CHAPTER IV

$Co_3O_4/\gamma\text{-}Al_2O_3$ AS A CATALYST FOR GREEN CHEMICALS PRODUCTION VIA CATALYTIC DEHYDRATION OF BIO-ETHANOL

4.1 Abstract

The catalytic dehydration of bio-ethanol is an effective route to transform alcohol to valuable hydrocarbons and chemicals such as olefins and aromatics. There are a variety of reactions that involve, after ethylene is formed as an intermediate, such as oligomerization, aromatization, and alkylation. Products can be, for examples, butylene, benzene, derivatives of benzene, and oxygenates. In this research, cobalt oxide-promoted alumina ($Co_3O_4/\gamma\text{-}Al_2O_3$) was examined, aiming to investigate the production of high valuable oxygenate compounds and hydrocarbons in bio-ethanol dehydration. The amount of Co loading was fixed at 5.0 wt%. The catalysts were characterized using SAA, XRD, and XPS, and tested in a fixed-bed reactor under atmospheric pressure at 500°C for 8 hours. Additionally, the gaseous products were analyzed using an on-line GC, and the oil products were analyzed using GCxGC-MS/TOF. With oxide loading, the amount of C_9 and C_{10}^{+} aromatics increased in the oil as ethylene decreased in the gas. The major components in the oil are oxygenate compounds, which consisted of ketones and alcohols such as 2-butanone, 2-pentanone, and phenol, together with hydrocarbons such as benzene, and a trace amount of p-xylene, ethyl-benzene, and naphthalene. The ratio of oxygenates and hydrocarbons was 19:1. Furthermore, XPS result indicated that Co_3O_4 mainly existed on $\gamma\text{-}Al_2O_3$, and after use, some of Co_3O_4 transformed to CoO.

4.2 Introduction

High cost solvents such as pentanones have increasingly been used for medical treatment, preparation of pharmaceuticals, and pesticides, and other industrial applications. Currently, available processes for producing pentanones are, for example, liquid phase oxidation of 2-pentanol and hexanoic acid, but gave high amounts of hazardous and toxic reagents that affect to the environment (He *et al.*,

2005). Moreover, the available processes are not only un-environmental friendly, but also composed of multi-steps that involved basic-catalyzed condensation to aldor species, followed by dehydrogenation of the intermediates on an acid catalyst, and then the last is selective hydrogenation, yielding unsaturated carbonyl compounds and generating a large amount of wastes. In the last decade, several types of catalyst were employed for pentanones production. For example, He *et al.*, (2005) employed Pd/MnOx-ZrO$_2$-ZnO catalyst for one step-synthesis of 2-pentanone from ethanol.

Alternatively, the catalytic dehydration of bio-ethanol is one of the available processes, which has potential to synthesize a high cost solvent, like 2-pentanone. The advantages of bio-ethanol dehydration are no waste generation, low pollution, greener, and environmental friendly route. Additionally, it not only has a lot of advantages, but also gives the hydrocarbons in gasoline range as co-products.

As aforementioned, a simple catalyst such as cobalt oxide-modified alumina is an interesting catalyst to produce high cost solvent from the catalytic dehydration of bio-ethanol. Since cobalt oxide was employed in methanol oxidation (Zafeiratos *et al.* 2010) Therefore, the aim of this work was to examine the formation of oxygenate compounds and hydrocarbons in the catalytic dehydration of bio-ethanol using Co$_3$O$_4$/Al$_2$O$_3$ catalyst. Additionally, the catalyst was characterized using surface area analyzer (SAA), X-ray diffraction (XRD), and X-ray-Photoelectron Spectroscopy (XPS).

4.3 Experimental

4.3.1 Catalyst Preparation

γ-Al$_2$O$_3$ (γ-Alumina) used in this work was supplied form Sigma Aldrich, Singapore. Cobalt (II) nitrate hexahydrate was used as the cobalt precursor. A metal solution of cobalt nitrate was loaded on the support using incipient wetness impregnation technique until the amount of 5.0 wt% Co loading was achieved. After impregnation, the wet catalyst was dried at 110°C overnight, and then calcined until 600°C, 10°C/min and held for 3 hours. The calcined catalyst was pelletized, crushed, and sieved to 20-40 mesh particles.

4.3.2 Catalytic Testing

The catalytic dehydration of bio-ethanol was performed in a continuous isothermal fixed-bed U-tube reactor controlled at $500^{\circ}C$ under atmospheric pressure for 8 hours. The high purity grade bio-ethanol (99.5%) was fed by a syringe pump with carrier gas, helium, through the catalyst bed. The gaseous product was passed through an online-GC, and the liquid condensed in a cooling unit was collected, and the oil was extracted from the liquid product by using carbon disulfide.

4.3.3 Product Analysis

The gaseous products were analyzed by using a GC-TCD (Agilent 6890N) to determine the gas composition, and GC-FID (Agilent 6890N) was used to determine the bio-ethanol and oxygenate contents. The extracted oils were analyzed by using Gas Chromatography (Agilent technology 7890) with Time-of-Fight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS) equipped with the 1st GC column was a non-polar Rtx®-5sil MS (30 m × 0.25 mm × 0.25 µm), and the 2nd GC column was an Rxi®-17 MS column (1.790 m × 0.1 mm ID ×0.1 µm) to determine the composition.

4.3.4 Catalyst Characterization

The Brunauer-Emmett-Teller (BET) technique was used to determine the specific surface area, total pore volume, and pore size of catalysts using Thermo Finnigan/Sorptomatic 1990 surface area analyzer. The pore size distribution was calculated using BJH method. The X-ray diffraction of catalysts was determined using Rigagu SmartLab® in BB/Dtex mode with CuKα radiation. The machine collected the data from 10°-80° (2θ) at 5°/min with the increment of 0.01°. X-ray Photoelectron Spectroscopy (XPS) spectra were obtained using a AXIS ULTRADLD. The system was equipped with a monochromatic Al x-ray source and hemispherical analyzer. The spectrometer was operated with the pass energy of 160 and 40 eV for wide and narrow scan, respectively. All peaks were calibrated from referring C 1s spectra located at 284.7 eV.

4.4 Results and Discussion

### 4.4.1 Catalyst Characterization

The BET surface area and pore volume decrease when cobalt is loaded on alumina as shown in Table 1. The decreases in surface area and pore volume of a catalyst, prepared by using incipient wetness impregnation technique, suggest that cobalt solution was adsorbed deeply in the pores of alumina, resulting in the formation of cobalt oxide particle inside the pores.

The XRD patterns are shown in Figure 1 to confirm the characteristic of alumina and the existing of cobalt oxide on alumina surface. The peaks located at $2\theta = 37.34°$, $45.65°$ and $67.51°$ are the characteristics of alumina (Liu *et al.*, 2012), and the peaks detected at $2\theta = 31.37°$, $45.41°$, $59.37°$ and $65.22°$ correspond to the oxide form of Co_3O_4 (Batista *et al.*, 2003). These results can confirm the characteristics of gamma phase of the alumina, and are the basic evidence supporting the chemical state of cobalt oxide catalyst.

Additionally, in order to further confirm the chemical state of the cobalt oxide, X-ray Photoelectron Spectroscopy was employed, and the results are shown in Figure 2 (A) and (B) for fresh and spent catalyst, respectively. The XPS spectrum of fresh catalyst display that the Co $2p_{3/2}$ binding energies at 779.4 and 781.5 eV are assigned to Co_3O_4 and CoO on the γ-alumina surface (Biesinger *et al.*, 2011), and accounted for 69.2% and 30.8%, respectively. Moreover, there is a characteristic satellite peak of Co_3O_4 located at 786.5 eV (Khassin *et al.*, 2012). The XPS spectrum of the spent catalyst is illustrated in Figure 2 (B). The Co $2p_{3/2}$ binding energy at 781.8 eV is assigned to CoO (Biesinger *et al.,* 2011), and the two-overlapped characteristic satellite peaks of CoO are also observed at 786.3 and 790.9 eV (Khassin *et al.*, 2012), respectively. Furthermore, from the XPS study, it is observed that there is a change of binding energy taking place after the catalytic testing. This implies that Co_3O_4 is entirely reduced to CoO during the reaction testing.

Table 4.1 Physical properties of alumina and cobalt-promoted alumina

Sample	Surface Area $(m^3/g)^a$	Pore Volume $(cm^3/g)^a$	Pore Diameter $(nm)^b$
Al_2O_3	206.4	0.1792	47.58
Co_3O_4/Al_2O_3	171.8	0.1406	45.34

[a]determined using BET method
[b]determined using B.J.H method
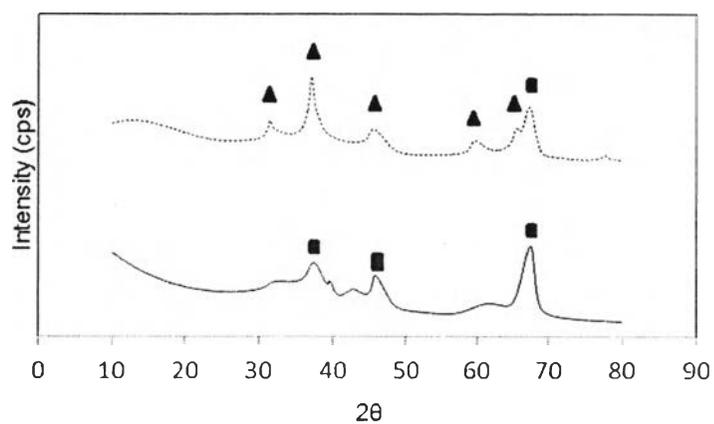
Figure 4.1 XRD pattern of alumina (bottom) and Cobalt-promoted alumina (top) (▲ = Co_3O_4 and ■ = Al_2O_3).
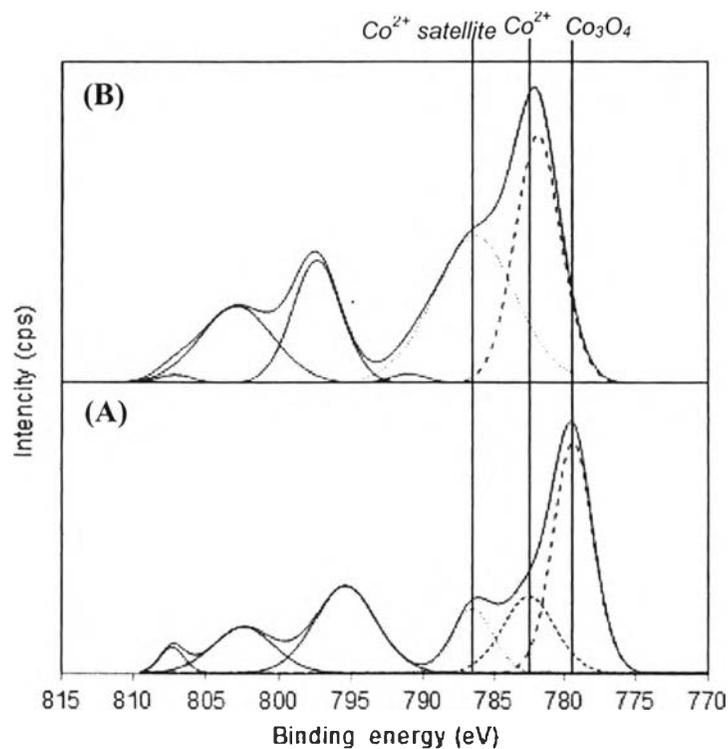
Figure 4.2 Co $2p_{3/2}$ XPS spectra of (A) fresh and (b) spent 5wt% cobalt oxide-promoted γ-alumina.

4.4.2 Effect of Alumina on The Catalytic Dehydration of Bio-ethanol

It was found that γ-alumina gave ethanol conversion 98.0%. Moreover, with the use of γ-alumina yielded ethylene as the major product in gas. Additionally, the composition of extracted oils is shown in Table 2. The results shows that extracted oil contains mainly oxygenate compounds. The major of oxygenate compounds are alcohols (i.e. phenol), with ketones (i.e. 2-butanone, 2-pentanone, 2-hexanone, and 3-hexanone) as co-products. For hydrocarbons, benzene, toluene, mixed-xylenes, C_9, and C_{10}^+ aromatics are traces of components.

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Table 4.2 Gaseous product distribution from bio-ethanol dehydration

Sample	Concentration (wt%)							
	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	CO_2
Non-catalyst	0.0	99.1	0.6	0.2	0.0	0.1	0.0	0.0
Al_2O_3	0.0	96.0	0.5	1.0	0.0	0.5	0.0	2.1
Co_3O_4/Al_2O_3	3.2	81.3	1.2	2.2	0.0	0.7	0.0	11.2

Data were taken at the eight hour of time-on-stream

4.4.3 Effect of Co_3O_4 on γ-Al_2O_3

In the case of Co_3O_4-promoted γ-alumina, it can be observed that methane, ethane, propylene, and butylene are insignificantly enhanced, but ethylene is suppressed in the gaseous products. Moreover, as shown in Table 2, the oxygenate compounds and hydrocarbons are accounted for 95.5% and 4.5 % in oil, respectively. As compared to parent alumina, Co_3O_4-promoted catalyst enhanced oxygenates rather than hydrocarbon production. The composition of oxygenate compounds were identified using GCxGC-TOF/MS, and it was found that oxygenate compounds are composed of alcohols, ketones, and a trace of esters.

The majority of phenol products is 3-methyl-phenol as shown in Figure 4(A). It consists of almost 50% of all phenol compounds. The total content of all phenol and its derivatives in oxygenate products is 78.7%. In addition, 2-pentanone is found as the main product in ketones, and it holds almost 80% of all ketone compounds. The formation of oxygenate compounds, especially 2-pentanone, from ethanol was explained by He *et al.,* 2005. When ethanol is fed and passed over a metal oxide catalyst, hydrogen at hydroxyl group of ethanol is firstly adsorbed on oxygen vacancies, and then ethoxy species are formed. Moreover, the ethoxy species can undergo dehydrogenation, via α-H abstraction, and subsequent electron transfer to metal cation, yielding acetaldehyde (Idriss *et al.,* 2000). Additionally, acetaldehyde itself can undergo condensation reaction to form aldor species which are thermodynamically transformed to acetone, and yield formaldehyde as a co-product. Likewise, acetaldehyde and acetone can react to one another, forming 2-

pentanone via acetaldehyde-acetone condensation and hydrogenation with water as a by-product. High molecular weight pentanones can be formed when 2-pentanone further undergo condensation with other acetones, as shown in Figure 3.

Table 4.3 Liquid product distribution from bio-ethanol dehydration

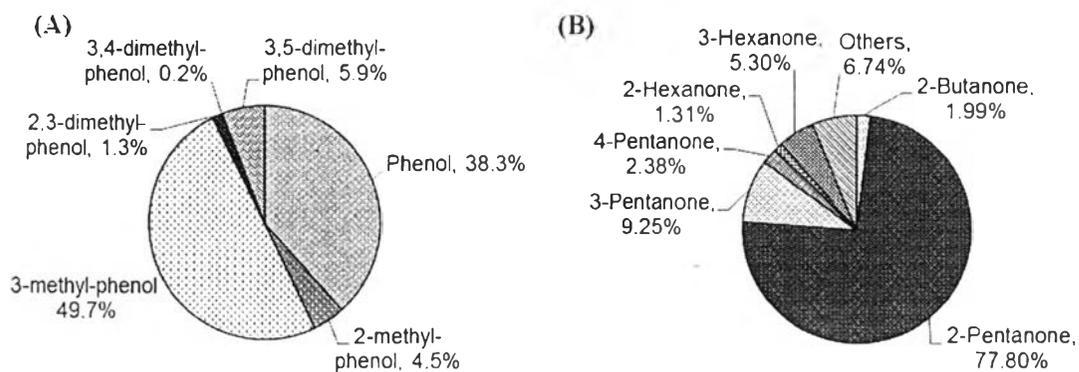| Sample	Non-catalyst	Al_2O_3	Co_3O_4/Al_2O_3
Product distribution (wt%)			
Oxygenates	89.0	92.1	95.5
Non-aromatics	1.44	0.60	0.00
Benzene	4.28	5.18	2.08
Toluene	0.31	0.64	0.38
p-Xylene	0.20	0.24	0.30
o-Xylene	0.02	0.16	0.09
m-Xylene	0.03	0.22	0.09
Ethylbenzene	0.12	0.37	0.10
C_9 aromatics	0.10	0.07	0.45
C_{10}^+ aromatics	4.53	0.38	1.04

Data were taken at the eight hour of time-on-stream

Figure 4.3 Compositions of phenols (A) and ketones (B) found in oxygenate compounds (wt%) from using Co_3O_4/Al_2O_3.

$$CH_3CH_2OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + 2H_{(a)}$$

Ethanol   Acetaldehyde

$$CH_3\overset{O}{\overset{\|}{C}}H \longrightarrow CH_3CH\overset{\bullet}{\underset{OH}{CH_2}}\overset{O}{\overset{\|}{C}}H \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2-OH$$

Aldor   Keto

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2-OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + H\overset{O}{\overset{\|}{C}}-H$$

Acetone   Formaldehyde

$$CH_3\overset{O}{\overset{\|}{C}}H + CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{H_2} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 + H_2O$$

2-pentanone

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow[H_2]{CH_3\overset{O}{\overset{\|}{C}}CH_3} \text{Higher pentanones} + H_2O$$
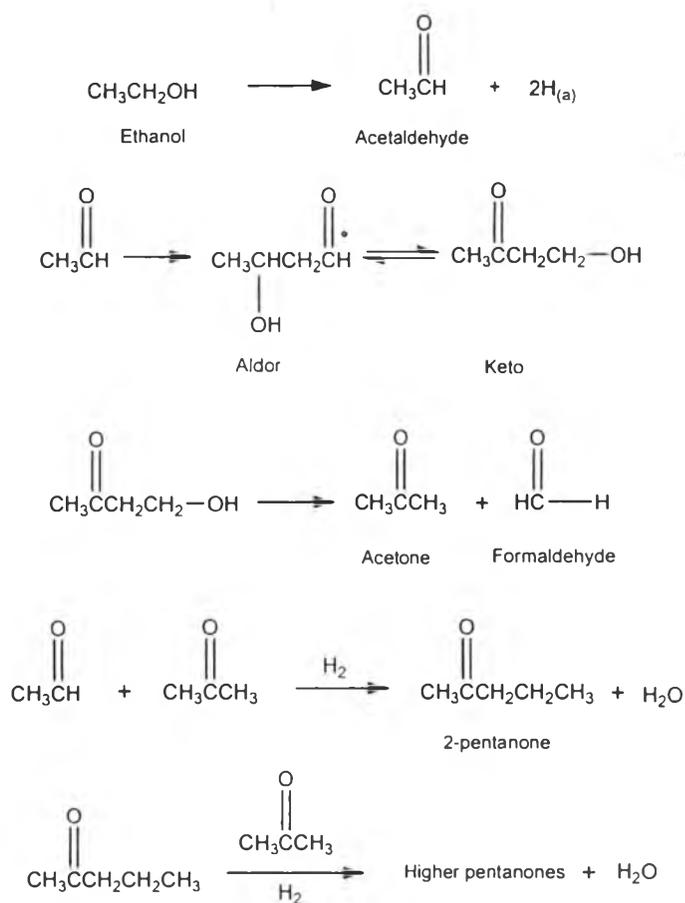
Figure 4.4 Reaction pathways of ethanol to 2-pentanone (He et al., 2005).

Additionally, the formation of oxygenate compounds is occurred by ethanol adsorbed at the vacancy of metal oxide surface, leading to ethoxy species formation. Zafeiratos et al. (2010) found that cobalt oxide could be reduced by methanol, forming carbon dioxide and water as by-product. This implies that Co_3O_4 is reduced by ethanol during the catalytic testing, forming ethoxy species that adsorbed on the metal oxide surface. The carbon dioxide formation in the gaseous products supports the explanation.

In addition, the hydrocarbon products obtained from using Co_3O_4 as a promoter are slightly suppressed as compared to the parent alumina. The hydrocarbons are composed of benzene, toluene, mixed-xylenes C_9, C_{10}^+-aromatics, and a trace of non-aromatics. Among the hydrocarbons, C_9 and C_{10}^+-aromatics are insignificantly enhanced while benzene, toluene, and mixed-xylenes are suppressed;

indicating that these hydrocarbons are further converted to C_9 and $C_{10}{}^+$-aromatics inside the pores of alumina. Furthermore, as seen in Table 1, ethylene that decreases in the gaseous products is believed to be an important intermediate to directly transform to propylene and then to aromatics.

4.5 Conclusions

Cobalt oxide-promoted alumina was examined in the catalytic dehydration of bio-ethanol in order to examine the formation of oxygenates and hydrocarbons. From our study, it was revealed that cobalt oxide can be used to produce 2-pentanone, which is used in many applications in industry and has high value. The obtained oxygenate compounds were composed of phenols, ketones, and a trace of esters. Moreover, the hydrocarbons were composed of non-aromatics, benzene, toluene, mixed-xylenes, C_9, and $C_{10}{}^+$-aromatics. Additionally, XPS analysis revealed that the fresh cobalt oxide-promoted catalyst was not pure Co_3O_4 at initial, but contained a mixture of CoO and Co_3O_4. However, Co_3O_4 was entirely reduced to CoO after use, during the formation of ethoxy species in the catalytic dehydration of bio-ethanol.

4.6 References

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