figure 3.4**.

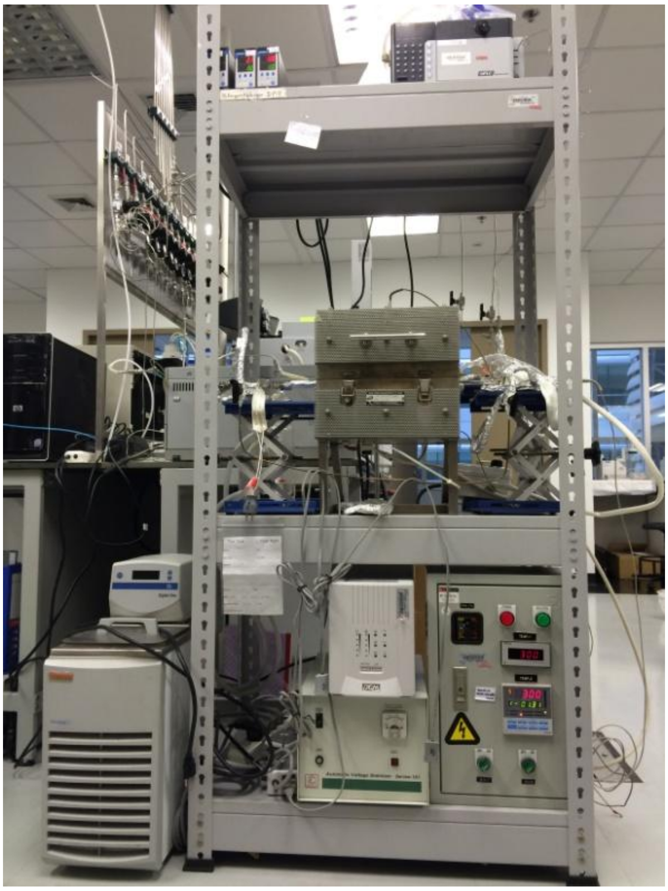

Figure 3.4 Catalytic dehydrogenation of ethanol system.

3.3.2 Calculation Procedure

The catalysts were evaluated for their performance based on several criteria, such as ethanol conversion ($X_{Ethanol}$) and product yield ($Y_{Product}$). Ethanol conversion and product selectivity are defined according to **Equations 3.1** and **3.2**, respectively.

3.3.2.1 Percentage of ethanol conversion ($X_{Ethanol}$)

The ethanol conversion from dehydrogenation reaction is described as an amount of ethanol reactant has reacted per the ethanol feed, which is defined in **Equation 3.1**.

$$X_{Ethanol} = \left(\frac{F_{ethanol,in} - F_{ethanol,out}}{F_{ethanol,in}}\right) \times 100\% \qquad \textbf{(3.1)}$$

Where, $F_{ethanol,in}$ and $F_{ethanol,out}$ are the molar feed flow rate and molar outlet flow rate of ethanol, respectively.

3.3.2.2 Yield of product ($\mathbf{Y_{Product}}$)

The definition of selectivity of product is shown in **Equation 3.2**, which is the term of flow rate product i per the total flow rate of the products.

$$Y_{product\ ,i}(\%) = \left(\frac{F_{product\ \ ,i}}{F_{ethanol\ ,in}}\right) \times 100\% \qquad \textbf{(3.2)}$$

Where $F_{product\ ,i}$ is the molar flow rate of product i, and $F_{ethanol\ ,in}$ is the molar feed flow rate of ethanol.

CHAPTER 4

RESULTS AND DISCUSSION

The chapter is divided into two sessions: the catalyst characterization and the catalyst activity testing. The catalysts were characterized by means of XRD, BET, TPR, and SEM. The catalyst activity testing studied the catalyst behavior towards the catalytic dehydrogenation of ethanol to acetaldehyde and hydrogen production. The results of each part are described as below:

4.1 Catalyst Characterization

4.1.1 Surface Area and Pore Analysis

The specific surface area, total pore volume, and average pore diameter of all prepared catalysts after being reduced in 10% v/v H_2 in N_2 for 3 hours were analyzed by the Brunauer, Emmett and Teller (BET) measurement and are summarized in **Table 4.1**. 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 is 302 m^2g^{-1}. After doping silica with Cu, Ag, and mixed Cu-Ag, the specific surface of all prepared catalysts decreased whereas pore volume and pore diameter increased. This was due to particles of metals blocking the silica pores. Moreover, when increasing percentage of metal loading, specific surface area decreased. By comparing the effect of catalyst preparation between the impregnation and the microwave-assisted technique, it was found that the specific surface area and total pore volume of all catalysts prepared by microwave-assisted technique higher than catalysts prepared by impregnation technique, whereas the pore size diameter is insignificantly changed. Therefore, it can be concluded that the microwave-assisted technique was better than conventional impregnation technique for preparing catalysts in this work.

Table 4.1 The results of BET surface area and pore size analysis.

No.	**Catalyst**	**Surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore diameter (nm)**
1	SiO_2 (support)	302.30	0.61	3.67
Typical impregnation technique				
2	2.5 wt.% Cu/SiO_2	215.50	1.58	27.72
3	5 wt.% Cu/SiO_2	257.20	1.16	16.43
4	10 wt.% Cu/SiO_2	151.60	1.22	27.89
5	2.5 wt.% Ag/SiO_2	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/SiO_2	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
Microwave-assisted technique				
11	2.5 wt.% Cu/SiO_2*	227.00	1.87	27.92
12	5 wt.% Cu/SiO_2*	273.70	1.30	27.90
13	10 wt.% Cu/SiO_2*	249.10	2.13	27.91
14	2.5 wt.% Ag/SiO_2*	298.70	1.90	27.92
15	5 wt.% Ag/SiO_2*	263.20	1.51	27.78
16	10 wt.% Ag/SiO_2*	154.40	1.56	27.80
17	2.5 wt.% Cu-Ag/SiO_2*	276.20	1.52	27.86
18	5 wt.% Cu-Ag/SiO_2*	291.40	1.47	27.35
19	10 wt.% Cu-Ag/SiO_2*	140.10	1.25	27.76

4.1.2 Phase Identification of Prepared Catalyst

The crystalline phase of the synthesized catalysts after reduced in 10% v/v H_2 in N_2 for 3 hours were analyzed using X-ray powder diffraction. The XRD patterns of synthesized catalysts i.e. Cu/SiO_2, Ag/SiO_2 and $Cu\text{-}Ag/SiO_2$ are shown in **Figures 4.1**, **4.2**, and **4.3**, respectively.

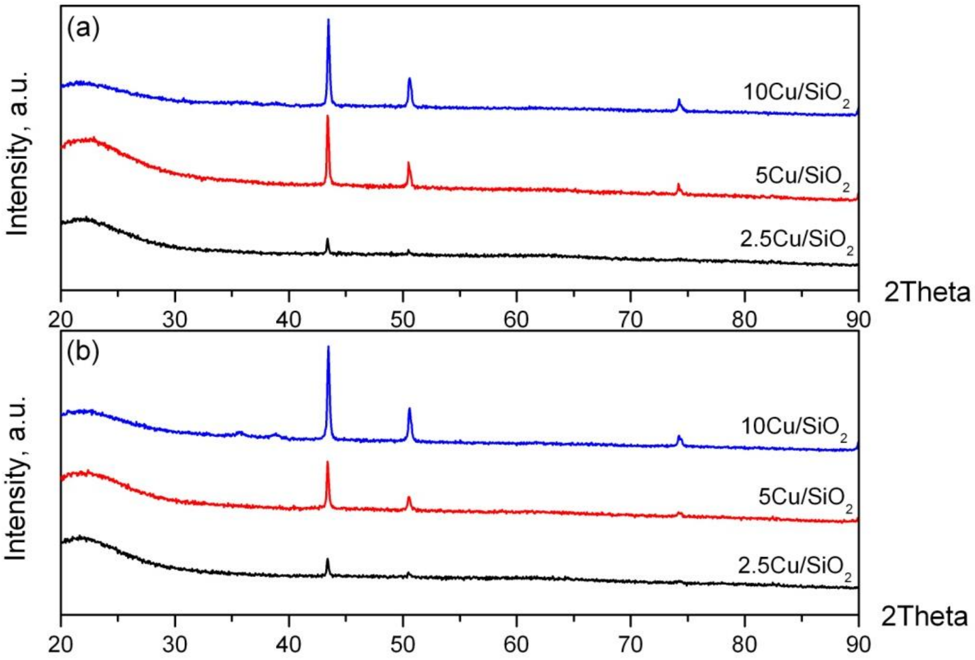

Figure 4.1 XRD patterns of copper doped on silica support catalyst after reduced in 10% v/v H_2 in N_2 at 300°C for 3 hours at different copper loadings: (a) typical impregnation technique and (b) microwave-assisted technique.

Figure 4.1 shows XRD patterns of copper doped on silica support catalyst (Cu/SiO_2) at different copper loadings. The Cu/SiO_2 catalyst prepared by typical impregnation technique and microwave-assisted technique are shown in **Figures 4.1(a)** and **4.1(b)**, respectively. From both figures, it can be identified that the synthesized catalysts prepared by typical impregnation technique have the same XRD pattern as the synthesized catalysts prepared by microwave-assisted technique. For the pattern of Cu/SiO_2 catalyst precursor after reduced, the silica supports present a broad background peak in the region 2θ between 20^o and 30^o which associated with amorphous silica, used as a support in this work. The Cu/SiO_2catalyst after reduced shows three main diffraction peaks related to crystalline copper (Cu) metal phase. A strong diffraction peak at 2θ of

43.4° along with two weak ones at 50.5 and 74.1°, which are attributed to (1 1 1), (2 0 0) and (2 2 0) planes respectively. Thus, it can be deduced that the copper species in the catalyst after being pretreated with H_2 at 300°C for 3 hours have been converted from a copper oxide to Cu metal. The peak intensity of crystalline copper metal increased when the copper loading in synthesized catalyst increased in the both cases of synthesized catalysts prepared by typical impregnation technique and microwave-assisted technique. The dramatic increase in peak intensity with increasing metal content may reflect the growth in crystal size.

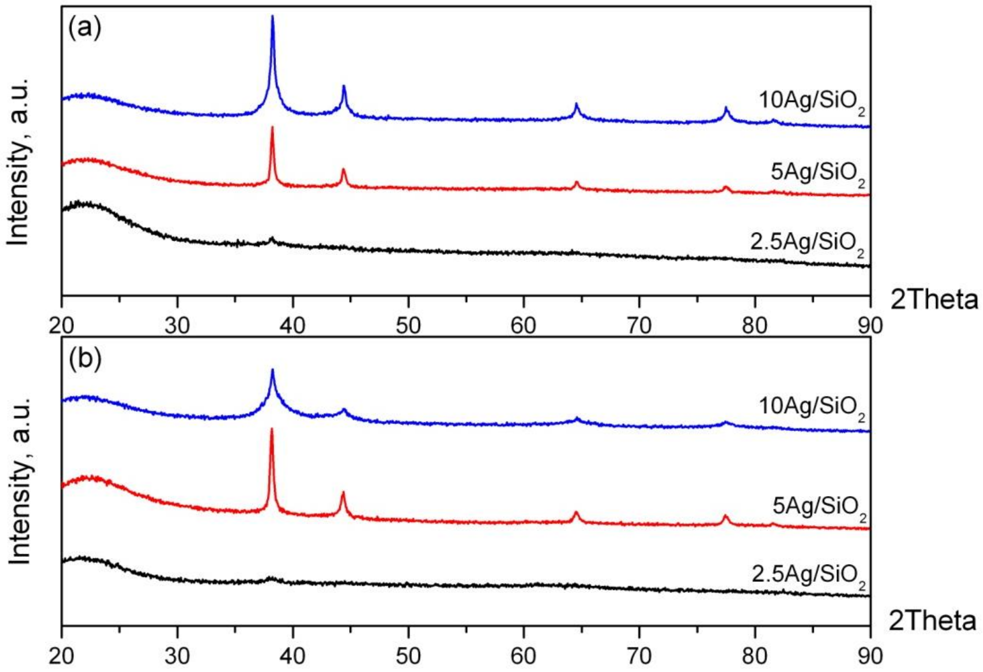

Figure 4.2 XRD patterns of silver doped on silica support catalyst after reduced in 10% v/v H_2 in N_2 at 300°C for 3 hours at different silver loadings: (a) typical impregnation technique and (b) microwave-assisted technique.

The XRD pattern of silver supported on a silica support catalyst (Ag/SiO_2) at different silver loadings prepared by typical impregnation technique and microwave-assisted technique are shown in **Figures 4.2(a)** and **4.2(b)**, respectively. Two catalyst preparation techniques give the same XRD pattern. At low silver loading (2.5 wt.%), the catalysts have no diffraction peaks of metallic silver. This indicates the amorphous and/or very small particle size of silver particle. After increasing silver loading, XRD patterns show four diffraction peaks related to crystalline metallic silver (Ag) phase at $2\theta = 38.2°$, 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 silver oxide can be converted to silver metal after reducing at 300°C with 10% v/v H_2 for 3 hours.

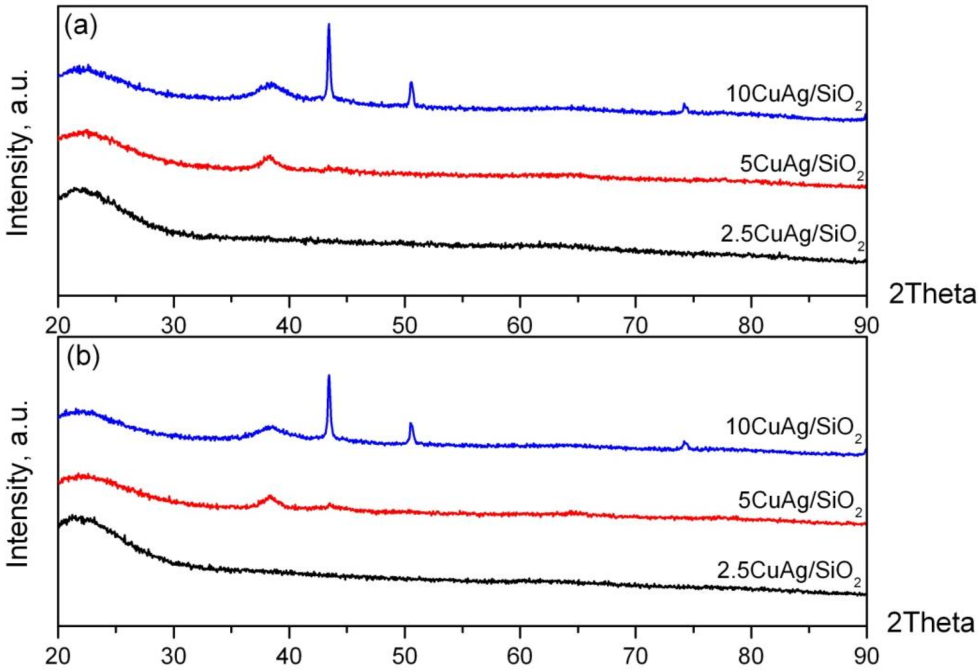

Figure 4.3 XRD patterns of bimetallic copper and silver doped on silica support catalyst after being reduced in 10% v/v H_2 in N_2 at 300°C for 3 hours at different total metal loadings: (a) typical impregnation technique and (b) microwave-assisted technique.

XRD patterns of bimetallic catalyst copper and silver doped on silica support catalyst at different metal loadings prepared by typical impregnation technique and microwave-assisted technique are shown in **Figures 4.3(a)** and **4.3(b)**, respectively. For bimetallic catalysts, both Cu and Ag metal crystalline peak are detected. The metallic copper and silver peak positions do not change when compared with monometallic catalysts. Moreover, it was found that there is no alloy of Ag and Cu but mixture or aggregates of the metallic Ag and the metallic Cu are produced. At the low bimetallic loading, no detectable peak was found at the position of crystalline metallic Cu and Ag phase because the catalyst has a low content in each metal. When the total metal loading is increased, peak position of crystalline Cu and Ag metal phase are more evident.

4.1.3 Reduction temperature of catalysts

The temperature-programmed reduction (TPR) is a thermal method used in the analysis of metal oxide reduction. TPR can reveal not only the reducibility and stability of the metal-supported or unsupported catalysts, but also the more profound surface chemical information i.e. metal species, metal distribution, and even quantitatively the loading of different metal surface species. In the present work, TPR was carried out from 25 to 850°C at a rate of 10°C per minute for all the synthesized catalysts. The TPR profiles obtained from the copper, silver and bimetallic copper-silver based on silica catalysts are illustrated in **Figures 4.4**, **4.5**, and **4.6**, respectively.

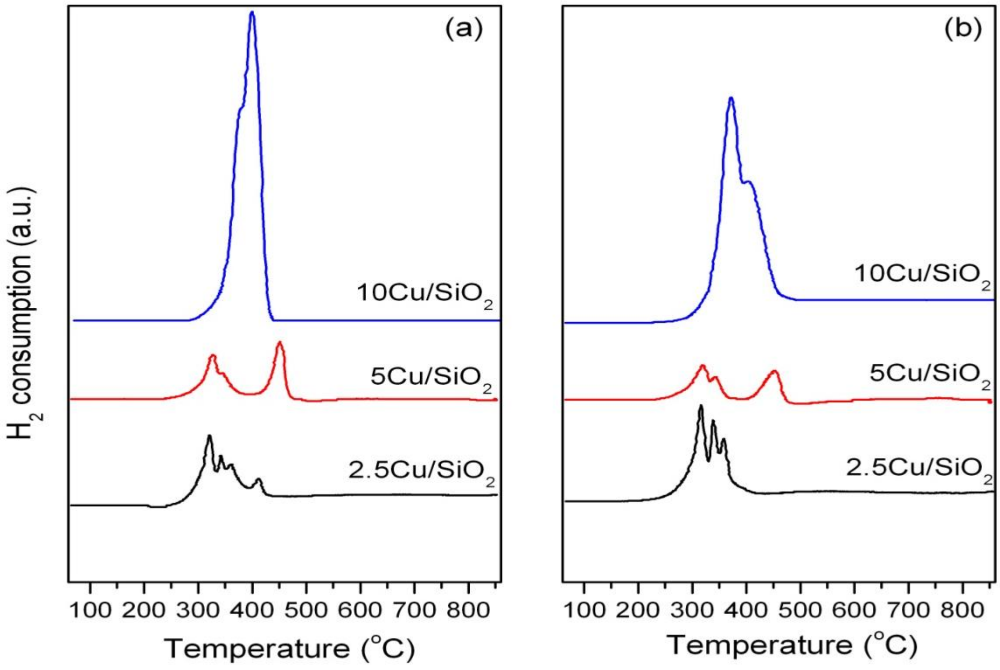

Figure 4.4 TPR profiles of copper doped on silica support catalyst at different copper loadings: (a) typical impregnation technique and (b) microwave-assisted technique.

H_2-TPR profiles of Cu/SiO$_2$ samples prepared by typical impregnation technique and microwave-assisted technique with 2.5, 5, and 10 wt.% copper loadings are shown in **Figures 4.4(a)** and **4.4(b)**, respectively. The observed shift in reducing temperature may be due to different copper particle sizes, different interactions between copper oxide and silica and different copper oxide dispersions. The H_2-TPR profiles of 2.5wt% Cu/SiO$_2$ in the both preparation techniques show three overlapping peaks at 320, 340 and 360°C, which is an indication of the existence of more than one copper oxide species in this catalyst. The reduction of pure CuO as reported in the literature occurs between 290 and 390°C [33-35]. While the higher copper content, 5 wt% Cu/SiO_2 exhibits two peaks, at 320 and 450°C. TPR peaks below 320°C are related to the reduction of well dispersed Cu oxide species, indicating a strong CuO–SiO_2 interaction. The peak at 450°C could be assigned to the reduction of CuO due to weak interactions with the SiO_2 surface or bulk CuO. Finally, the H_2-TPR profile of 10 wt% Cu/SiO_2 catalysts prepared by typical impregnation and microwave-assisted technique present the same peak position in the range of 300 to 450°C. They show a single broad peak, centered at 400 and 370°C, respectively. This indicates the reducibility of the combination peak between the interaction of CuO with the SiO_2 surface and bulk CuO , and suggests the presence of the large particle size of CuO in the catalyst.

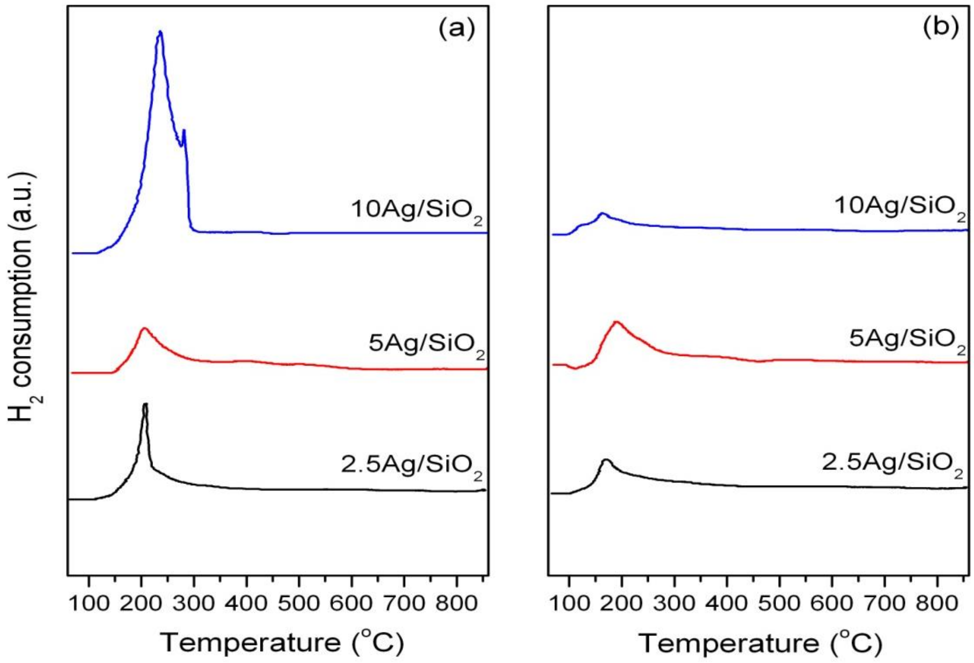

Figure 4.5 TPR profiles of silver doped on silica support catalyst at different silver loadings: (a) typical impregnation technique and (b) microwave-assisted technique.

Figures 4.5(a) and **(b)** depict the TPR profiles for Ag-based catalysts prepared by typical impregnation techniques and microwave-assisted techniques, respectively. From the figure, all Ag/SiO_2 catalysts show only one peak reduction of Ag_2O. For Ag/SiO_2 prepared by typical impregnation technique, Ag loading of 2.5% and 5% show the reduction peak at 205°C while, for 10% Ag/SiO_2, the reduction peak shift to 235°. As the silver content increased, the signals shifted to high temperatures, suggesting that the reduction peak at the relatively lower temperature is attributed to the reduction of small Ag_2O particles, while the reduction peak at higher temperature is related to the reduction of large Ag_2O particles and strong interaction with the support. The low temperature peaks attribute to the reduction of large Ag_2O clusters interacting weakly with the support, which is typically easier to reduce than small metal oxide particles. While the Ag/SiO_2 catalyst prepared by microwave-assisted technique presented similar H_2-TPR profiles with Ag/SiO_2 catalyst prepared by typical impregnation technique, they have lower reduction temperatures and lower H_2 consumption in the case of Ag loading. It suggests that the particle size of Ag in the Ag/SiO_2 catalyst prepared by microwave-assisted technique is smaller than Ag/SiO_2 catalyst prepared by typical impregnation technique and could have higher Ag dispersion on catalyst surface.

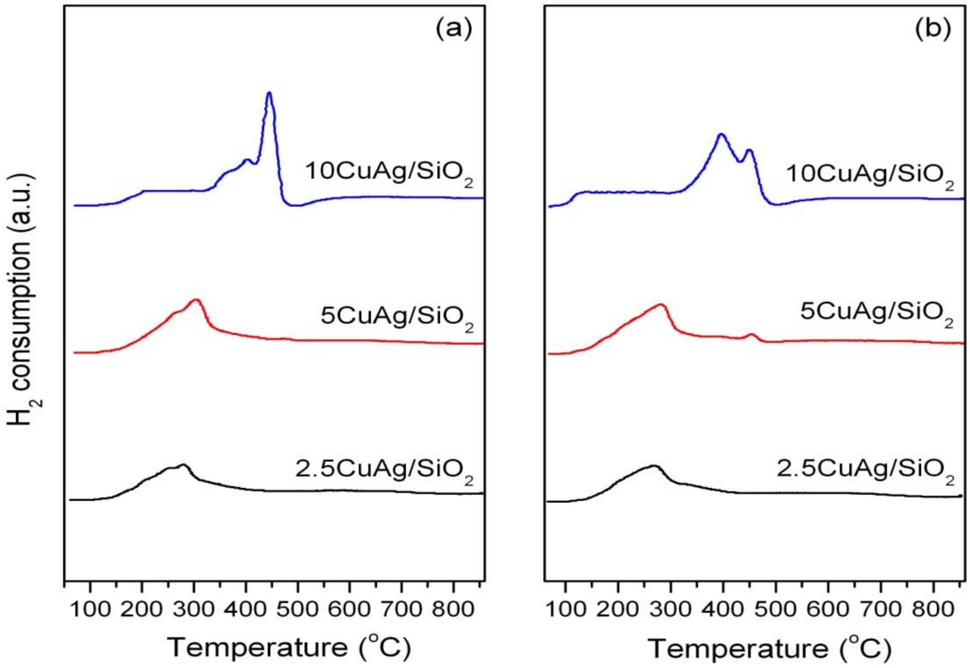

Figure 4.6 TPR profiles of bimetallic copper and silver doped on silica support catalyst at different total metal loadings: (a) typical impregnation technique and (b) microwave-assisted technique.

For the bimetallic Cu-Ag catalyst, H_2-TPR profile of bimetallic catalyst prepared by typical impregnation and microwave-assisted techniques are shown in **Figures 4.6(a)** and **4.6(b)**, respectively. From both figures, it was found that the reduction temperature of bimetallic catalyst was the combination of the reduction temperature region between the copper and the silver. The reduction temperature signals shifted to high temperatures when the metal content increased.

4.2 Catalytic activity toward ethanol dehydrogenation

4.2.1 Effects of metal and reaction temperature

At the first step, monometallic copper and silver doped on silica support were chosen to study catalytic activity for ethanol dehydrogenation. The catalytic activity testing for acetaldehyde and hydrogen production from dehydrogenation of ethanol were carried out at four different temperatures, ranging from 250 to 400°C. It was observed that acetaldehyde and hydrogen were the only products obtained in this study. No presence of other product was detected, showing that the dehydrogenation of ethanol to acetaldehyde and hydrogen, as shown in following equation:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

Different copper and silver loading were carried out in order to elucidate the effect of metal loading on the dehydrogenation of ethanol to produce acetaldehyde and hydrogen. **Figures 4.7** and **4.8** show the ethanol conversion and product yields of acetaldehyde and hydrogen from dehydrogenation reaction of ethanol implemented in temperature range of 250-400°C in the presence of 2.5, 5, and 10 wt.% of Cu/SiO_2 and Ag/SiO_2, respectively. In case of copper doped on silica support (Cu/SiO_2) catalysts prepared by typical impregnation technique, as shown in **Figure 4.7**, the values of ethanol conversion and product yield of Cu/SiO_2 catalysts increased with increasing the copper loading from 2.5 to 5 wt.% and slightly decreased when copper loading increased to 10 wt.%. In addition, the ethanol conversion and product yield increased when the reaction temperature increased from 250 to 400°C excepted at 10 wt.% Cu/SiO_2 catalyst increased with temperature enhancement from 250 to 300°C and dramatically decreased after the reaction temperature higher than 300°C, as seen in **Figure 4.7(c)**. This is probably due to copper loading increasing as a result of low metal dispersion (as suggested in **Table 4.1**) or deactivation of the catalyst from the sintering of copper at high temperature.

Among all catalysts, 5 wt.% Cu/SiO_2 showed the highest ethanol conversion and product yields (acetaldehyde and hydrogen) for all reaction temperatures, from which at 400°C ethanol conversion, acetaldehyde and hydrogen yields of 48.22, 39.05 and 46.05% can be achieved respectively.

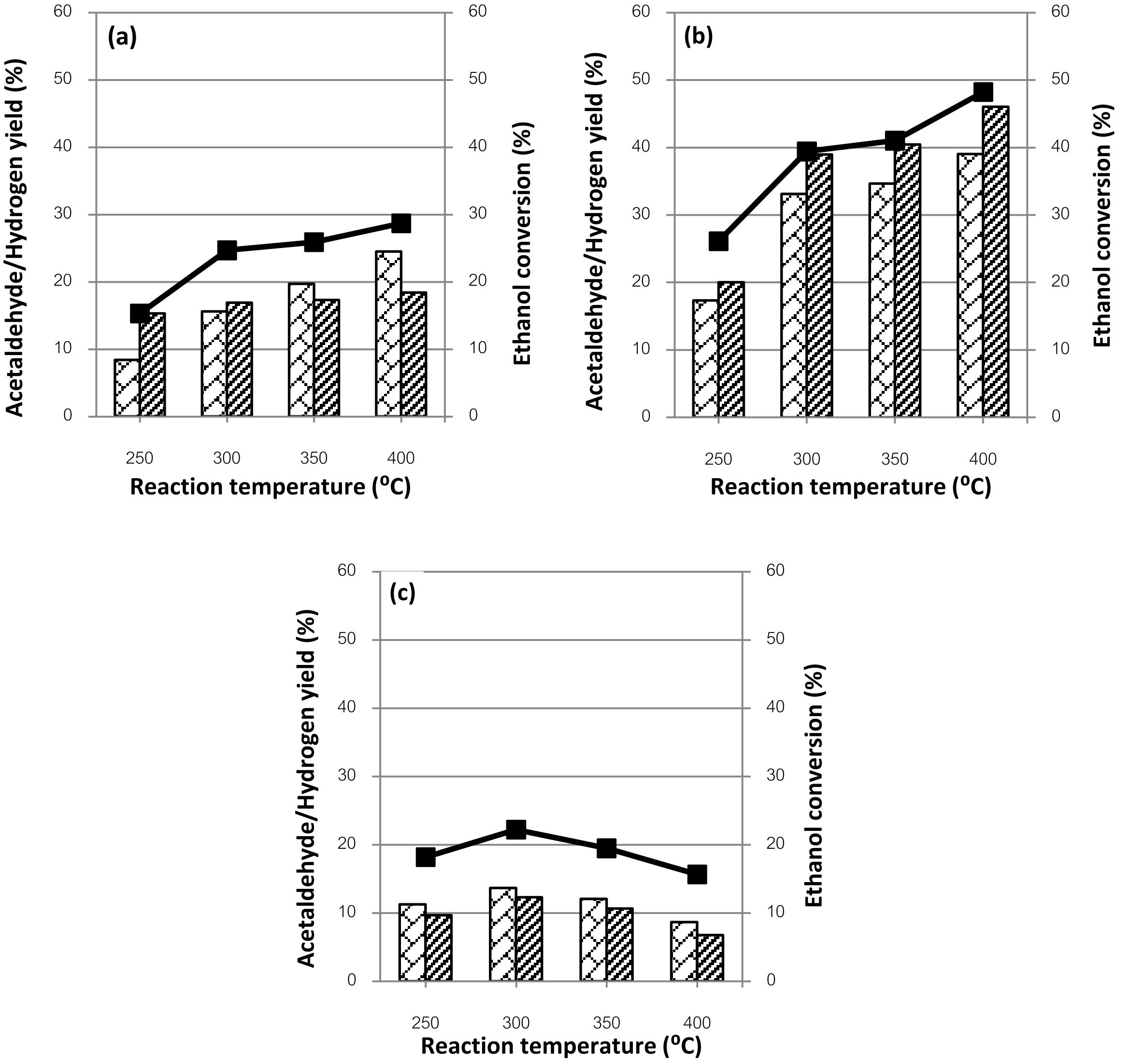

Figure 4.7 Ethanol conversion, acetaldehyde and hydrogen yield as a function of reaction temperature for ethanol dehydrogenation reaction over 2.5 wt.% Cu/SiO_2 (a), 5 wt.% Cu/SiO_2 (b) and 10 wt.% Cu/SiO_2 (c) catalyst prepared by typical impregnation technique (■ ethanol conversion, ▧ acetaldehyde yield and ▨ hydrogen yield).

In the case of Ag/SiO_2, as shown in **Figure 4.8**, it was found that the ethanol conversion and product yield increased when the reaction temperature increased from 250 to 400°C. The highest catalyst performance of Ag/SiO_2 was 10 wt.% silver loading at all reaction temperatures, **Figure 4.8 (c)**. The highest ethanol conversion, acetaldehyde and hydrogen yield were 56.62, 44.42, and 49.88%, respectively at a reaction temperature of 400°C, which is relatively higher than Cu/SiO$_2$ at the same reaction condition. This reveals that Ag is more active toward ethanol dehydrogenation as compared to Cu.

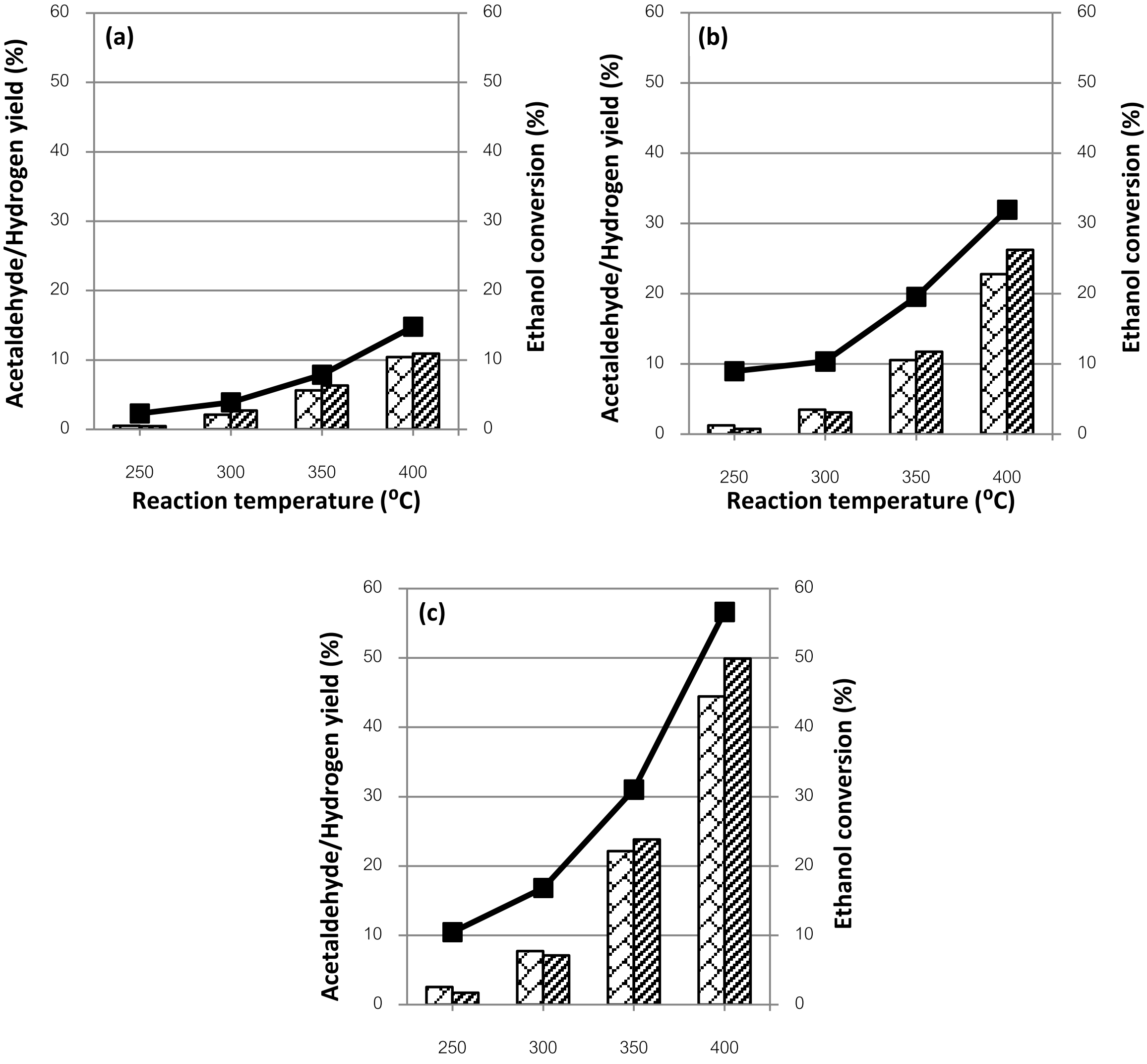

Figure 4.8 Ethanol conversion, acetaldehyde and hydrogen yield as a function of reaction temperature for ethanol dehydrogenation reaction over 2.5 wt.% Ag/SiO$_2$ (a), 5 wt.% Ag/SiO$_2$ (b) and 10 wt.% Ag/SiO$_2$ (c) catalyst prepared by typical impregnation technique (■ ethanol conversion, ▧ acetaldehyde yield and ▨ hydrogen yield).

Cu-Ag/SiO$_2$ catalysts were then tested for comparison. It is noted that bimetallic catalysts have been widely used in industrial processes for many years because of their unique catalytic properties. In the present work, it was found that bimetallic Cu-Ag/SiO$_2$

offers improvement in catalyst activity toward the dehydrogenation of ethanol compared to single use of copper and silver alone as shown in **Figure 4.9**. It was also observed that the catalyst activity of bimetallic Cu-Ag/SiO_2 increased with increasing total metal loading and reaction temperature. This result suggests the benefit of using Cu to partially replace Ag to in terms of catalyst activity improvement and catalyst cost reduction since the price of copper precursor was much cheaper than sliver metal precursor.

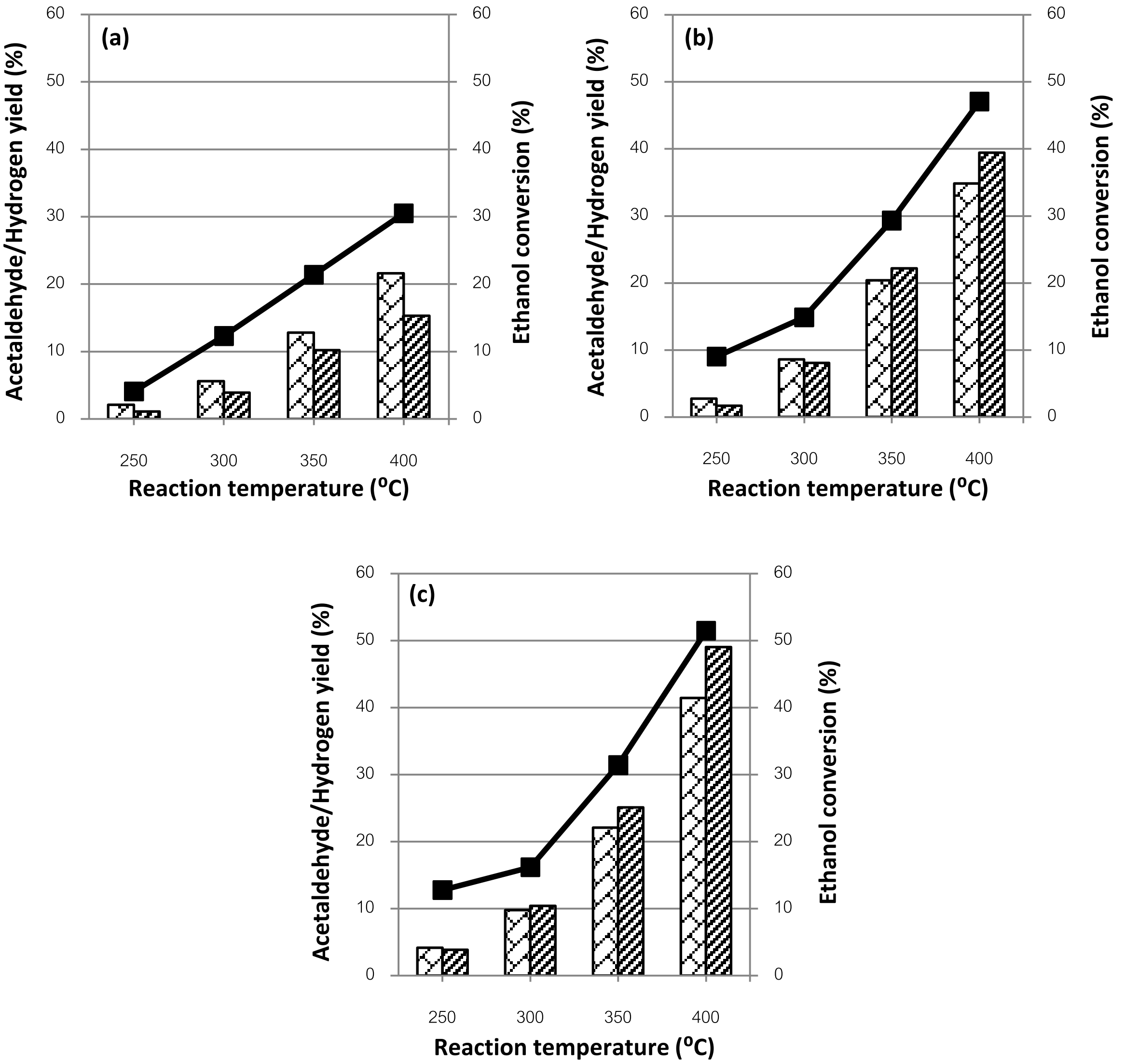

Figure 4.9 Ethanol conversion, acetaldehyde and hydrogen yield as a function of reaction temperature for ethanol dehydrogenation reaction over 2.5 wt.% Cu-Ag/SiO_2 (a), 5 wt.% Cu-Ag/SiO_2 (b) and 10 wt.% Cu-Ag/SiO_2 (c) catalyst prepared by typical impregnation technique (■ ethanol conversion, ☒ acetaldehyde yield and ▨ hydrogen yield)

4.2.2 Effects of catalyst preparation technique

Microwaves have been found to be useful in organic synthesis, material processing and waste remediation. Microwave heating is internal heating, as opposed to conventional heating, which is external heating. Thus, the application of microwaves,which caused rapid and even heating, opensup new opportunities in chemistry, materials scienceand other areas [36]. Recently, microwave heating has been developing as an effective method for the preparation of catalysts [37, 38] and can provide (i) rapid drying, (ii) moisture levelling leading to a uniform distribution of metal in the support, (iii) physically strong pellets compared to conventionally heated catalysts, and (iv) a change in the activity of the catalyst compared to its conventionally prepared analogues [39]. Microwave heating thus offers the possibility of developing catalysts with uniform pellet strength and enhanced catalyst activity. In the present study, silica supported mono- and bimetallic Cu-Ag catalysts prepared by microwave-assisted technique were selected to investigate and compare the catalyst activity which were prepared by convention impregnation method.

All mono- (Cu and Ag) and bimetallic Cu-Agcatalysts prepared by microwave-assisted technique were tested in the dehydrogenation of ethanol under the same conditions as conventional impregnation catalysts to confirm the effects of catalyst preparation for the catalystis properties and activity. The results catalyst activity testing (ethanol conversion, acetaldehyde and hydrogen yield) of all catalysts prepared by microwave-assisted technique are shown in **Figures 4.10-4.12**. The sub-figure in each figure, (a), (b) and (c) show the catalyst activity over 2.5, 5 and 10 wt.% of metal loading in monometallic (Cu and Ag) and bimetallic (Cu-Ag) respectively.

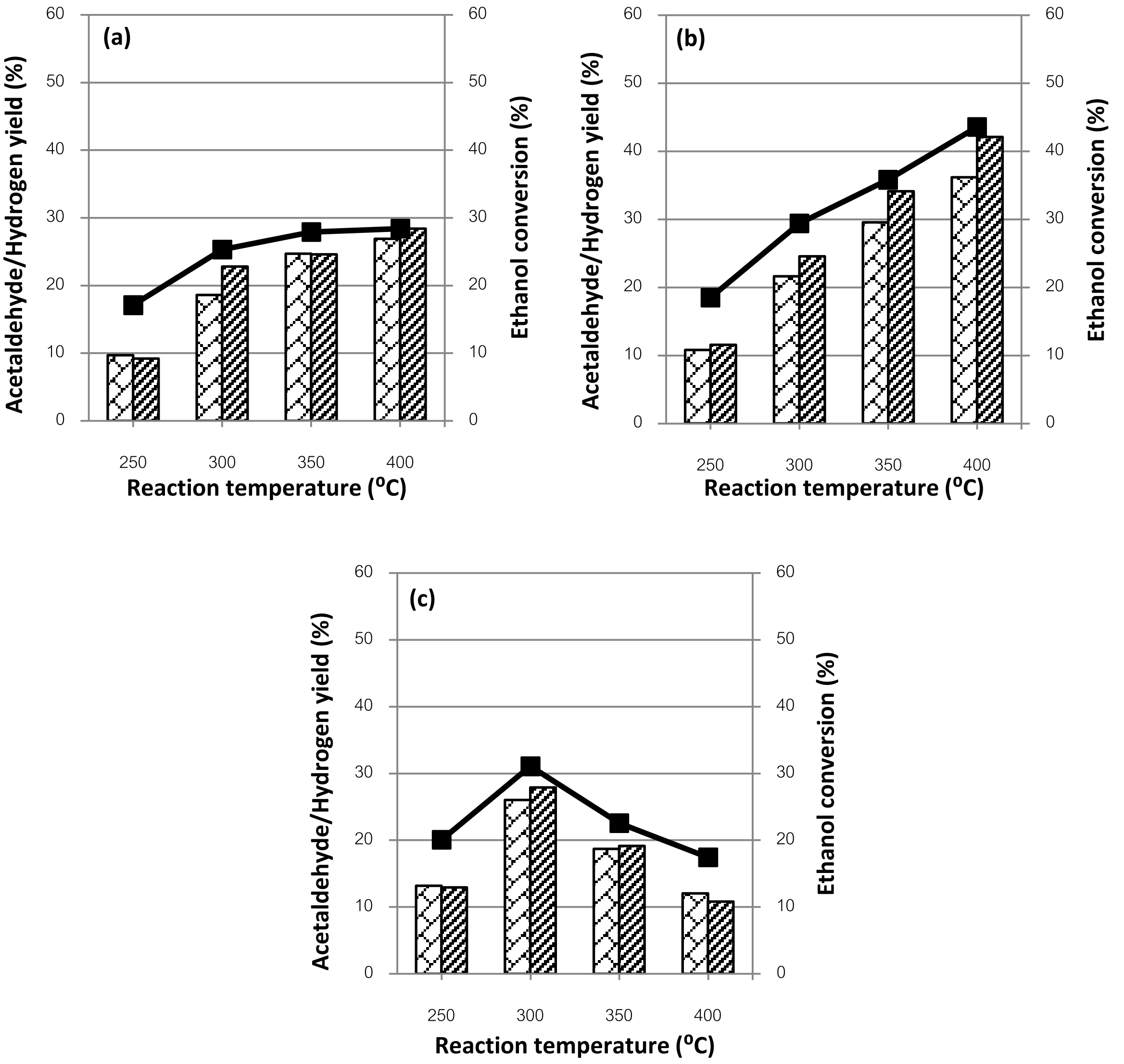

Figure 4.10 Ethanol conversion, acetaldehyde and hydrogen yield as a function of reaction temperature for ethanol dehydrogenation reaction over 2.5 wt.% Cu/SiO_2 (a), 5 wt.% Cu/SiO_2 (b) and 10 wt.% Cu/SiO_2 (c) catalyst prepared by microwave-assisted technique (■ ethanol conversion, ⊠ acetaldehyde yield and ▨ hydrogen yield).

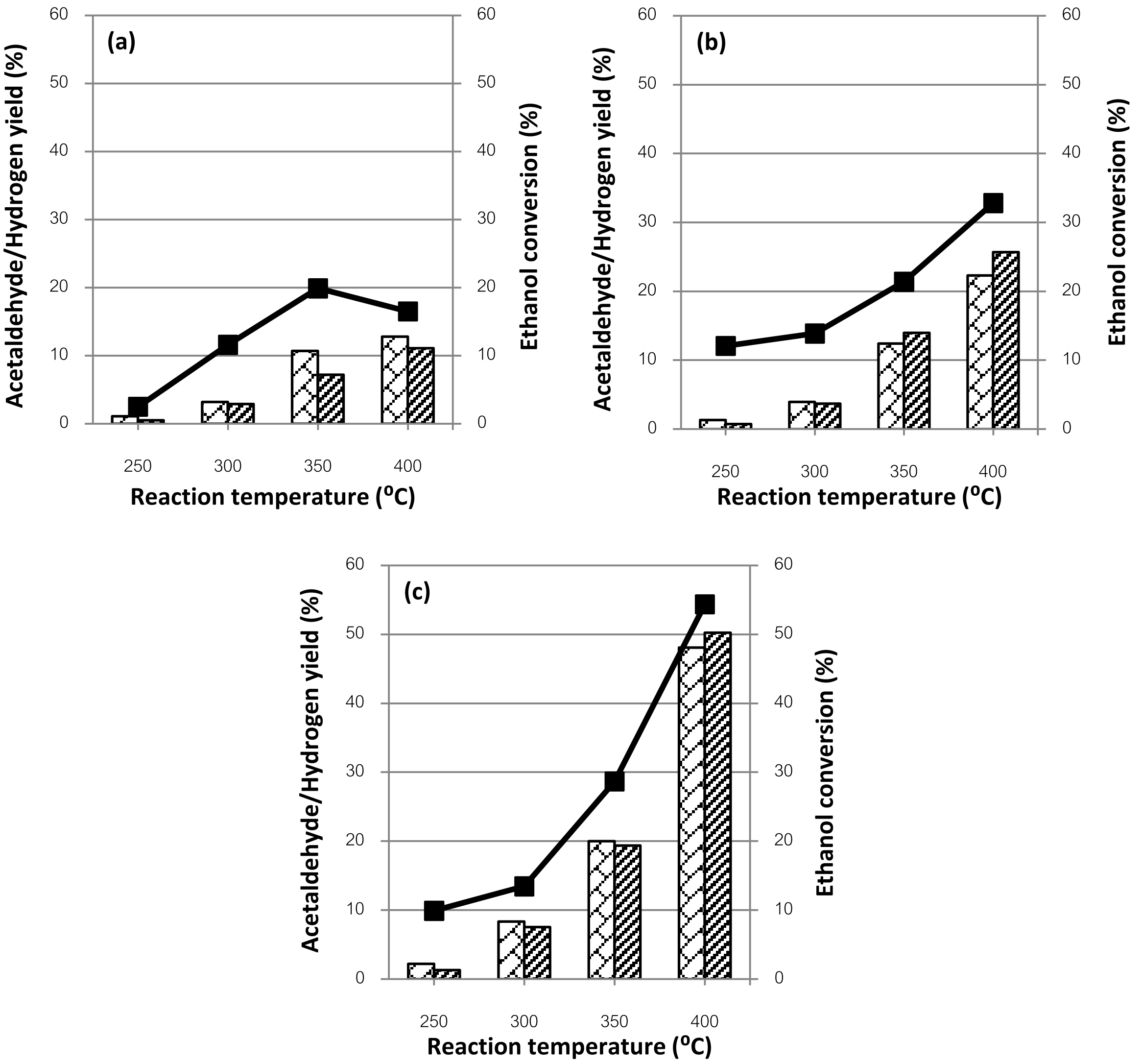

Figure 4.11 Ethanol conversion, acetaldehyde and hydrogen yield as a function of reaction temperature for ethanol dehydrogenation reaction over 2.5 wt.% Ag/SiO_2 (a), 5 wt.% Ag/SiO_2 (b) and 10 wt.% Ag/SiO_2 (c) catalyst prepared by microwave-assisted technique (■ ethanol conversion, ⊠ acetaldehyde yield and ▨ hydrogen yield).

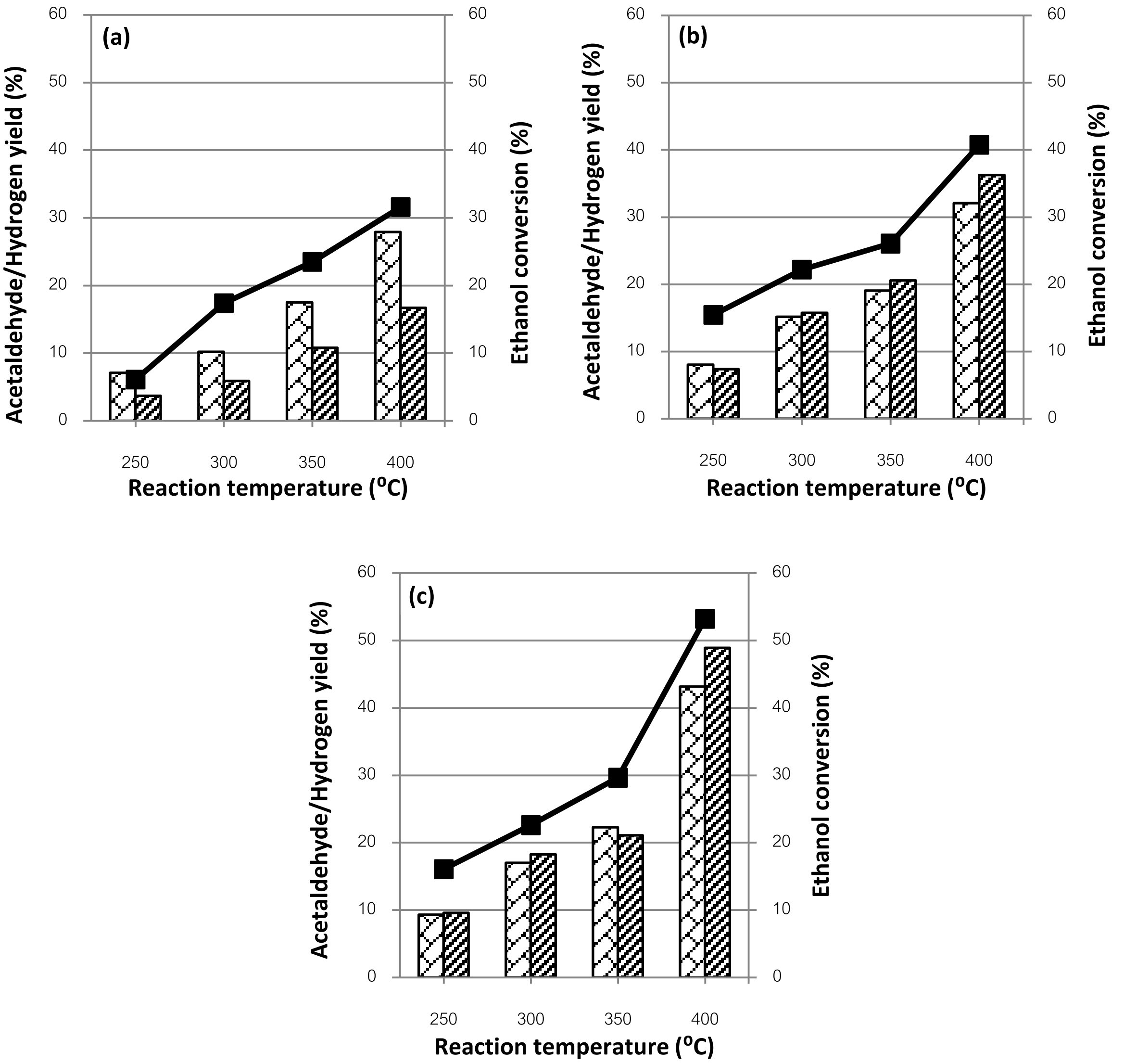

Figure 4.12 Ethanol conversion, acetaldehyde and hydrogen yield as a function of reaction temperature for ethanol dehydrogenation reaction over 2.5 wt.% Cu-Ag/SiO_2 (a), 5 wt.% Cu-Ag/SiO_2 (b) and 10 wt.% Cu-Ag/SiO_2 (c) catalyst prepared by microwave-assisted technique (■ ethanol conversion, ⊠ acetaldehyde yield and ▨ hydrogen yield).

It can be seen that all catalysts prepared by the microwave-assisted method had better activity than catalysts prepared by the conventional impregnation method. It is suggested from the catalyst characterization that the microwave-assisted technique helps the catalyst to gain higher metal dispersion. When the catalyst have higher dispersion, the opportunity to react with the reactant on the active site of the catalyst is greater. However, at high reaction temperature, the activities of catalysts prepared from microwave-assisted method are in the same range as those prepared by conventional impregnation method, which could be due to the effect of thermal sintering that damages the good metal dispersion.

After studying the catalyst activity of all catalysts, it was found that the good candidate catalysts are 10 wt.% Ag/SiO_2 and bimetallic Cu-Ag/SiO_2 catalyst since they show the highest ethanol conversion and product yield. Therefore, the production yield from ethanol dehydrogenation over 10 wt.% Ag/SiO_2 and bimetallic Cu-Ag/SiO_2 catalyst prepared by typical impregnation and microwave-assisted technique at 400°C was studied for pro-long reaction (12 hours) in order to test and confirm the catalyst activity, stability, and deactivation which are important factors for the commercial application. The result catalyst activity, stability and deactivation of 10 wt.% Ag/SiO_2 and bimetallic Cu-Ag/SiO_2 catalyst prepared by typical impregnation and microwave-assisted technique at 400°C are shown in **Figure 4.13**. Clearly, the catalyst prepared by microwave-assisted technique exhibit higher catalyst stability and activity for both 10 wt.% Ag/SiO_2 and 10 wt.% Cu-Ag/SiO_2. Among all catalysts, Cu-Ag/SiO_2 prepared by microwave-assisted technique shows the highest acetaldehyde yield of 43.16 % with the lowest deactivation percentage of 5.02 % after 12 h of operation.

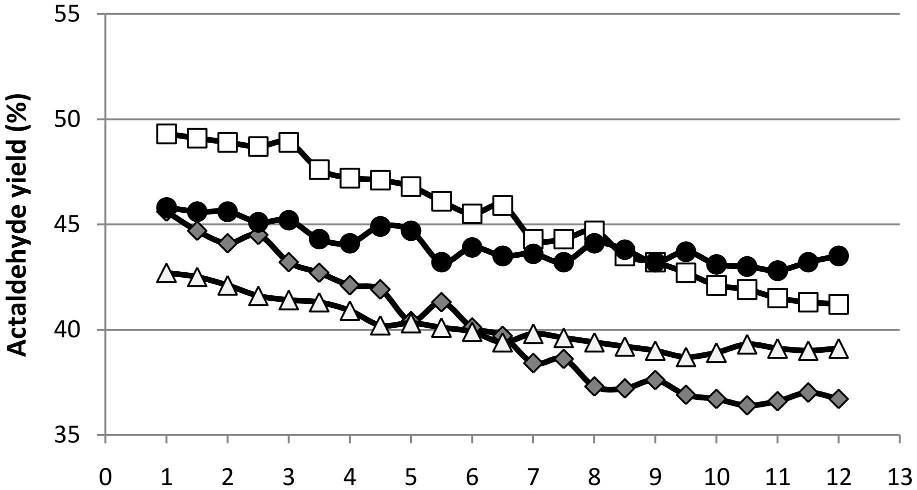

Figure 4.13 Acetaldehyde yield as a function of time over synthesized catalyst for dehydrogenation of ethanol operated at 400°C (♦ 10 wt.% Ag/SiO_2, ▲10 wt.% Cu-Ag/SiO_2 prepared by typical impregnation technique, and ■ 10 wt.% Ag/SiO_2, ● 10 wt.% Cu-Ag/SiO_2 prepared by microwave-assisted technique).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research work is studied acetaldehyde and hydrogen production through a catalytic dehydrogenation of ethanol. The monometallic Cu, Ag, and bimetallic Cu-Ag supported by SiO_2 were prepared with the different metal loading of 2.5-10% and applied as catalysts in this research. The catalysts were synthesized by conventional impregnation technique and microwave-assisted technique and tested activity in the ethanol dehydrogenation reaction under the operating temperature between 250 to 400°C. The catalytic dehydrogenation of ethanol was followed through a fixed bed continuous flow reactor at atmospheric pressure. Catalyst physical and chemical characterizations by nitrogen adsorption measurements (BET), X-ray diffraction (XRD), and temperature-programmed reduction (TPR) were carried out in order to elucidate the effect of active metal types, metal loading, and catalyst preparation methods on the ethanol dehydrogenation activity and stability.

The studies revealed that types of active metals, metal loading, and catalyst preparation methods had a significant influence on the reactivity. For all different metal loading (2.5, 5, and 10 wt.% of Cu, Ag, and mixed Cu-Ag) prepared by conventional impregnation technique, it was found that the catalyst performance in term of activity increased with increasing metal loading and reaction temperature except over 10 wt.% Cu/SiO_2 catalyst. This was probably due to Cu loading increasing as a result of large particle size and poor dispersion of Cu metal on support surface. In addition, bimetallic material used to improve the catalyst properties and activity. Bimetallic $Cu\text{-}Ag/SiO_2$ enhanced reaction activity higher than monometallic Ag. Moreover, comparison the catalyst preparation methods between conventional impregnation and microwave-assisted technique on the catalyst activity, it was also found that the catalysts prepared by microwave-assisted technique gave better activity than catalyst prepared by conventional impregnation technique, which could be mainly due to the dispersion improvement of metal over support by this preparation.

Among all catalysts, bimetallic Cu-Ag/SiO_2 prepared by microwave-assisted technique showed the highest activity and stability after 12 h of reaction. So, it was an active and selective catalyst for catalytic dehydrogenation of ethanol to produce acetaldehyde and hydrogen, which will be useful in commercialization application.

5.2 Recommendations for future research

The possible reactions of ethanol conversion should be evaluated for examining the type and amount of by-products that occur.

The temperature programmed oxidation (TPO) technique used for analyzing of Cu/SiO_2, Ag/SiO_2 and bimetallic Cu-Ag/SiO_2 catalysts deactivation should be further investigated in order to affirm coke deposition in dehydrogenation of ethanol. In addition, X-ray diffraction (XRD) was introduced to analyze the properties of the fresh and used catalysts, such as carbon formation, particle size and crystallinity of metal.

The effect of time course on catalyst stability of all Cu/SiO_2, Ag/SiO_2 and bimetallic Cu-Ag/SiO_2 in different metal loadings should be compared and the best catalyst selected for the dehydrogenation of ethanol in terms of catalyst activity and stability.

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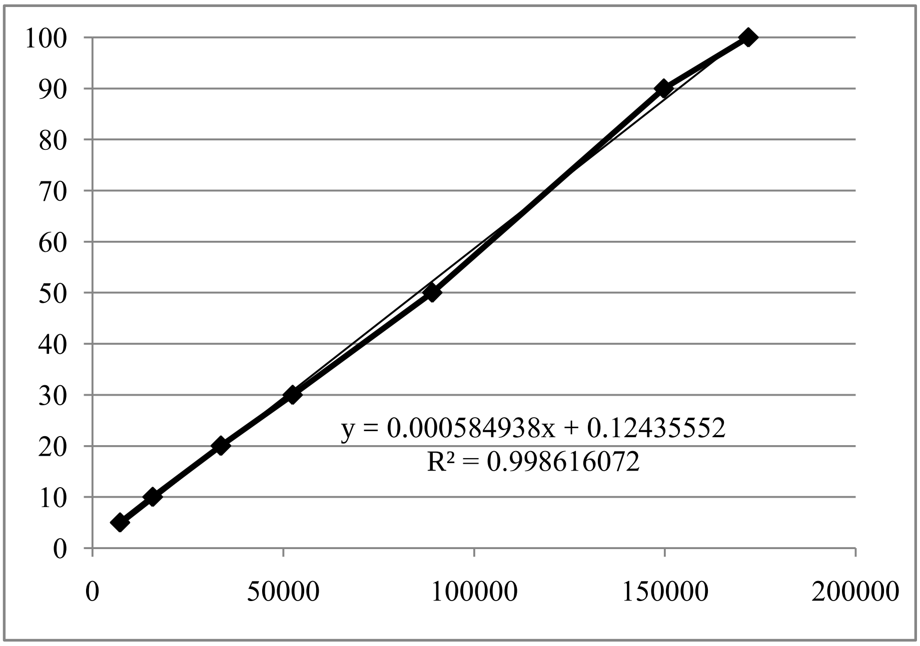
APPENDIXES

APPENDIX A

A.1 Standard Calibration Curve

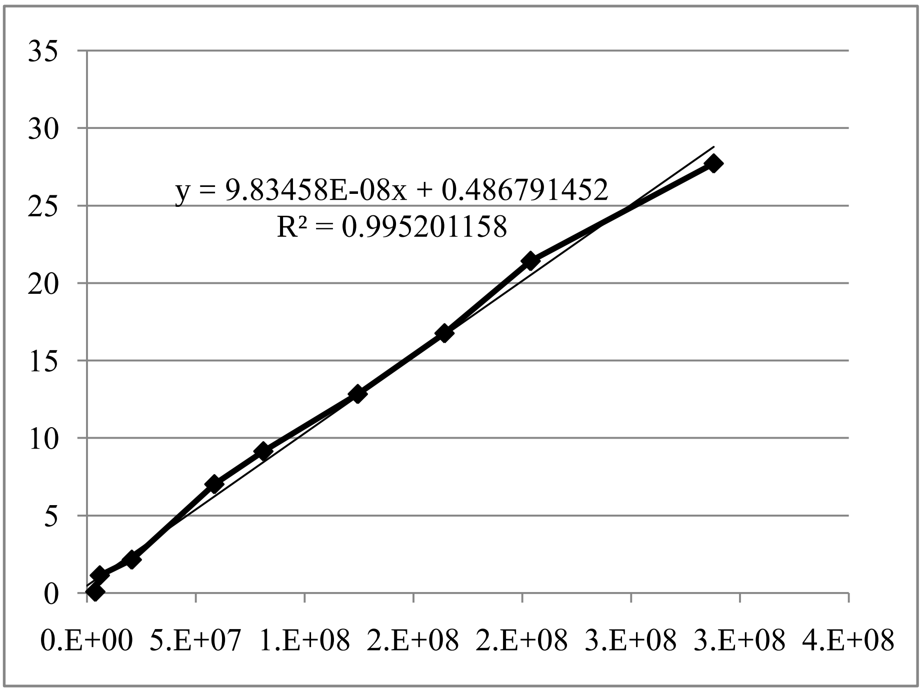
- Hydrogen

%v/v H_2 in N_2	% purity (%mole/mole)	Peak area NO. 1	Peak area NO. 2	Mean Peak area
5	5	7,209.20	7,189.50	7,199.35
10	10	15,950.20	15,688.70	15,819.45
20	20	33,627.20	33,744.00	33,685.60
30	30	52,057.30	52,876.20	52,466.75
50	50	89,249.80	88,853.30	89,051.55
90	90	149,792.50	149,732.20	149,762.35
100	100	171,645.20	172,254.10	171,949.65



- Acetaldehyde

% purity (%mole/mole)	**Peak area NO. 1**	**Peak area NO. 2**	**Mean Peak area**
27.72	287,933,457.40	287,845,351.40	287,889,404.40
21.42	204,537,220.50	202,989,532.50	203,763,376.50
16.76	163,227,483.00	165,208,283.00	164,217,883.00
12.84	124,573,950.60	124,106,216.60	124,340,083.60
9.14	81,134,575.70	80,882,131.70	81,008,353.70
7.02	57,859,304.25	59,154,714.25	58,507,009.25
2.16	21,003,456.60	20,183,058.60	20,593,257.60
1.15	5,856,738.40	5,832,240.40	5,844,489.40
0.08	3,834,829.70	3,818,765.70	3,826,797.70



APPENDIX B

B.1 Adsorption and desorption isotherms of prepared catalysts

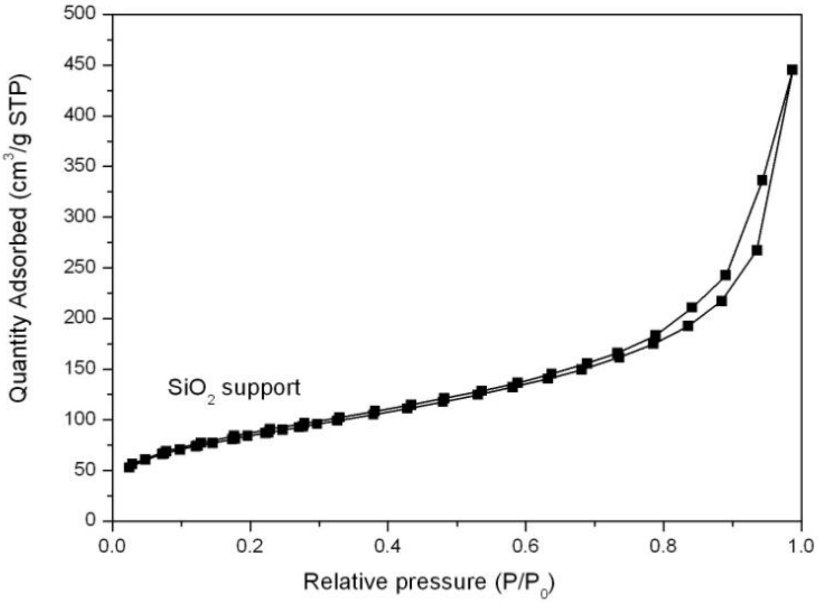


Figure B.1 Adsorption and desorption isotherms of silica support.

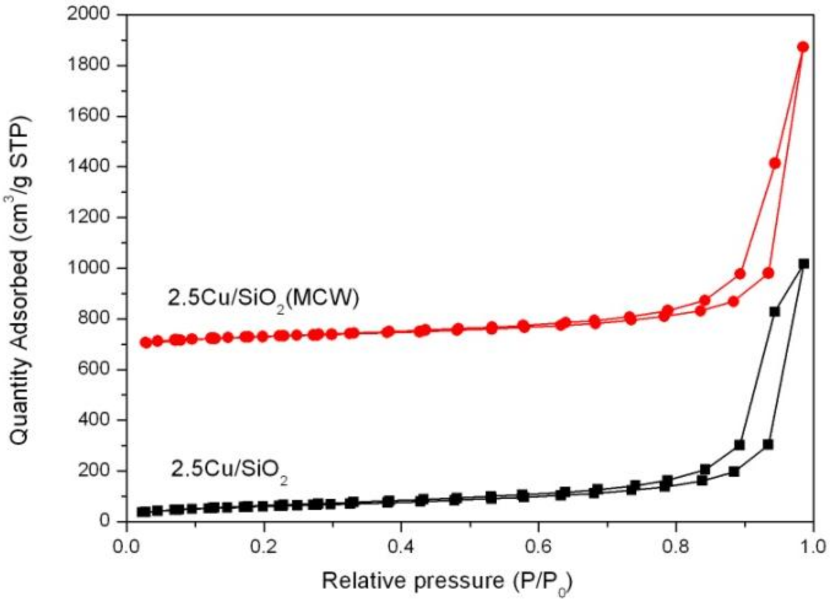


Figure B.2 Adsorption and desorption isotherms of 2.5 wt.% copper doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

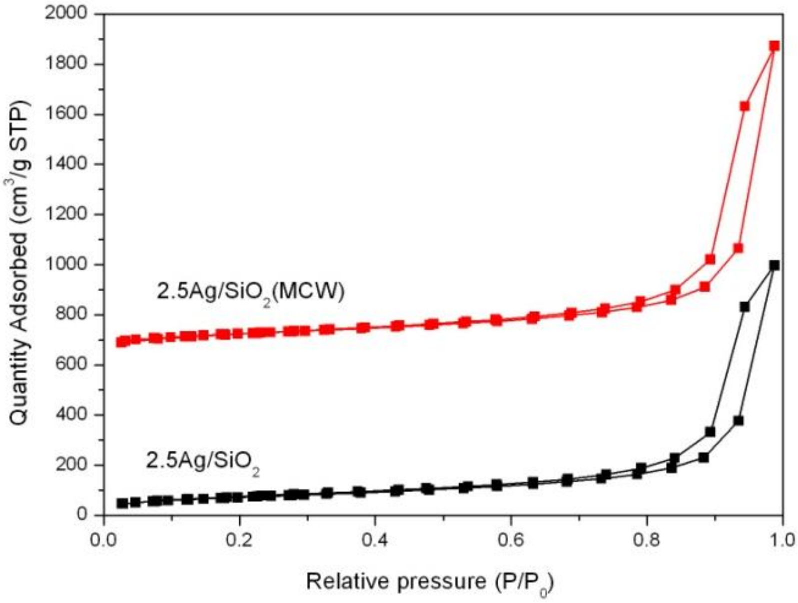


Figure B.3 Adsorption and desorption isotherms of 2.5 wt.% silver doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

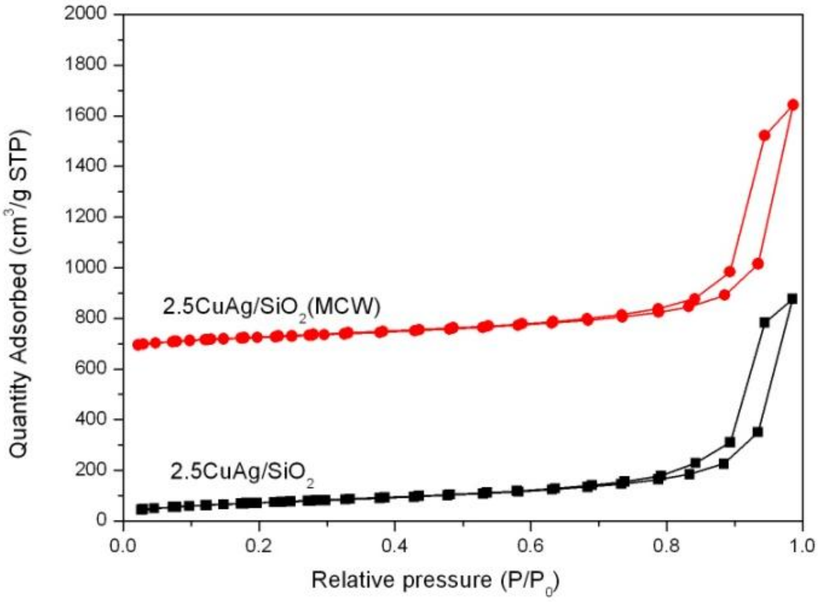


Figure B.4 Adsorption and desorption isotherms of 2.5 wt.% copper and silver doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

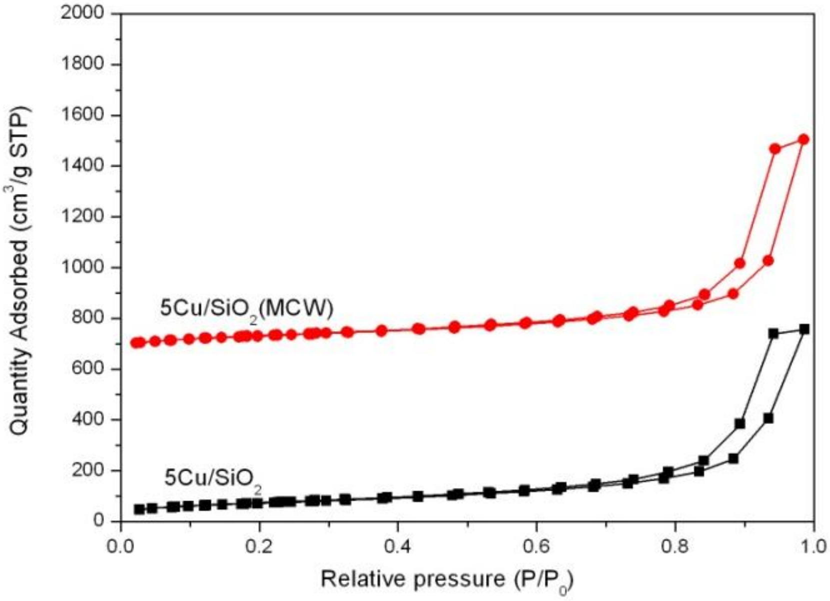


Figure B.5 Adsorption and desorption isotherms of 5 wt.% copper doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

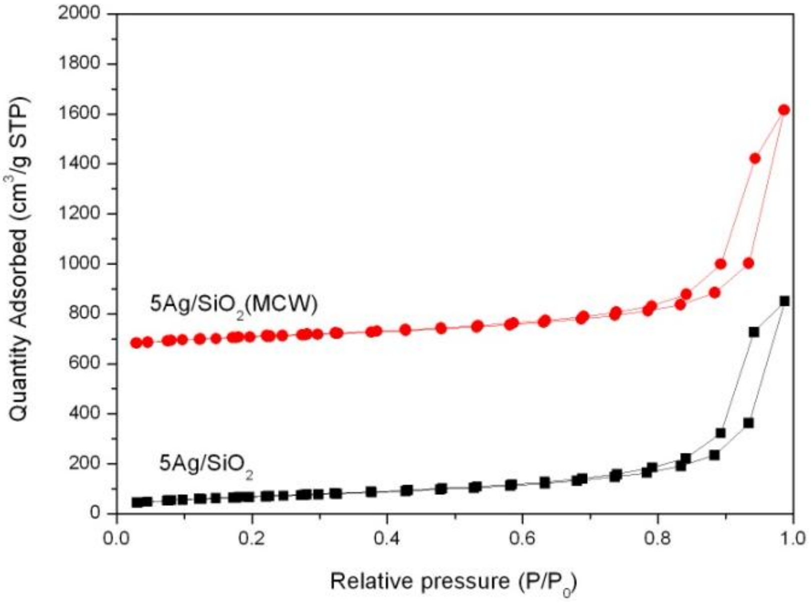


Figure B.6 Adsorption and desorption isotherms of 5 wt.% silver doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

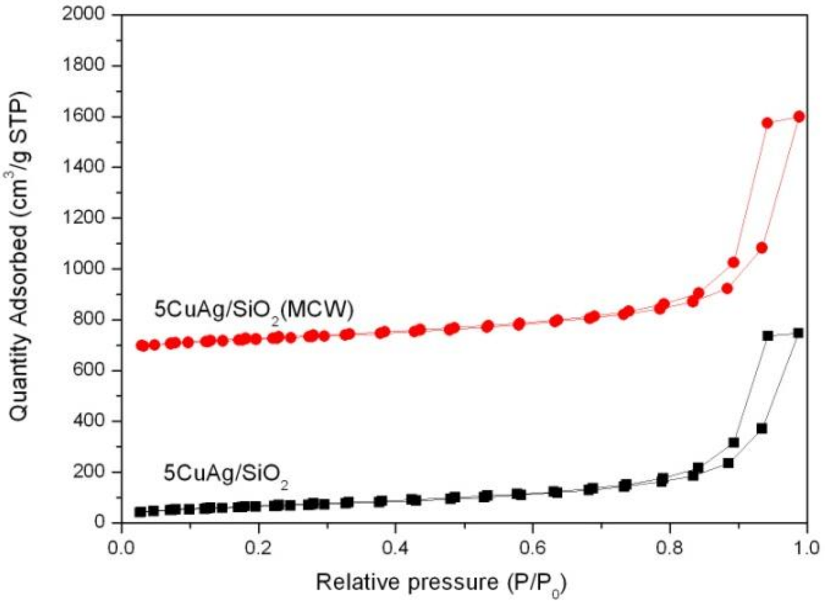


Figure B.7 Adsorption and desorption isotherms of 5 wt.% copper and silver doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

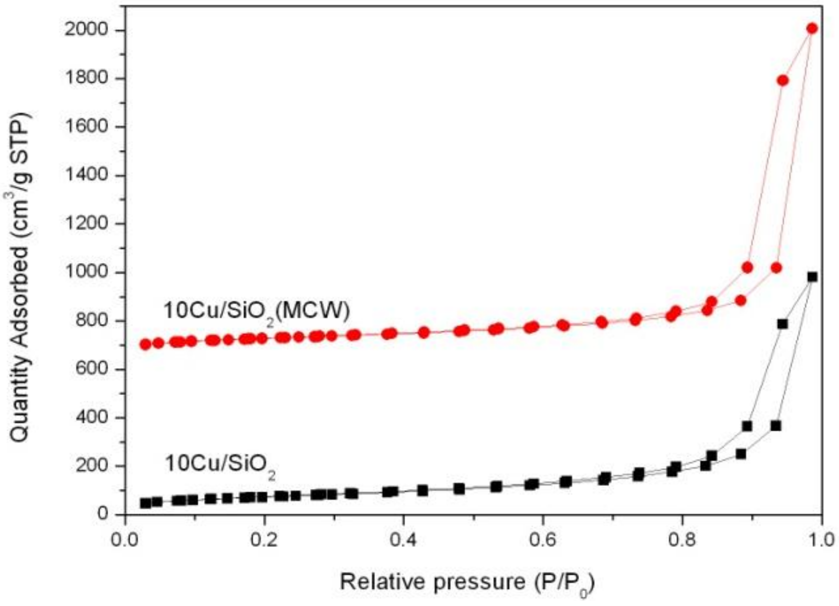


Figure B.8 Adsorption and desorption isotherms of 10 wt.% copper doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

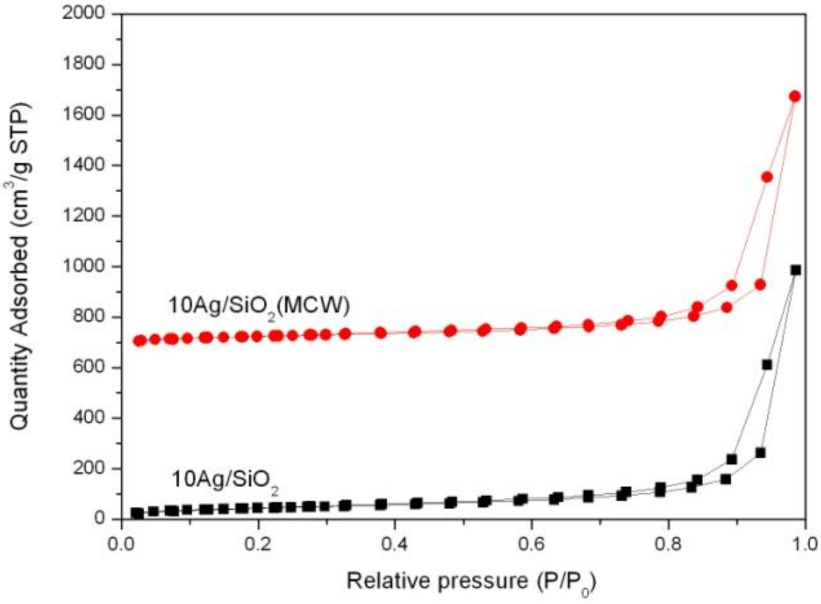


Figure B.9 Adsorption and desorption isotherms of 10 wt.% silver doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.

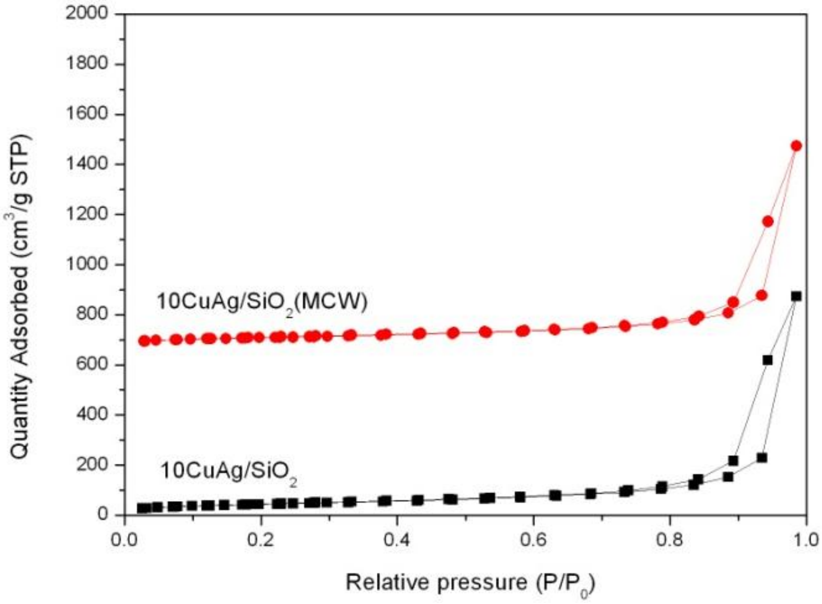


Figure B.10 Adsorption and desorption isotherms of 10 wt.% copper and silver doped on silica support: (■) typical impregnation technique and (●) microwave-assisted technique.