BIO-CHEMICALS FROM CONVERSION OF BIO-ETHANOL USING VARIOUS SINGLE OXIDES

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ABSTRACT
Bio-ethanol is mainly produced by the fermentation process from biomass materials. Although mostly used as biofuels, it can be also used for the production of value-added chemicals such as acetaldehyde, acetone, 1,3-butadiene, and 1-butanol. The catalytic conversion of bio-ethanol can be generally divided into two pathways; dehydration and dehydrogenation. In this work, the catalytic conversion of bio-ethanol was investigated using MgO, CuO and ZnO as basic oxide catalysts, aiming to investigate the production of bio-chemicals from bio-ethanol conversion. The gaseous products were analyzed using GC-FID, and the liquid products were analyzed using GC-MS/TOF. It was found that MgO, CuO, and ZnO enhanced the dehydrogenation of ethanol. The major components in the oils were oxygenate compounds, which consisted of aldehydes, esters, and ethers, such as acetaldehyde, crotonaldehyde, ethyl acetate, and 1,1-diethoxyethane. The results indicated that MgO gave the highest selectivity to acetaldehyde.
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INTRODUCTION
The catalytic conversion of bio-ethanol is an important reaction for the production of valuable chemicals. It can be also used for the production of value-added chemicals such as acetaldehyde, acetone, 1,3-butadiene, and 1-butanol. Chieregato _et al_. (2015) studied about the catalytic conversion of ethanol in the Lebedev and Guerbet reactions by using MgO at 250°C and 400°C. The MgO catalyst showed pure basic properties. They found that at the reaction at a low temperature gave low ethanol conversion while MgO resulted in high ethanol conversion at a higher temperature. Furthermore, Makshina _et al_. (2012) investigated the catalytic conversion of ethanol into 1,3-butadiene using $MgO-SiO_2$ catalysts doped with the transition metal oxide (MO_x); namely, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ag. These transition metal oxides were used with the aim at increasing the acetaldehyde production and reducing the ethylene formation. It was found that undoped $MgO-SiO_2$ produced ethylene and acetaldehyde as the main products because MgO enhanced dehydrogenation and aldol condensation reactions whereas SiO_2 catalyzed dehydration. Moreover, the results showed that both acetaldol and crotonaldehyde as the reaction intermediates led to 1-butanol or 1,3-butadiene. Additionally, the acid-base properties of a catalyst have an important role for the product distribution. Moreover, the catalytic conversion of bio-ethanol to value chemicals needs the different sites of catalysts. In this work, the effect of metal oxides; that are, MgO, CuO, and ZnO, on the catalytic conversion of bio-ethanol was investigated. Moreover, possible reaction pathways

promoted by using MgO, CuO, and ZnO that consist of different acid-base properties were investigated.

EXPERIMENTAL

A. Catalyst Preparation and Characterization

MgO, CuO and ZnO supplied from Sigma Aldrich, Singapore. The catalysts were pelletized and sieved to 20-40 mesh particles. The specific surface area, pore volume, and pore diameter of catalysts were determined by using the Brunauer-Emmett-Teller (BET) technique. Moreover, the total acidity and basicity were evaluated using Temperature Programmed Desorption of Ammonia (NH_3-TPD) and Temperature Programmed Desorption of carbon dioxide (CO_2-TPD), respectively.

B. Catalyst Testing

The catalytic conversion of bio-ethanol was carried out in a stainless steel U-tube reactor. The bio-ethanol (99.5%) was fed into the reactor using a syringe pump with helium gas as a carrier gas. The catalytic conversion of bio-ethanol was investigated at reaction conditions: temperature = 400 ℃, WHSV = 9.4 $g_{ethanol}/g_{catalyst}$ h^{-1}, and reaction time = 3 hours. The products coming out from U-tube reactor were condensed in ice-water cooling system to collect the liquid product, and the non-aqueous product was extracted from the liquid product by using carbon disulfide, and the gaseous products were kept in a gas sampling bag (Chinniyomphanich *et al*., 2015).

C. Product Analysis

The liquid products were analyzed by using a gas chromatography equipped with a Mass Spectrometry of Time of Flight type (1D GC-TOF/MS), Agilent 7890. Helium was used as the carried gas, and nitrogen was used in the cooling system. The conditions were set as followed: initial temperature of 40 ℃, 2.5 ℃/min heating rate, final temperature of 250 ℃ held for 5 min, and split ratio at 1:25. Moreover, the gaseous products were analyzed by gas chromatography (Agilent Technologies 6890 Network GC system) using HP-PLOT Al_2O_3 column (50 m x 0.32 mm ID and 20 μm film thickness) equipped with a flame ionization detector (FID) to determine hydrocarbon gases. The chemical products obtained from ethanol conversion were classified into two groups; dehydration and dehydrogenation products.

RESULTS AND DISCUSSION

A. Catalyst Characterization

The physical properties of catalysts are displayed in Table 1. The BET surface area, pore volue, and pore diameter were determined by Barrette-Joyner-Halenda (BJH) and Braunamer-Emmet-Teller (BET) method. Additionally, the basicity of catalysts was characterized using the temperature programmed desorption of CO_2. The CO_2-TPD profiles of MgO, CuO, and ZnO are displayed in Figure 1. The profiles have only one peak around 50-650 ℃. The peaks are observed at 193.2 ℃, 358.4 ℃, and 618.2 ℃ using MgO, ZnO, and CuO, respectively. Moreover, the basic strength are increased in the following order: ZnO < MgO < CuO. In addition, the total acidity was characterized using the temperature

programmed desorption of ammonia. Figure 2 illustrates the TPD-NH$_3$ profiles of MgO, CuO, and ZnO catalysts. For MgO, the profile has only one peak at 233 ℃. In the profile of CuO, the first peak locates at 164 ℃, and the second one is located at 231 ℃. For ZnO, the first peak is observed at 230 ℃, the second peak locates at around 380 ℃, and the third one is observed at 421 ℃. It is found that ZnO gives the highest acid strength than others. Table 2 shows the total basicity and acidity of MgO, CuO, and ZnO. It is noticed that CuO has the highest basicity of around 0.092 mmol/g. Hence, the total basicity are increased in the following order: ZnO < MgO < CuO. Moreover, the total acidity are increased in the following order: MgO < CuO < ZnO.

Table 1 Physical properties of catalysts.

Catalyst	Surface Area (m^2/g)[a]	Pore Volume (cm^3/g)[a]	Pore Diameter (nm)[b]
MgO	0.0082	0.0046	2232
CuO	0.1304	0.0187	574.1
ZnO	2.6430	0.0596	90.19

[a] Determined by BET method
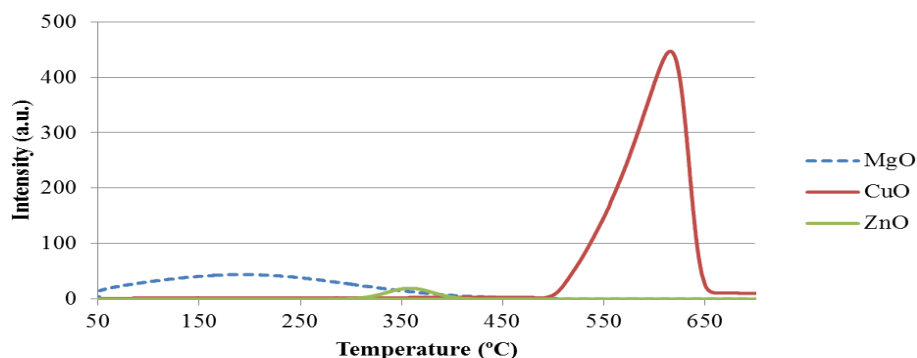
[b] Determined by B.J.H. method

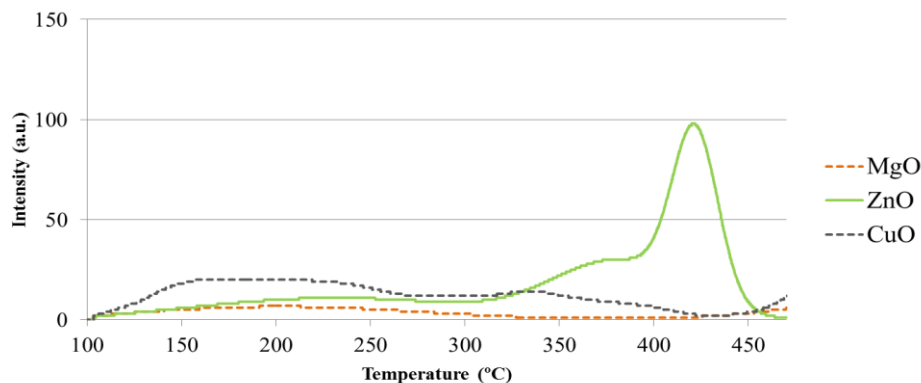**Figure 1** CO$_2$-TPD profiles of MgO, ZnO, and CuO catalysts.

Figure 2 NH$_3$-TPD profiles of MgO, ZnO, and CuO catalysts.

Table 2 Total basicity and acidity of MgO, CuO, and ZnO catalysts.

Catalysts	Density of base (mmol/g)	Density of acid (mmol/g)	Ratio of total basicity: total acidity
MgO	0.032	0.004	8.000
CuO	0.092	0.019	4.842
ZnO	0.013	0.029	0.448

B. Catalytic Activity Testing

The catalytic conversion of bio-ethanol using MgO, CuO, and ZnO catalysts are shown in Figure 3. The results indicate that ZnO catalyst gives the highest ethanol conversion up to 50% at 3 hours time-on-stream. Table 3 shows the yield of aqueous, non-aqueous, and gas products obtained from the catalytic conversion of bio-ethanol using MgO, CuO, and ZnO catalysts. As compared to the non-catalytic case, the gas yield is increased from 7.92% to 17.9%, 15.6%, and 18.7% with using MgO, CuO and ZnO, respectively It is found that ZnO gives the highest selectivity to gaseous products among the others. Furthermore, the concentration of hydrocarbon gas in gaseous products is presented in Figure 4. It is noticed that ethylene is the major component obtained from all catalysts, especially with using ZnO. The selectivity to ethylene is decreased from 63.1% to 45.0% with using MgO catalyst. Moreover, the extracted oils are composed of two main components; namely, dehydration and dehydrogenation products. The dehydrogenation products are then classified into six groups; namely, alcohols, aldehydes, ketones, esters, ethers, and acids. Figure 5 illustrates the selectivity of each group in dehydrogenation products obtained from the catalytic and non-catalytic conversion of bio-ethanol at 3 hours. It is observed that all catalysts give similar groups of components of dehydrogenation products. It is found that MgO catalyst gives the highest selectivity to aldehydes up to 94.7 %. Therefore, the aldehydes selectivity is increased in the following order: CuO < ZnO < MgO.
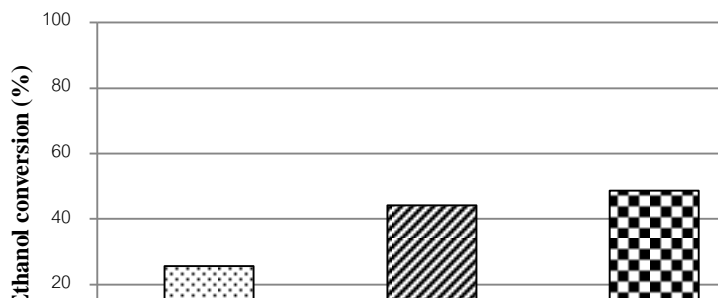

Figure 3 Ethanol conversion of MgO, CuO, and ZnO.

Table 3 Yield of products obtained from MgO, CuO, and ZnO catalysts.

Sample	%Relative yield		
	Aqueous	Non-aqueous	Gas
Non-catalyst	10.7	5.74	7.92
MgO	13.5	8.47	17.9
CuO	15.0	17.9	15.6
ZnO	16.2	17.2	18.7

Moreover, the aldehydes are composed of two components; namely, acetaldehyde and crotonaldehyde. Figure 6 shows the product yield of acetaldehyde and crotonaldehyde obtained from using MgO, CuO, and ZnO catalysts. Among all catalysts, MgO gives the highest acetaldehyde yield, followed by ZnO and CuO. This indicates that MgO catalyst favors to produce around 17% acetaldehyde. Therefore, the yield of acetaldehyde at 3 hours can be ranked as follows: ZnO < CuO < MgO. The possible reaction pathways are displayed in Figure 7. This can be explained that MgO catalyst enhances the dehydrogenation of acetaldehyde, resulting in the increasing production of acetaldehyde and crotonaldehyde. On the other hand, CuO catalyst promotes different reactions from MgO catalyst, resulting in the increasing formation of 1,1-diethoxyethane. Moreover, the use of ZnO catalyst promotes both the dehydration and dehydrogenation of ethanol, resulting in the increasing formation of acetaldehyde and ethylene.
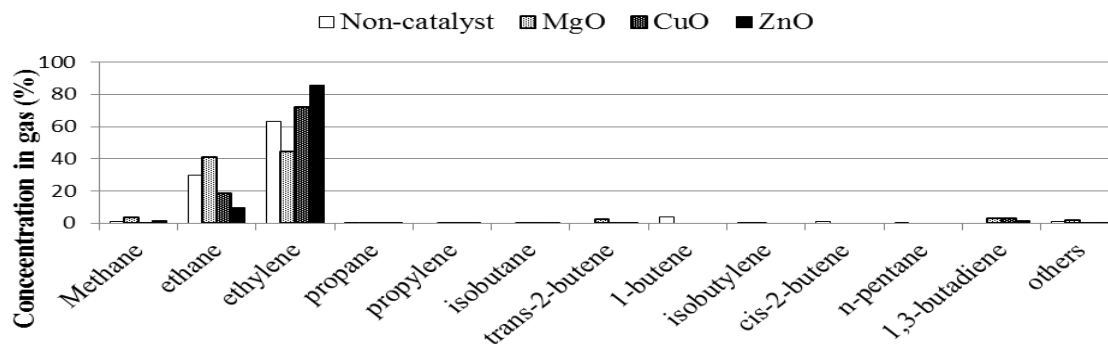

Figure 4 Concentration of hydrocarbon gases in gaseous products using MgO, CuO, and ZnO catalysts at 3 hours time-on-stream.

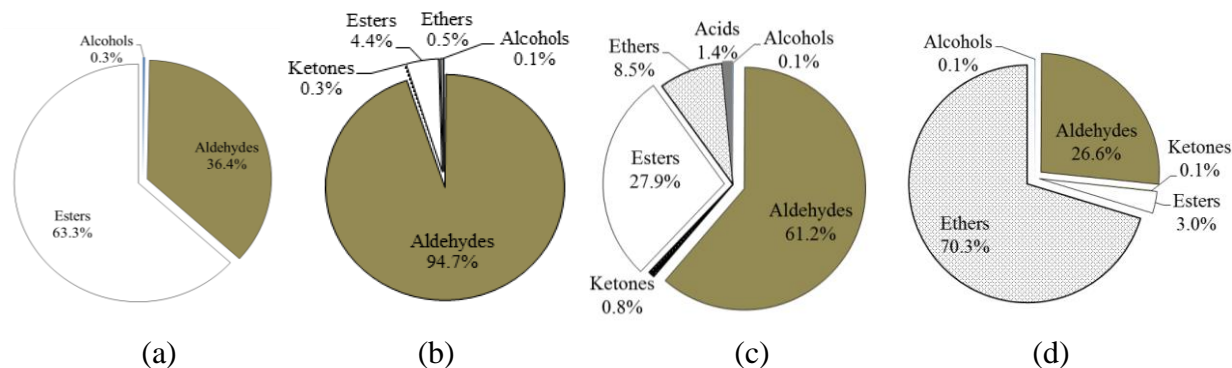(a)   (b)   (c)   (d)

Figure 5 Composition of dehydrogenation products obtained from; (a) Non-catalyst, (b) MgO, (c) CuO, and (d) ZnO at 3 hours time-on-stream.
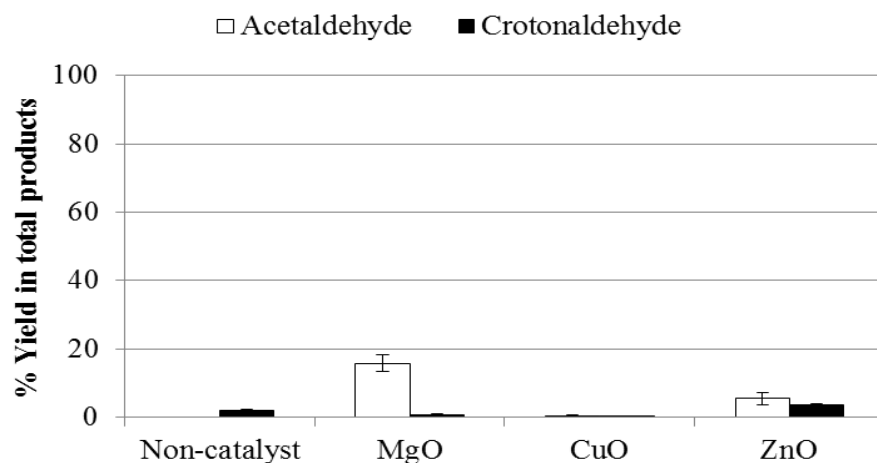

Figure 6 Yield of acetaldehyde and crotonaldehyde obtained from using MgO, CuO, and ZnO catalysts.
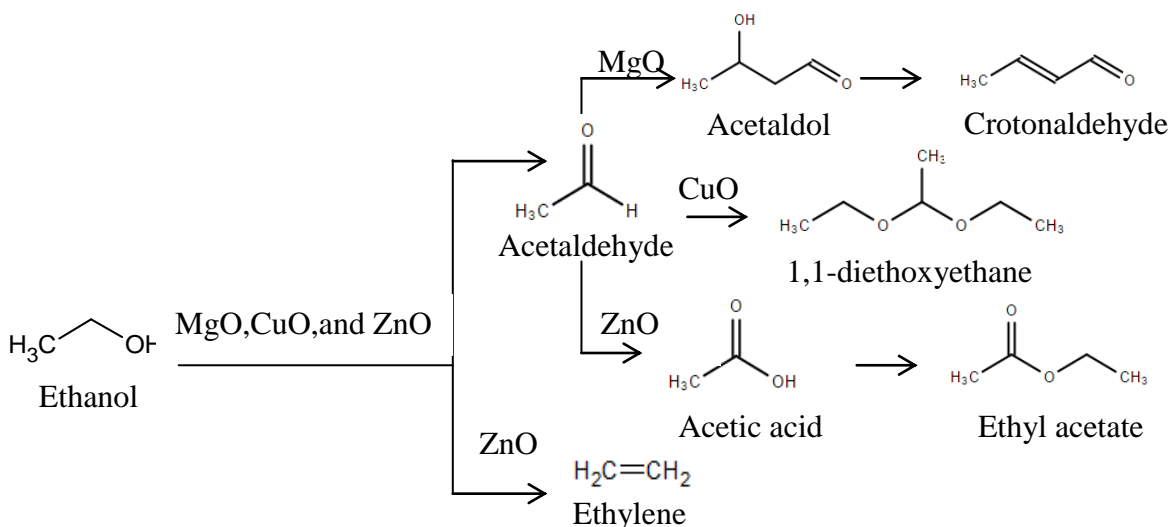

Figure 7 Possible reaction pathways for the catalytic conversion of ethanol to chemicals promoted by using MgO, CuO, and ZnO catalysts.

CONCLUSIONS

The effect of metal oxides; that are, MgO, CuO, and ZnO, on the catalytic conversion of bio-ethanol and the selectivity of products was studied. It was observed that all catalysts enhanced the dehydrogenation of ethanol, resulting in the increasing formation of acetaldehydes. The highest ethanol conversion was achieved at 50% by using ZnO catalyst. It was found that each catalyst promoted different reaction pathways and selectively produced different products. MgO catalyst produced aldehydes with the highest proportion

of dehydrogenation products. Additionally, the catalytic activity on acetaldehyde production depended on the acid-base properties of catalysts. ZnO catalyst produced the highest selectivity to ethylene due to its higher density of acid than the others. The mostly-pure basic density of MgO catalyst was found to enhance the acetaldehyde formation with the highest selectivity.

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