PRODUCTION OF HIGHER ALCOHOLS FROM ETHANOL OVER MgO BASED CATALYSTS

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A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENT FOR
THE DEGREE OF BACHELOR OF SCIENCE (INDUSTRIAL CHEMISTRY)
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
ACADAMIC YEAR 2017

การผลิตแอลกอฮอล์โมเลกุลใหญ่จากเอทานอล
โดยใช้ตัวเร่งปฏิกิริยาแมกนีเซียมออกไซด์

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ปริญญาวิทยาศาสตรบัณฑิต (เคมีอุตสาหกรรม)
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Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, has approved this special project submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in academic year 2017.

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ABSTRACT

In this special project, the conversion of ethanol to higher alcohols using magnesium oxide (MgO) synthesized by citric acid sol-gel method based catalysts was investigated in a continuous fixed-bed reactor. Ethanol can be converted to higher alcohol via Guerbet reaction, where H_2-transfer is an important step. H_2-transfer activity of the prepared catalysts was firstly tested with MPV (Meerwein–Ponndorf–Verley) reaction of isopropanol and propionaldehyde. MgO shows H_2-transfer activity, providing acetone and *n*-propanol as major products. In conversion of ethanol, MgO can convert ethanol to crotonaldehyde. However, those formed aldehydes are not completely hydrogenated to butanol because of low hydrogen on MgO surface, indicating not enough Lewis acid sites. On the other hand, cLDH with strong Lewis acid Al^{3+}, gives higher yield of higher alcohols and also provides higher yield of undesired products, ethylene and diethyl ether. Thus, MgO was further modified with 5 wt.% metal oxides (RuO_2/MgO and ZnO/MgO) by adsorption technique. It was found that number of acid-basic sites are found to correlate with product selectivity in Guerbet reaction. High Lewis acidity, RuO_2/MgO provided high ethanol conversion with high yield of undesired product diethyl ether. On the other hand, ZnO/MgO shows high activity for dehydrogenation of ethanol to acetaldehyde and aldol condensation to high molecular weight products (alcohols and carbonyls) with low yield of undesired product, diethyl ether because of stronger acid-basic sites. After that, the acid-base pair sites of, ZnO/MgO was further modified by increasing ZnO loading from 3 wt.% to 10 wt.%. The 5 wt.% and 10 wt.% ZnO/MgO show the high activity for aldol condensation (C8 and C10 carbonyls) while low yield of higher alcohols, because of H_2-transfer inhibition by the excessive acid sites (Zn^{2+}). On the other hand, 3 wt.% ZnO/MgO gives highest yield of higher alcohols due to appropriate acid-base pair sites

Keywords : aldol condensation, ethanol, Guerbet reaction, magnesium oxide (MgO), hydrogen transfer.

ACKNOWLEDGEMENTS

For the thesis completion, we would like to gratefully thank our advisor, Dr. Natthida Numwong for support, supervisions and encouragement throughout the thesis. Furthermore, we also sincere thanks our co-advisor, Assoc. Prof. Dr. Tawan Sooknoi for his knowledge and advices. We would not have achieved this thesis without all of the suggestions that we received from him.

We would also like to extend our sincere thanks to Asst. Prof. Dr. Panpailin Seeharaj and Dr. Amnat Permsubscul for serving as the committee and for their valuable comment and suggestions.

In addition, we are grateful for the supports from Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang and Catalytic Chemistry Research Unit for the equipment, chemicals and facilities.

Finally, we would like to sincere appreciation to all teacher, friends as well as the member of Catalytic Chemistry Research Unit for their advice, supports and encouragement.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Bioethanol is one of the world's most popular renewable resources. One of its interesting use is the conversion of ethanol to higher alcohols such as butanol, hexanol, etc. These higher alcohols are widely used as versatile additives and chemicals in modern petroleum and chemical industries [1]. For instance, C_2-C_5 alcohols ($C_nH_{2n+1}OH$, n=2-5) are attractive fuel as clean fuel additives to increase the octane number and reduce the polluted emissions of gasoline due to its good solubility in hydrocarbons and high heating value. On the other hand, C_{6+} alcohols ($C_nH_{2n+1}OH$, $n \geq 6$) are usually applied in the field of manufacturing of plasticizers, lubricants and detergents [2].

An important reaction to produce higher alcohols from ethanol is "Guerbet reaction". In these reaction, ethanol is adsorbed on the catalyst surface and dehydrogenated to acetaldehyde, follows by aldol condensation of aldehydes to larger unsaturated aldehyde. Final step is hydrogen transfer, which promotes the formation of higher alcohol from unsaturated aldehyde. The reaction mechanism is considered to be on both acidic and basic active sites [3].

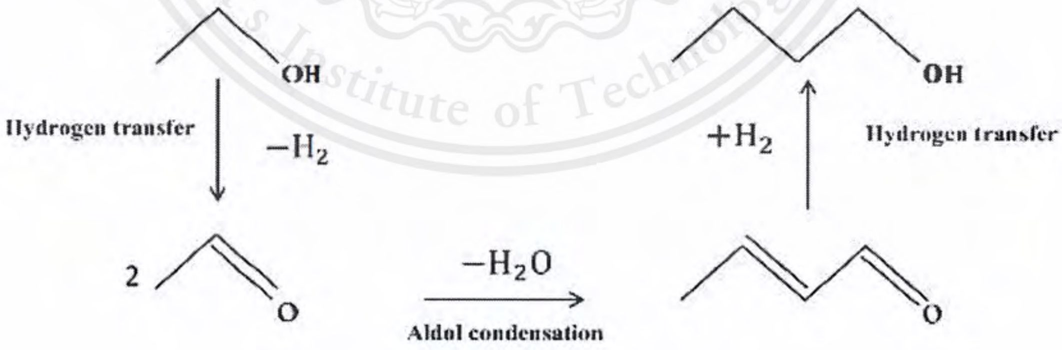


Figure 1.1 Guerbet reaction

Magnesium oxide (MgO) or magnesia, is a white hygroscopic solid mineral that occurs naturally as periclase and is a source of magnesium. It has an empirical formula of MgO and consist of lattice of Mg^{2+} ions and O^{2-} ions held together by ionic bonding [4]. MgO has Brønsted basic site that can promote aldol condensation in Guerbet reaction [4].

The isolated O^{2-} ion on MgO surface would be unable to form ethoxide intermediates. Thus, the incorporation of small amounts of metal cations to MgO drastically increased the acetaldehyde formation rate because of the generation of new surface Lewis acid-strong base pair sites [4].

In this study, MgO was used as catalyst to produce higher alcohols from ethanol. In addition, incorporation of metal oxide RuO_2 and ZnO in MgO was also performed to induce Lewis acid site, which has predominant H_2-transfer characteristic in Guerbet reaction. The sol-gel method was used in this study to obtain high surface area MgO. The metal oxide incorporated MgO, catalysts were prepared by adsorption technique. The ethanol conversion was investigated in continuous fixed-bed reactor. The activity and selectivity of the prepared catalysts were determined.

1.2 Objectives

1.2.1. To obtain highly selective and stable catalyst for production of higher alcohols from ethanol.

1.2.2. To understand the effect of incorporated metal oxide on the catalyst activity, selectivity and stability.

1.2.3. To understand the reaction pathway and mechanism of ethanol conversion to higher alcohols over MgO catalysts.

1.3 Scopes of study

1.3.1. Synthesis of high surface area magnesium oxide (MgO) by sol-gel method.

1.3.2. Preparation of metal oxide incorporated MgO catalysts by adsorption method.

1.3.3. Characterization of catalysts by nitrogen adsorption (BET), NH_3-temperature programmed desorption (NH_3-TPD), CO_2-temperature programmed desorption (CO_2-TPD), X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-Ray analysis (SEM-EDX)

1.3.4. Study the conversion of ethanol to higher alcohol in continuous fixed bed reactor.

1.3.5. Study the effect of incorporated metal oxides on activity, selectivity and stability of magnesium oxide (MgO) catalysts.

1.3.6. Analysis liquid products by on-line gas chromatography with flame ionization detector (GC-FID)

1.4 Expected result

We expect that our study could be an alternative way in improving catalyst with high activity and selectivity for the conversion of ethanol to higher value products for chemical industry.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Alcohol

In chemistry, an alcohol is any organic compound in which the hydroxyl functional group functional group (-OH) is bound to a saturated carbon atom .Alcohols are classified into primary, secondary (*s-*, *sec-*) and tertiary (*t-*, *tert-*) based upon the number of carbon atoms connected to the carbon atom that bears the hydroxyl functional group [5].

In general, the hydroxyl group makes the alcohol molecule polar. Those groups can form hydrogen bonds to one another and to other compounds. Because of hydrogen bonding, alcohols tend to have higher boiling points than comparable hydrocarbons and ethers [6].

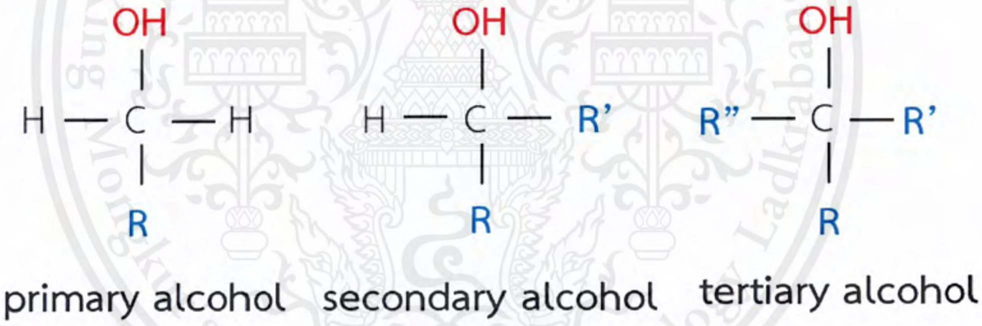


Figure 2.1 The structure of alcohols

2.2 Ethanol

Ethanol or ethyl alcohol, also called drinking alcohol, is the principal type of alcohol found in alcoholic beverages, produced by the fermentation of sugars by yeasts. It is a neurotoxic psychoactive drug and one of the oldest recreational drugs used by humans. It can cause alcohol intoxication when consumed in sufficient quantity. Its structural formula, CH_3CH_2OH is often abbreviated as C_2H_5OH, C_2H_6O or EtOH [7].

Ethanol melts at −114.1°C, boils at 78.5°C, and has a density of 0.789 g/mL at 20°C. Its low freezing point has made it useful as the fluid in thermometers for temperatures below − 40°C, the freezing point of mercury, and for other low-temperature purposes, such as for antifreeze in automobile radiators [8].

The chemical properties of ethanol are dominated by the -OH functional group, which can undergo many industrially important chemical reactions, e. g. , dehydration, halogenation, ester formation, and oxidation . Because ethanol can be produced efficiently not only by chemical synthesis from petroleum and coal-based feedstock, but also by fermentation of abundantly available organic materials, its commercial role as a raw material for various chemicals is of increasing importance. Conversion of ethanol to "alkochemicals" is an entirely new approach to producing familiar petrochemicals. Some of these routes are already being used industrially in large alcohol producing countries [9].

Ethanol is used as an automotive fuel by itself and can be mixed with gasoline to form gasohol. Ethanol is miscible in all proportions with water and with most organic solvents, which is useful as a solvent for many substances and in making perfumes, paints, lacquer, and explosives. Alcoholic solutions of nonvolatile substances are called tinctures; if the solute is volatile, the solution is called a spirit.

Furthermore, ethanol can be oxidized to form first acetaldehyde and then acetic acid. It can be dehydrated to form ether. For example, butadiene can be made from ethanol, and it is used in making synthetic rubber [8].

2.3 Higher alcohol

2.3.1 Butanol

n-Butanol or n-butyl alcohol or normal butanol is a primary alcohol with a 4-carbon structure and the formula C_4H_9OH. Its isomers include isobutanol, 2-butanol, and tert-butanol . Butanol is one of the group of " fusel alcohol" , which have more than two carbon atoms and have significant solubility in water [10].

Butanol is a liquid at standard temperature and pressure, with a boiling point of approximately 117.6°C and a melting point of approximately −89.9°C [11].

Butanol is an alcohol that is produced through petrochemical processes, but can also be produced, like ethanol, through fermentation of sugars derived from corn and agricultural crops. Butanol is a four carbons alcohol; ethanol is a two carbons alcohol. Ethanol is primarily sold as a fuel blend stock for gasoline. *n*-butanol is sold primarily as a chemical. *n*-butanol is a superior global chemical with over 8 billion pounds of annual demand in England. Isobutanol is primarily marketed as a fuel blend stock similar to ethanol today and correspondingly has a much lower value as a fuel [12].

2.3.2 Hexanol

1-Hexanol is an organic alcohol with a six-carbon chain and a condensed structural formula of $CH_3(CH_2)_5OH$. This colorless liquid is slightly soluble in water, but miscible with diethyl ether and ethanol. Two additional straight chain isomers of 1-hexanol, 2-hexanol and 3-hexanol, exist, both of which differing by the location of the hydroxyl group. Many isomeric alcohols have the formula $C_6H_{13}OH$. It is used in the perfume industry [13].

2.3.3 Octanol

1-Octanol also known as octan-1-ol is the organic compound with the molecular formula of $CH_3(CH_2)_7OH$. It is a Fatty alcohol. Many other isomers are also known generically as octanols. 1-Octanol is manufactured for the synthesis of esters for use in perfumes and flavorings. Esters of octanol, such as octyl acetate, occur as components of essential oils. It is used to evaluate the lipophilicity of pharmaceutical products [14].

2-Octanol [$CH_3(CH_2)_5CH(OH)CH_3$], is obtained by the alkaline hydrolysis of castor oil. It is used as a solvent in the paint industry, as a wetting agent in the textile industry, and as a component of brake fluids [15].

2.3.4 Benzyl alcohol

Benzyl alcohol is an aromatic alcohol with the formula $C_6H_5CH_2OH$. It is a colorless liquid with a mild pleasant aromatic odor.

It is produced naturally by many plants and is commonly found in fruits and teas. It is also found in a variety of essential oils including jasmine, hyacinth, and ylang-ylang.

Benzyl alcohol is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. Thus, it can be used in paint strippers especially, when combined with compatible viscosity enhancers to encourage the mixture to cling to painted surface. It is also a precursor to a variety of esters, used in soap, perfume, and flavor industries. It is also used as a photographic developer [16].

2.4 Aldehyde

Aldehydes are represented by the general formula RCHO, where R can be hydrogen or an aliphatic, aromatic, or heterocyclic group. According to IUPAC nomenclature, aldehydes are identified by the ending "al." However, many of them still are called by their common names.

The polarity of the carbonyl group of aldehydes not only facilitates the typical aldehyde reactions-addition of nucleophiles, reduction, and oxidation but it also makes the α-hydrogen atom acidic. For these reasons, aldehydes can undergo a wide variety of reactions [17].

2.4.1 Acetaldehyde

Acetaldehyde (CH_3CHO) was observed in 1774 by SCHEELE during reaction of black manganese dioxide and sulfuric acid with alcohol. Its constitution was explained in 1835 by LIEBIG who prepared pure acetaldehyde by oxidation of ethanol with chromic acid and designated this product “aldehyde” a concentration of the term “alcohol dehydrogenates”.

Acetaldehyde is mobile, low-boiling, highly flammable liquid with a pungent odor. Because of its high chemical reactivity, acetaldehyde is an important intermediate in the production of acetic acid, acetic anhydride, ethyl acetate, peratic acid, butanol, 2-ethylhexnaol, pentaerythritol, chlorinated acetaldehyde (chloral), glyoxal, alkyl amines, pyridines and other chemicals.

Occurrence: Acetaldehyde is an intermediate in the metabolism of plant and animal organisms, in which it can be detected in small amounts. Lager amounts of acetaldehyde interfere with biological processes. As an intermediate in alcoholic fermentation processes it is present in small amounts in all alcoholic beverages, such as beer, wine, and spirits. Acetaldehyde also has been detected in plant juices and essential oils, roasted coffee, and tobacco smoke [18].

Acetaldehyde is used as an intermediate in the production of acetic acid, acetic anhydride, cellulose acetate, vinyl acetate resins, acetate esters, pentaerythritol, synthetic pyridine derivatives, terephthalic acid and peracetic acid [19].

2.4.2 Butanal

Butyraldehyde, also known as butanal, is an organic compound with the formula (CH_3CH_2C OH). This compound is the aldehyde derivative of butane. It is a colorless flammable liquid with an acrid smell. It is miscible with most organic solvents. Butyraldehyde can be produced by the catalytic dehydrogenation of *n*-butanol. At one time, it was produced industrially by the catalytic hydrogenation of crotonaldehyde, which is derived from acetaldehyde. Upon prolonged exposure to air, butyraldehyde oxidizes to form butyric acid [20].

2.4.3 Hexanal

Hexanal, also called hexanaldehyde or caproaldehyde is an alky aldehyde used in the flavor industry to produce fruity flavors. Its scent resembles freshly cut grass, like cis-3-hexennal [21].

2.4.4 Benzaldehyde

Benzaldehyde (C_6H_5COH) is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde and one of the most industrially useful [22]. Benzaldehyde is commonly employed to confer almond flavor to foods and scented products. It is sometimes used in cosmetics product [23].

2.5 Guerbet reaction

An important reaction to produce higher alcohols from ethanol is “Guerbet reaction”. The Guerbet reaction of alcohols is the oldest and best understood material in the class of compounds first synthesized by Marcel Guerbet [24].

In these reaction, ethanol is adsorbed on the catalyst surface and dehydrogenated to acetaldehyde, follows by aldol condensation of aldehydes to larger unsaturated aldehyde. Final step is hydrogen transfer, which promotes the formation of higher alcohol from unsaturated aldehyde. The reaction mechanism is considered to be on both acidic and basic active sites [3].

Dehydrogenation starts by alcohol chemisorptions on acid- basic site pairs, which cleave O-H bonds to form surface alkoxide intermediates bound to the acid center.

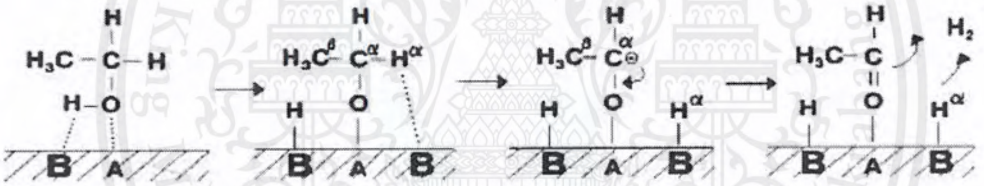


Figure 2.2 .Dehydrogenation of alcohols to the corresponding aldehydes [4].

The α-hydrogen in the alkoxide group is then abstracted by a neighboring basic site in order to form adsorbed aldehydes. Aldol condensation reactions on Mg_yAlO_x samples involved also the formation of a carbanion intermediate on Lewis acid-strong Brønsted base pair sites as shown in **Figure 2.3**.

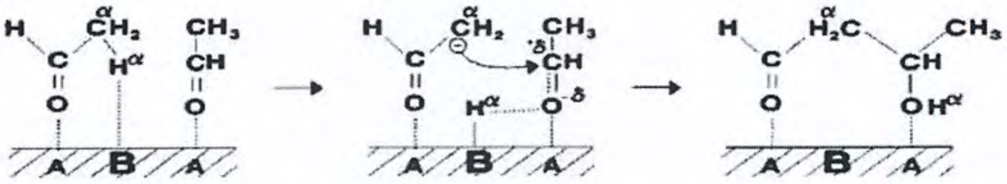


Figure 2.3 Aldol condensation [4].

After aldol condensation, the product of aldol condensation will be dehydrated to crotonaldehyde. Finally, crotonaldehyde will be hydrogenated to 1-butanol as shown in **Figure 2.4**.

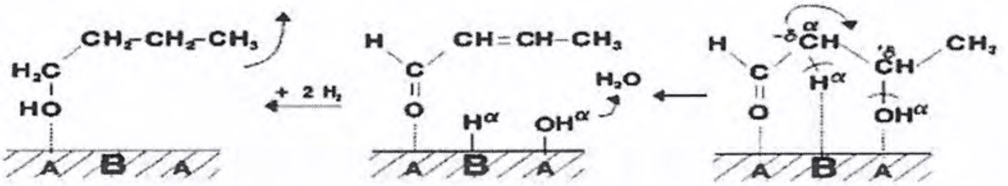


Figure 2.4 Dehydration of the aldol product, and hydrogenation of the unsaturated condensation products [4].

2.6 Catalyst

Catalytic conversion of ethanol to n-butanol involves the Guerbet reaction, where a primary aliphatic alcohol is converted into its β-alkylated dimer alcohol with loss of one equivalent of water. In 1931, ethanol coupling was first observed on mixtures of MgO, Al_2O_3 and CuO_x. Metal oxides are promising catalysts for ethanol conversion because they give high product selectivity and controllable synthetic processes; for instance, Mg-Al oxide catalysts with different structures show high selectivity for n-butanol in ethanol conversion. Mixed metal oxides catalysts have acid and base sites, which active in aldol condensation reactions [25].

2.6.1 Magnesium oxide

Magnesium oxide (MgO), or magnesia, is a white hygroscopic solid mineral that occurs naturally as periclase and is a source of magnesium. It has an empirical formula of MgO and consists of a lattice of Mg^{2+} ions and O^{2-} ions held together by ionic bonding. MgO has Brønsted basic site that can promote aldol condensation in Guerbet reaction.

The isolated O^{2-} ion on MgO surface would be unable to from ethoxide intermediates. Thus, the incorporation of small amounts of metal cations to MgO drastically increased the acetaldehyde formation rate because of the generation of new surface Lewis acid-strong base pair sites [4].

The application of MgO is largely. It can be used in agricultural, chemical, construction, environmental, and other industrial applications [26].

However, MgO can be used in catalytic industry as base catalyst. For example, the activity for both the aldol condensation of citral with acetone and the glycerolysis of methyl oleate diminished with the MgO calcination temperature because these reactions were essentially promoted on strongly basic O^{2-} sites [4].

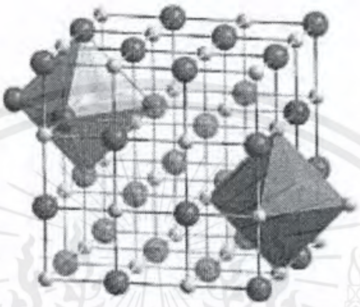


Figure 2.5 The structure of magnesium oxide [4].

2.6.2 Acid-basic catalysts

Acid-basic catalyst is a catalyst with both acid and basic functions in the structure so-called bifunctional catalyst. The catalytic mechanism can be categorized into two types depending on how the acid and basic interact with substrate. Both acid and basic can interact independently or step by step with different mechanisms, which are further categorized as simultaneous and successive acid–base interaction, respectively.

Simultaneous acid–base interaction can be further divided into two types. The first one is the simultaneous interaction that the acid and basic interact with the substrate in such a way that the basic pushes the electron pair to one part of the substrate and the acid pulls the electron pair from the other part of the substrate called “concerted mechanism”. Another one is the simultaneous interaction that the acidic site interacts with one substrate molecule and the basic site with a different substrate molecule. Both interactions occur simultaneously but independently.

For the successive interaction case, the substrate interacts with a certain catalytic site to form an intermediate, which interacts successively with the other type of catalytic site to form another intermediate or final product. The acid and the base take different roles successively in the catalytic process [27].

2.7 Literature reviews

Bioethanol is one of the world's popular renewable resources. One of its interesting uses is the conversion of ethanol to higher alcohols such as butanol, hexanol, etc. These higher alcohols are widely used as versatile additives and chemicals in modern petroleum and chemical industries [28].

Ethanol is one of the most well-known renewable chemical sources in the industrial, which is acquired from several ways such as the fermentation of agricultural products or via petrochemical processes. Ethanol has been widely used in organic synthesis and industrial in various ways. Ethanol can be converted to higher molecular weight alcohols so-called Guerbet alcohols. These higher alcohols are used as high added-value solvents, surfactants, lubricants and fuel [29].

In 2013, Zhu, H., et al. studied the synthesis of metal modified NiO based catalyst using $Ni(NO_3)_2{\cdot}6H_2O$, NH_4VO_3, $Ti[OCH(CH_3)_2$, $Zr(OBu)_4$, H_2WO_4, citric acid, and $(NH_4)_2$ MoO_4. The mixed Ni–Me–O oxides catalysts, where the Me is Zr, Ti, V, Mo, W, with the Me/(Ni + Me) atomic ratio of 5%, were prepared by sol–gel method. The Ni_{95} $–V_{05}$ oxide catalyst was prepared by dissolving 6 g of $Ni(NO_3)_2{\cdot}6H_2O$, 0.122 g of NH_4VO_3 and 12 g of citric acid in 100 mL of water. The obtained blue solution was kept at 80°C under stirring conditions for 24 h, and then evaporated at 80°C in an open system to remove water. The gel formed from the water evaporation was further dried at 120°C and 140°C, respectively for 2 h, and lastly dried at 160°C for 12 h. The resulting black xerogel was calcined by heating from room temperature to 450°C with a ramping rate of 1°C/min, and then kept at 450°C for 4 h in static air. The BET surface area of these materials is in the range of 90–105 m^2/g, which is larger than that of NiO from other synthesis methods. As evidenced from the results, the sol–gel method can produce

NiO with small particle size and large surface area compared with precipitation and hydrothermal synthesis [30].

Nakayama, T., et al. studied the preparation of Ni/MgO by using different methods such as sol-gel with citric acid, sol-gel without citric acid, co-precipitation. They found that BET surface area of Ni/MgO at the same %Ni content (70 wt.%), prepared by sol-gel with citric acid has the highest surface area compared with those of catalysts prepared by different methods (47 m^2/g). The surface of the Ni/MgO prepared by sol-gel without citric acid is 25 m^2/g. The surface area prepared by co-precipitation is lower than that of sol-gel method, 23 m^2/g [31].

In 2015, Ndou A.S., et al. investigated dimerization of ethanol to butanol over alkali earth metal oxides and modified MgO catalysts for the synthesis of fine chemicals from alcohols. Higher alcohols are produced through Guerbet reaction which is an important industrial process that is used to increase the carbon number of alcohols. In this reaction, a primary or secondary alcohol react with itself or another alcohol to produce a higher alcohol. MgO was calcined in air at 230°C for 6 h. The catalytic experiments were carried out in a vertical fixed-bed glass reactor. Using MgO as catalyst in this reaction provided 18.39% yield of butanol [32].

In 1998, Di Cosimo J.I., et al. found that the nature, density and strength of surface basic sites on hydrotalcite Mg-Al mixed oxide depend on its composition. The incorporation of small amounts of Al to MgO increase ethanol reaction rate by about one order of magnitude. It appears that Al^{3+} cations drastically increase the surface density of active Lewis acid-strong base pair site. Calcined Mg-Al hydrotacites with low Al content, improved a higher density of basic sites. Ethanol dehydration rates increase abruptly on samples containing a high density of both Al^{3+}-O^{2-} pair and low- and medium strength basic site [4].

In 2016, Panjanapongchai T.,et al. studied the production of higher alcohols from ethanol over layered double hydroxide (LDH) catalysts. They suggested that it is important to tune and balance the number and strength of acid and basic sites, in order to obtain high selectivity of desired products in the Guerbet reaction. Calcined LDHs with Mg/Al ratio 3:1 showed highest activity for higher alcohols production from ethanol. Moreover, they found that reduced 10 wt.% Cu-2 wt.% Zn/cLDHs showed the existence of acid sites, which affect dehydration of ethanol to ethylene. Nevertheless, increasing the loading of the metal cause lower yield of both ethylene and higher alcohol. This may be the effect of the alloy obscures acid and basic sites, which suppresses both dehydration and aldol condensation. In addition, the Ru adsorbed cLDHs promotes aldol condensation and hydrogenation of carbonyl compounds for production of higher alcohols (C4 alcohols). Thus, the selectivity of products in ethanol conversion depends mainly on catalyst composition [33].

In 2009, I. Marcu., et al. studied the conversion of ethanol into 1-butanol and 1,1-diethoxyethane over Cu-Mg-Al mixed oxide catalysts obtained from layer double hydroxides (LDH) precursors. They found that Mg/Al ratio of LDH does not play important role on the catalytic properties of the studied catalyst, but the copper content proves very important. The main pathway is the condensation of ethanol with acetaldehyde resulting in ethyl acetate formation. The increased of the copper content leaded to the decreased of strong and the total basicities of the catalysts. and the selectivity for *n*-butanol increased when the number of strong basic sites increased [34].

In 2008, T. Tsuchida., et al. studied the reaction of ethanol over hydroxyapatite (HAP) [$Ca_{10}(PO_4)_6(OH)_2$] catalysts with different Ca/P molar ratios, HAP-1 (Ca/P ratio=1.59), HAP-2 (Ca/P ratio=1.62), HAP-3 (Ca/P ratio=1.65), HAP-4 (Ca/P ratio=1.67). They found that the distribution of acid sites and basic sites on the catalyst surface varied with the Ca/P ratio of HAP. The yields of ethylene, 1-butanol, and 1,3-butadiene were correlated with the ratio of acid sites and basic sites. They compared the catalysts acid and basic properties with those of traditional base catalysts CaO and MgO, found that distribution of higher alcohols from ethanol over HAP by the Guerbet reaction can be expressed with simple probability [35].

In 2011, S. Ogo., et al. found that the product distributions in the catalytic conversion of ethanol at 300°C under atmospheric pressure depended on the kinds of component ions of the hydroxyapatite catalysts. 1-Butanol was the major products over the Ca-P and Sr-P hydroxyapatite catalysts. The Sr-P hydroxyapatite catalyst exhibited the highest 1-butanol selectivity at any ethanol conversions between 1 and 24%. On the other hand, ethylene was the major products over the Ca-V and Sr-V hydroxyapatite catalysts [36].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

Chemicals	Grade of purity	Manufacturers
1. Ethanol	99.99%	Carlo Erba
2. Methanol	99.99%	Fisher-Scientific
3. Nitrogen gas	High purity (99.99%)	Praxair
4. Air	High purity (99.99%)	Praxair
5. Distilled water	-	-
6. Magnesium nitrate hexahydrate $[Mg(NO_3)_2.6H_2O]$	98.0%	Panreac
7. Citric acid $[HOC(COOH)(CH_2COOH_2)]$	99.5%	Carlo
8. Propionaldehyde	98%	Lobal Chemie
9. Isopropanol	99.9%	Carlo Erba
10. Zinc nitrate hexahydrate $[Zn(NO_3)_2{\cdot}6H_2O]$	97.5%	Carlo Erba
11. Dichloro (p-cymene) ruthenium(II) dimer	-	Sigma-Aldrich
12. Toluene	99.5%	Lab-Scan
13. Acetone	99.8%	QReC
14. 2,2'-bipyridine ($C_{10}N_8N_2$)	99.0%	Sigma-Aldrich
15. Layered double hydroxides (LDH)	-	SCG Chemicals Company Limited

3.2 Apparatus

1. Syringe (10 mL)
2. Syringe pump
3. Magnetic stirrer
4. Laboratory glassware
5. Oven
6. Furnace
7. Hotplate & stirrer
8. Thermometer
9. Sieve
10. Catalytic testing rig
11. Mass flow controller
12. Temperature programmed desorption (TPD) system
13. Gas chromatograph with flame ionization detector (GC-FID)
14. Gas chromatograph-mass spectrometer (GC-MS) (Agilent Technologies, 689N Network GC system)
15. X-ray powder diffractometer (Shimadzu, XRD-6100, Scientific Instrument Service Center, KMITL)
16. Scanning electron microscopy with energy dispersive X-Ray analyser (SEM-EDX) (EVO®MA10, College of Data Storage Innovation, KMITL)

3.3 Experimental procedure

3.3.1 Catalyst preparation

3.3.1.1 Synthesis of MgO catalyst

Magnesium oxide (MgO) was synthesized by sol-gel method, 6 g of magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$) and 12 g of citric acid (C_6H_8O) were dissolved in 100 mL distilled water. This solution was kept at 80°C under stirring conditions for 24 h, and evaporated at 80°C in an open system to remove water. The gel formed from the water evaporation was further dried at 120°C and 140°C, respectively for 2 h, and lastly dried at 160°C for 12 h. The resulting catalyst was calcined by heating from room temperature to 500°C with a heating rate of 1°C/min for 4 hours before use as a catalyst.

3.3.1.2 Preparation of 5 wt.% RuO_2/MgO catalyst

A RuO_2/MgO catalyst was synthesized by adsorption technique. Before adsorption, MgO was calcined at 500°C for 4 h under 60 mL/min flow of air, with a heating rate of 1°C/min. The 1 M Ru precursor solution were prepared by dissolving 0.2428 g of dichloro (p-cymene) ruthenium(II) dimer in 150 mL of toluene and 50 mL of acetone. After that, 1 g of MgO was adsorbed with Ru precursor solution in capped-bottle until the color was changed from brown to orange, under a vigorous stirring at room temperature for 3 h. The mixture was centifuged and then dried in an oven at 100°C overnight to remove excess water until the catalyst was dried. Then, it was calcined in a muffle furnace at 500°C for 4 h under a flow of air (60 mL/min) with a heating rate of 1°C/min to obtain RuO_2/MgO catalyst.

3.3.1.3 Synthesis of *tris*-(bipyridine) zinc(II) nitrate [$Zn(bipy)_3(NO_3)_2$]

To prepare zine precursor for adsorption, 3.00 mmol of zinc(II) nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and 11.00 mmol of 2,2'-bipyridine ($C_{10}N_8N_2$) were dissolved in a minimum volume of methanol. The solution was stirred at ambient temperature for 2 hours and left for 24 hours for precipitation. The yellow crystals were collected and kept in a desiccator.

3.3.1.4 Preparation of ZnO/MgO catalysts

ZnO/MgO catalysts were prepared by adsorption technique (SEA: strong electronic adsorption). Before adsorption, the MgO were calcined at 500°C for 4 h under a flow of air (60 mL/min) with a heating rate of 1°C/min. After that 0.2, 0.5, and 1.0 g of *tris*-(bipyridine) zinc(II) nitrate, [$Zn(bipy)_3](NO_3)_2$] were dissolved in 200 mL of deionized water, in order to prepared 3 wt.%, 5 wt.% and 10 wt.% ZnO/MgO catalysts. 1.00 g of MgO was adsorbed with zinc precursor solution in capped-bottle for 3 hours, under a vigorous stirring at room temperature. The mixture was vacuum filtered, rinsed two times with deionized water, and dried in an oven at 100°C overnight. Afterward, the catalyst was calcined in muffle furnace at 500°C for 4 h under a flow of air (60 mL/min) with a heating rate of 1°C/min to obtain ZnO/MgO catalysts.

3.3.2 Catalyst characterization

3.3.2.1 Structural analysis using X-ray diffraction (XRD)

The crystalline phase of the prepared materials can be identified using XRD measurement . The sample was ground before it was packed on the sample holder .Analysis was done employing Rigaku diffractometer (Cu-K$_\alpha$ radiation, 40 kV, 30 mA), covering the range of 2θ = 20–80°, at the rate of 1.20°/step, and a scanning rate of 1 s/step.

3.3.2.2 Scanning electron microscopy with energy dispersive X-Ray analysis (SEM-EDX)

SEM-EDX was used for surface analytical techniques. The sample was manually dispersed on an SEM stub and then coated with a gold thin film. After that, the sample was placed in a chamber, which was evacuated from ambient pressure to below 10-4 Torr. Then, the sample holder was adjusted, tilted and moved in the X, Y and Z directions. Finally, sample surface was showed from almost any perspective.

3.3.2.3 Determination of specific surface area by nitrogen adsorption

Surface area of the catalysts can be determined by a gas adsorption analyzer (Autosorb-1C, Quantachrome). Approximately 0.05 g of the sample was loaded into the cell, which was attached to the outgassing station equipped with a heating mantle. The temperature was raised to 300°C during outgassing pr^{oc}ess. After that, nitrogen gas was introduced to the sample cell where the adsorption can be measured at the range of the partial pressure (P/P_0) from 10^{-6} to 1.0. The adsorption isotherm and corresponding surface area were analyzed using ***BET equation*** as shown in **Equation 3.1**

$$\frac{1}{\upsilon\left[\left(\frac{p_0}{p}\right)-1\right]} = \frac{c-1}{\upsilon_m c}\left(\frac{p}{p_0}\right) + \frac{1}{\upsilon_m c} \qquad \text{Equation 3.1}$$

Where P and P_0 are the equilibrium and the saturation pressure of adsorbents at the temperature, υ is monolayer adsorbed gas quantity, and c is the BET constant. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption to multilayer adsorption with the following hypotheses; (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer.

3.3.2.4 Determination of acidity of the catalysts by NH_3-temperature programmed desorption (NH_3-TPD)

The acid function of the catalyst was identified using NH_3-TPD measurement. Sample (0.2 g) was preheated in the flowing air zero at 450°C for 2 h and evacuated and then it was exposed to 20 kPa of 1% NH_3/He gas at 30°C until saturation coverage was reached. After that the sample was flushed with He at room temperature for 1 h, the temperature was then increased at a linear rate of 10°C/min from 50 to 500°C under vacuum.

3.3.2.5 Determination of basicity of the catalyst by CO_2-temperature programmed desorption (CO_2-TPD)

The basic function of the catalyst was identified using CO_2-TPD measurement. Sample (0.2 g) was preheated under the flowing of air zero at 450°C for 2 h and evacuated and then it was exposed to 20 kPa of pure CO_2 gas at 30°C until saturation coverage was reached. After that the sample was flushed with He at room temperature for 1 h, the temperature was then increased at a linear rate of 10°C/min from 50 to 500°C under vacuum.

3.3.3 Catalytic activity testing

Before testing the catalytic activity in ethanol conversion of each catalyst, MPV reaction of isopropanol and propionaldehyde at 380°C using 0.3 g of catalyst in a fixed-bed continuous-flow glass reactor (8 mm) was investigated. The catalyst powders were pelletized and crushed to the desired size (600-850 μm). After that, it was packed into a glass tube reactor and covered with glass wool and glass beads. The reactor was located at the center of a vertical tube furnace. Nitrogen was used as carrier gas. Gas flow rate was controlled by a mass flow controller and was checked by a bubble flow meter. After that the catalytic activity in ethanol conversion of each catalyst was carried out at 380°C, with the same reaction condition and reactor set-up as in MPV testing. The scheme of catalytic testing rig is shown in **Figure 3.1**. Before the catalytic reaction, the as-prepared catalyst was pretreated at 500°C for 1 h under air zero flow (30 mL/min). Feed (isopropanol, propionaldehyde, or ethanol) was introduced into the reactor using a syringe pump at 1.0 mL/h. The catalytic testing was conducted for a total time on stream (TOS) of 6 h. The product effluents were analyzed online through a gas chromatograph, previously calibrated for the reaction products response.

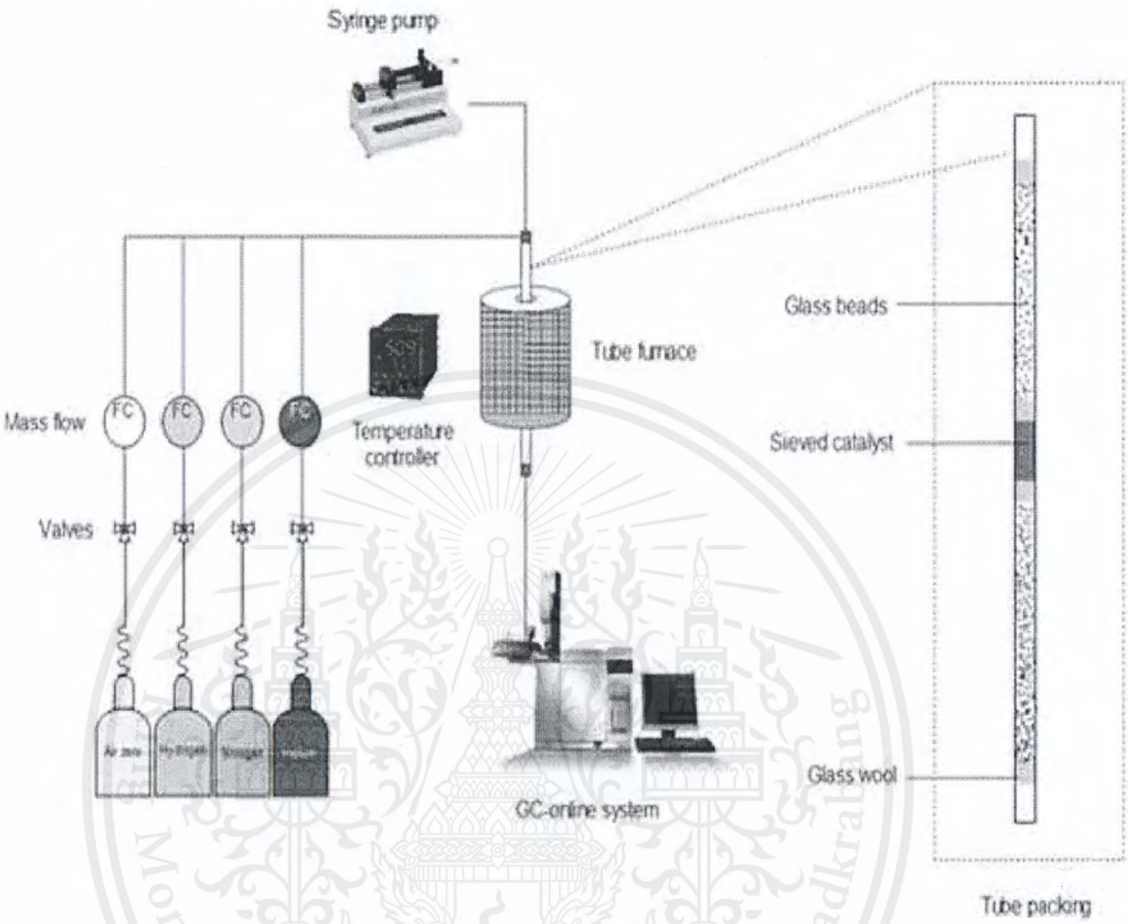


Figure 3.1 Catalytic activity testing rig

3.3.4 Products analysis

The products identification was confirmed by online gas chromatograph equipped with a flame ionized detector (GC-FID, Agilent). The products were collected in a gas sampling loop, and then periodically injected into GC column with an inert carrier nitrogen gas. The temperature of the injection port was set at 200°C, 35°C for column oven, and 250°C for FID detector. The GC temperature condition was started at 35°C, hold for 2 min then heated up to 200°C. Pressure of the carrier gas was fixed to 14 psi all time. The products were recorded as a chromatogram. Each peak areas from the chromatogram was measured and calculated. Compared with standard peak area, the species and composition of each products was determined.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 X-Ray Powder Diffraction (XRD)

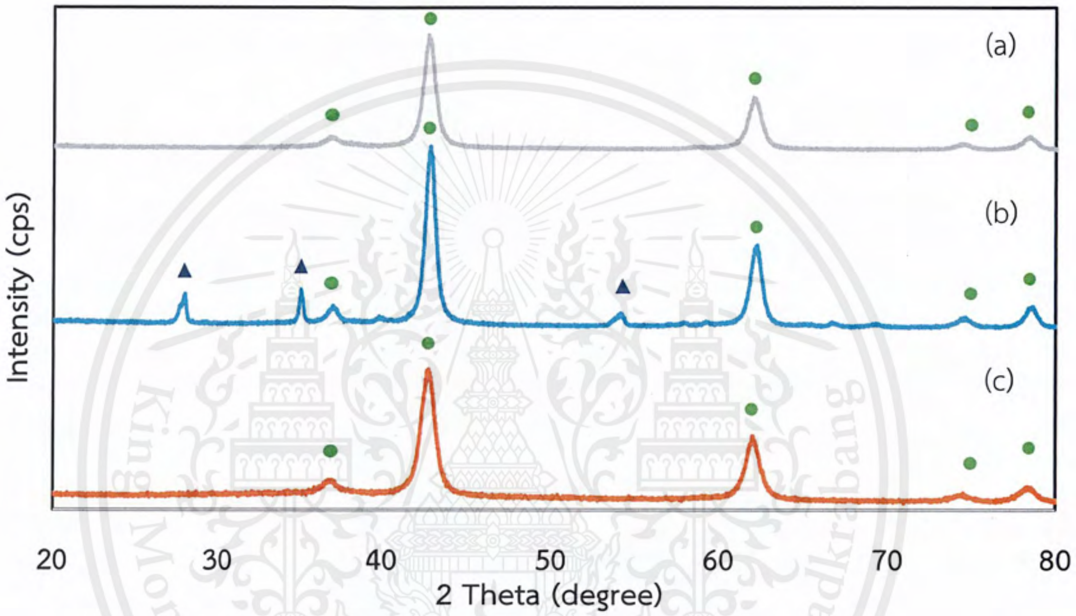


Figure 4.1 XRD pattern of (a) MgO synthesized by sol-gel method, (b) 5 wt.% RuO_2/MgO and (c) 5 wt.% ZnO/MgO

● MgO, ▲ RuO_2

As shown in **Figure 4.1 (a)** the synthesized MgO shows diffraction peaks at 2θ = 36.8°, 42.7°, 62.0°, 74.4° and 78.3° [37]. All of the observed diffraction peaks are well matched with the typical single crystalline phase of MgO in the JCPDS file for MgO (JCPDS Card No. 36-1451). No other peaks were detected in the XRD pattern within the detection limited of X-ray diffraction instrument, indicating the purity of the synthesized MgO powder. This indicated the successful synthesis of MgO. When 5 wt.% ruthenium oxide was incorporated into MgO, the major phases of RuO_2 are founded at 2θ= 27.9°, 34.9°, and 54.0° [38] **(Figure 4.1 (b))**. On the other hand, when 5 wt.% zinc oxide was incorporated, there are no diffraction peaks of zinc oxide were observed **(Figure 4.1 (c))**. This is presumably due to the higher dispersion of ZnO on MgO surface compared with RuO_2/MgO as can be confirmed by SEM-EDX results **(Figure 4.4)**.

4.1.2 Elemental composition, surface area, acid and basic characteristics of catalysts

The elemental composition, specific surface area, acidity, and basicity of the catalysts were determined by scanning electron microscopy with energy dispersive X-Ray analysis (SEM-EDX), BET measurement, and temperature programmed desorption (TPD), respectively. The results are shown in **Table 4.1**.

Table 4.1 Elemental composition, surface area, acid, and basic characteristics of catalysts

Catalyst	Surface area (m^2/g)	Elemental Composition (wt.%)			Acidity (mmol/g)	Basicity (mmol/g)
		Mg	O	Metal		
$MgO^{(a)}$	195.1	N/A	N/A	N/A	1.1	0.8
5 wt.% $RuO_2/MgO^{(b)}$	N/A	48.1	46.8	$5.2^{(d)}$	1.4	0.4
3 wt.% $ZnO/MgO^{(b)}$	N/A	51.0	45.4	$3.7^{(e)}$	1.3	1.1
5 wt.% $ZnO/MgO^{(b)}$	N/A	44.9	49.6	$5.6^{(e)}$	1.4	1.1
10 wt.% $ZnO/MgO^{(b)}$	N/A	46.2	39.6	$14.2^{(e)}$	1.0	1.1
$cLDH^{(c)}$	N/A	N/A	N/A	N/A	0.7	0.4

(a) prepared by sol-gel method using citric acid

(b) prepared by adsorption

(c) Layer double hydroxides calcined under a flow of air at 500°C, 4 h, supplied from SCG Chemicals Company Limited

(d) Ru

(e) Zn

The specific surface area of MgO synthesized by sol-gel method using citric acid is 195.1 m^2/g. It is almost three times higher surface area compared with the commercial MgO (63 m^2/g). It can be presumed that the combustion of citric acid contributes the formation of porosity. This leads to an increase in catalyst surface area, which is an important point of view for heterogeneous catalysis.

As can be seen in Table 4.1, the actual amount of metal is consistent with the calculated percentage of metal loading during catalyst preparation, suggesting a good catalyst preparation procedure.

As shown in **Table 4.1**, the MgO possesses both acid and basic properties, due to the presence of O^{2-} (Brønsted basic site) and Mg^{2+} (Lewis acid site) in the structure. **Table 4.1** presents that incorporation of MgO with ZnO by adsorption method, leads to an increase in the number of both acid and basic sites compared with MgO. However, the number of acid and basic sites are slightly increase when adding more percent loading of ZnO on MgO.

On the other hand, after incorporated MgO with RuO_2, the acidity is increased while the basicity is dropped, presumably due to agglomerated RuO_2 particles obscured the basic sites, as consistent with SEM-EDX results shown in **Figure 4.4 (a)**.

Figure 4.2 exhibits NH_3-TPD profiles of the prepared catalysts. It can be seen that incorporation of metal oxides on MgO surface leads to an increase in strong acid site, especially ZnO because of Lewis acid property of Zn.

Both acid and basic properties also presented in calcined layered double hydroxides (cLDH), due to the presence of Mg-O^{2-} pair (basic site) and Al^{3+} (acid site) in the LDH structure.

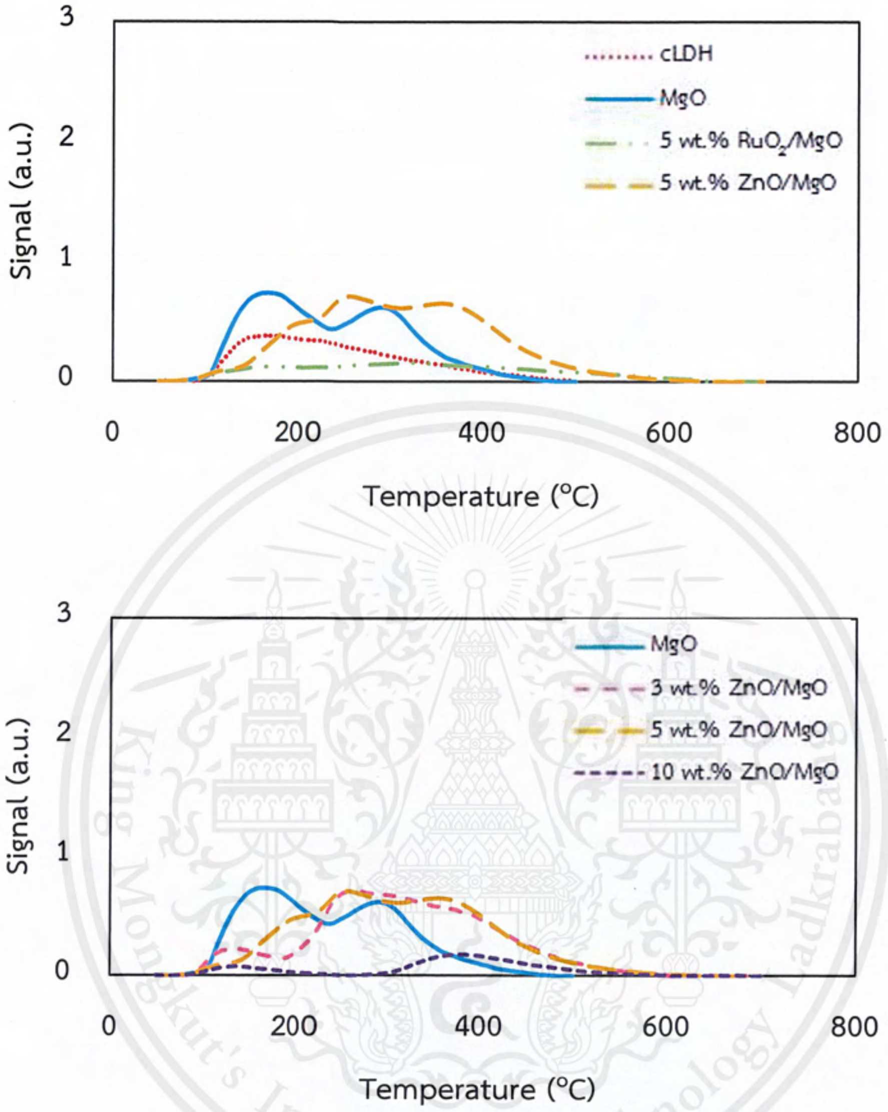


Figure 4.2 NH_3-temperature programmed desorption profile of catalysts

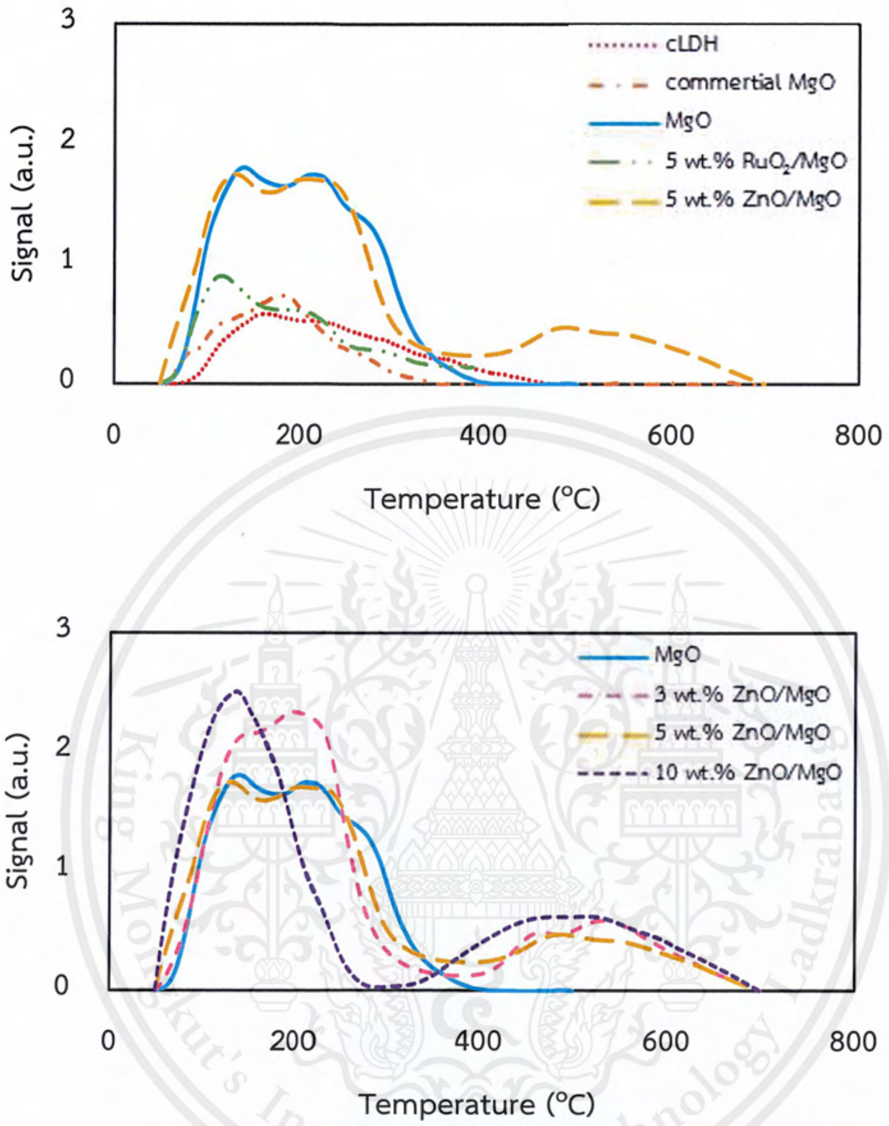


Figure 4.3 CO_2-temperature programmed desorption profile of catalysts

4.1.3 Dispersion of incorporated metal oxide on MgO

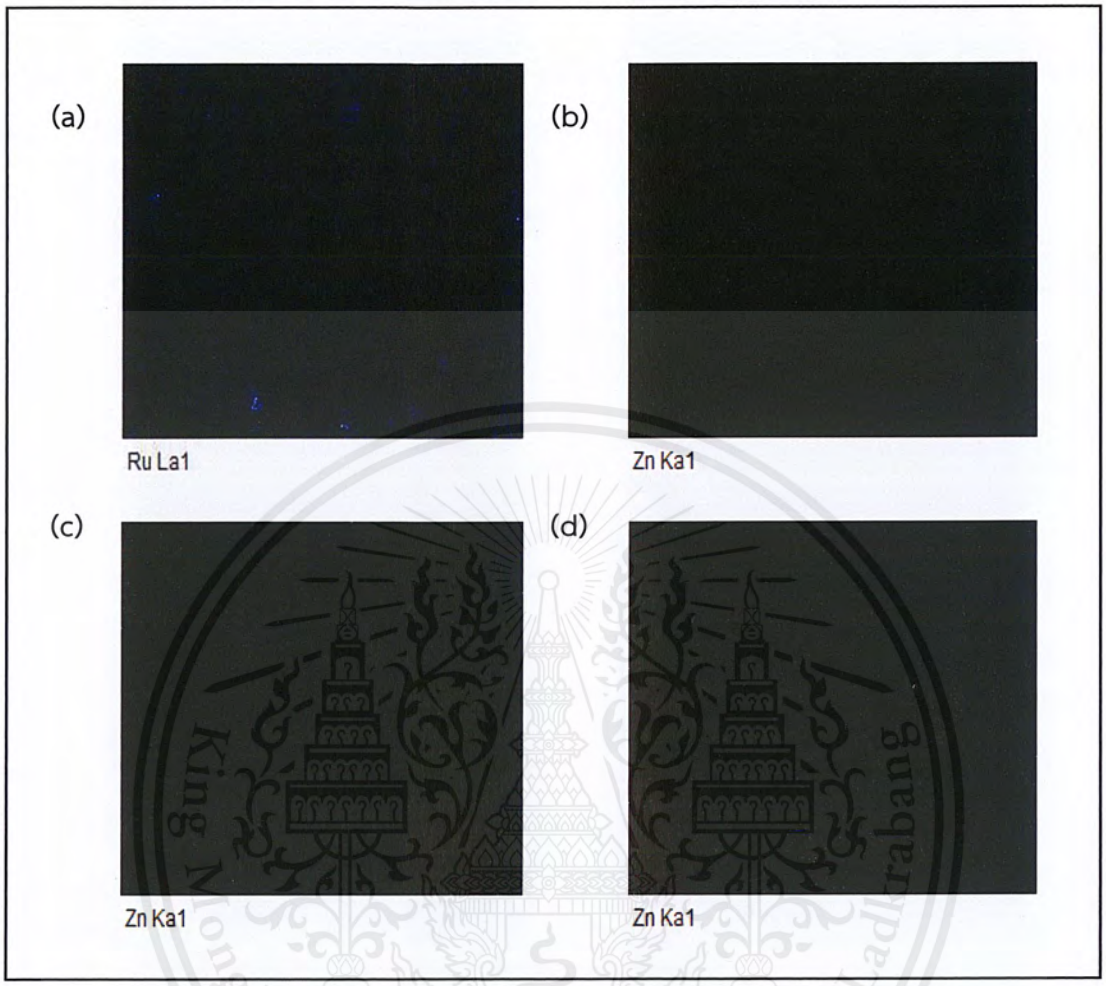
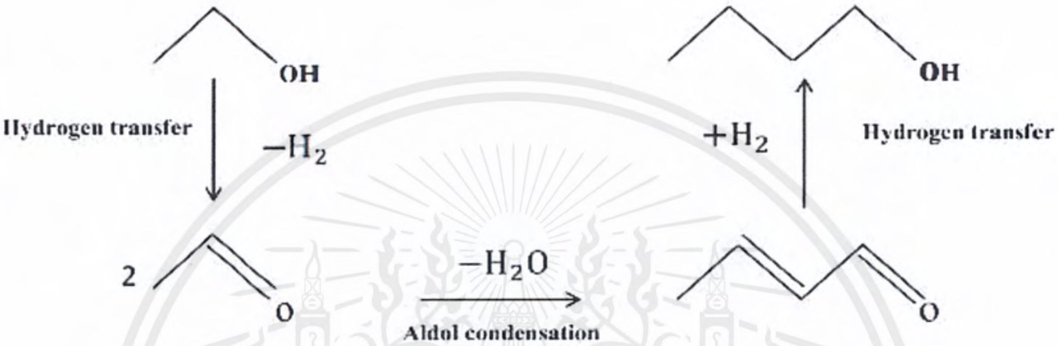


Figure 4.4 Elemental mapping obtained from SEM-EDX technique of (a) 5 wt.% RuO_2/MgO, (b) 3 wt.% ZnO/MgO, (c) 5 wt.% ZnO/MgO, and (d) 10 wt.% ZnO/MgO.

In order to indicate the dispersion of incorporated metal oxides on MgO surface, SEM-EDX was employed. As shown in **Figure 4.2 (a)** and **(b)**, at the same metal loading, the dispersion of ZnO on MgO surface is better than that of RuO_2. This is presumably due to non-polar solvent used in ruthenium precursor solution for catalysts preparation by adsorption, which leads to the agglomeration of ruthenium oxide on polar MgO surface. Comparing ZnO/MgO with different percent metal loadings, it can be seen that the lower the percentage of ZnO loading, the better the dispersion of ZnO on MgO surface. Accordingly, dispersion of metal oxide has an important effect to activity of the catalysts.

4.2 MPV reaction

According to Guerbet reaction, it composes of 3 steps in the conversion of ethanol to higher alcohols (**Scheme 4.1**). First step is dehydrogenation of ethanol to acetaldehyde. The second is aldol condensation of acetaldehydes to C4 aldehyde. Final is hydrogenation of C4 aldehyde to C4 alcohol.



Scheme 4.1 Guerbet reaction

It shows that H_2-transfer is an important step in Guerbet reaction to provide acetaldehyde intermediate and high yield of higher alcohols. Hence, H_2-transfer activity of the prepared catalysts was firstly tested with MPV (Meerwein–Ponndorf–Verley) reaction of isopropanol and propionaldehyde. MPV reaction of isopropanol and propionaldehyde over MgO catalyst was observed from yield of MPV products (acetone and *n*-propanol), as shown in **Figure 4.5**.

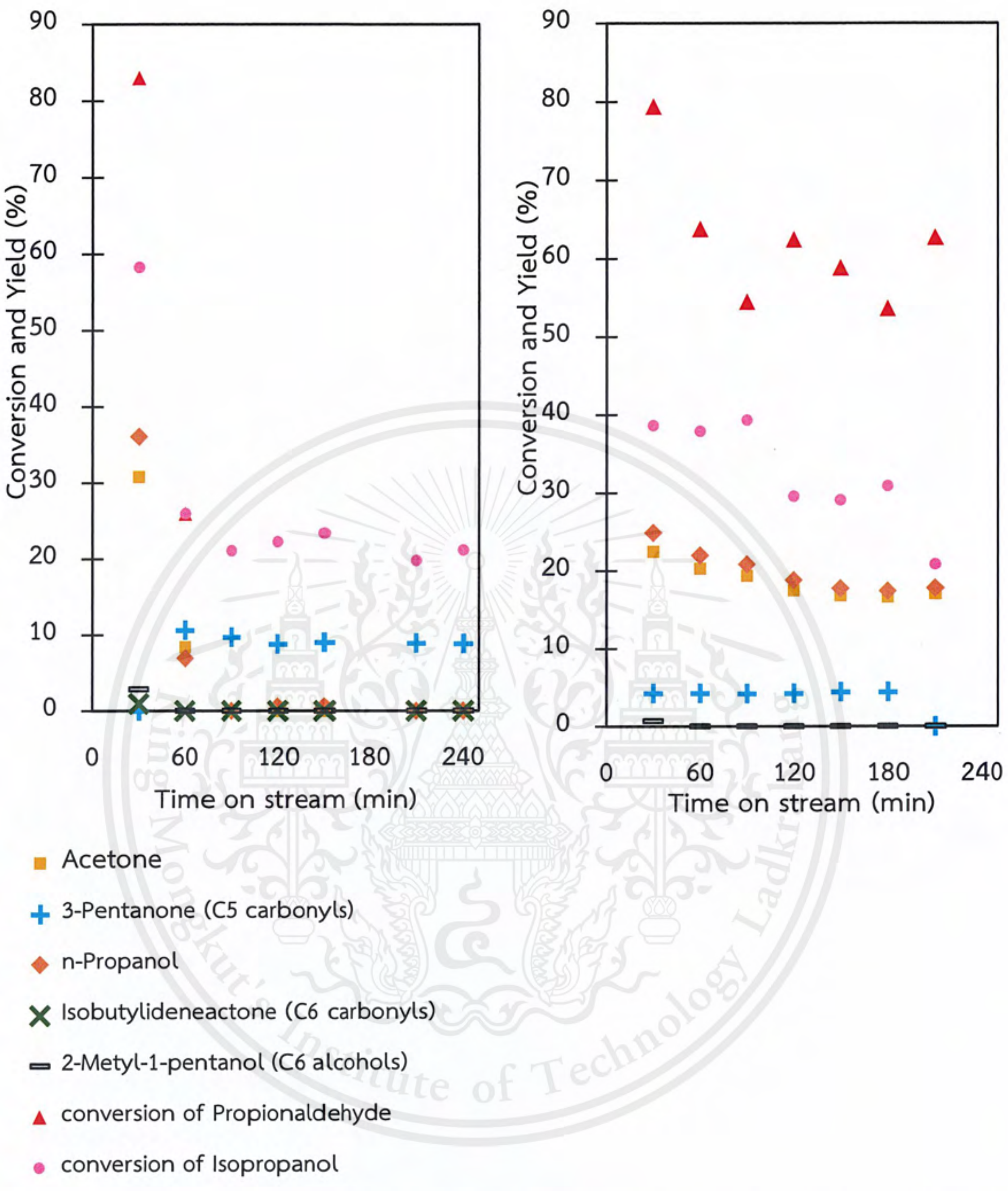
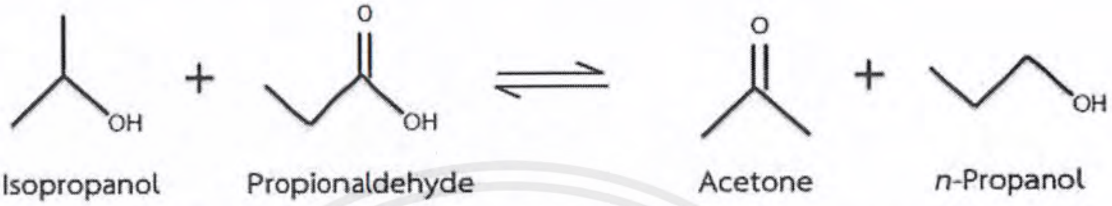


Figure 4.5 MPV reaction over MgO using (a) 1:1 isopropanol: propionaldehyde and (b) 2:1 isopropanol: propionaldehyde feed ratio *(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time of isopropanol: 20 g.h/mol, contact time of propionaldehyde: 22 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)*

It can be observed from **Figure 4.5 (a)** that at the beginning of the reaction (0.5-1 h time on stream) acetone and *n*-propanol, which are products from dehydrogenation of isopropanol and hydrogenation of propionaldehyde, respectively, are initially formed over MgO catalyst (**Scheme 4.2**). This indicated the H_2-transfer activity of MgO.

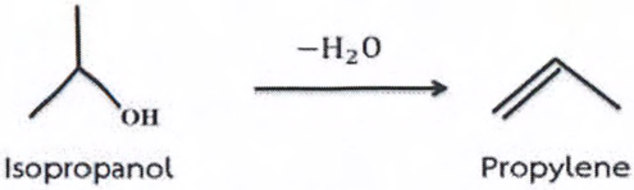


Scheme 4.2 MPV of reaction isopropanol and propionaldehyde

After 1 h of time on stream, a suddenly decrease in H_2-transfer activity of MgO could be detected with an increase of larger products (C5 ketones), which might be occurred from aldol condensation of propionaldehyde and sequentially cracking. These large molecular weight products could strongly adsorb on catalysts surface and prevented the entering of feed molecule. Hence, a decrease in H_2-transfer activity was detected.

Furthermore, the effect of isopropanol: propionaldehyde feed ratio (1:1 and 2:1) on H_2-transfer activity of the MgO catalyst was investigated. It obviously showed that the higher feed ratio, the higher yield of MPV products (acetone and *n*-propanol) was obtained (**Table 4.2**). This is because isopropanol acted as a hydrogen donor, donated hydrogen to propionaldehyde, promoted the formation of acetone and *n*-propanol, and sequentially suppressed the aldol condensation of propionaldehyde. Accordingly, MPV reaction over MgO using 2:1 isopropanol: propionaldehyde feed ratio presented higher stability compared with 1:1 **(Figure 4.5 (b))**.

From **Table 4.2**, it is noteworthy that no undesired propylene by-product was obtained over MgO catalyst, indicating that MgO does not possess any Brønsted acid site, which facilitates dehydration of *n*-propanol (**Scheme 4.3**).



Scheme 4.3 Dehydration of isopropanol

On the other side, calcined layered double hydroxides (cLDH) generated high yield of propylene, presumably due to the Brønsted acid site presented on the cLDH surface [33]. It is well-known that production of olefins from alcohol is catalyzed by Brønsted acid site [39-40].

Therefore, from the preliminary study on MPV reaction, MgO seems to be a promising catalyst for the production of higher alcohols from ethanol.

Table 4.2 Conversion and product yields of MPV reaction over MgO and cLDH catalysts.

Catalysts	MgO		cLDH
Isopropanol: Propionaldehyde	1:1	2:1	2:1
Conversion (%)			
Isopropanol	25.3	30.2	41.2
Propionaldehyde	8.0	61.3	49.1
Yield of Product (%)			
Propylene	-	-	15.4
Acetone	3.4	18.1	7.0
n-Propanol	3.9	19.3	16.2
C6 alcohols(a)	0.0	0.1	-
C7 alcohols(b)	-	-	0.7
C9 aromatic alcohols	-	-	3.4
C5 carbonyls(c)	8.2	3.9	0.6
C6 carbonyls(d)	0.2	-	-

(a) : 2-methylpentanol
(b) : 2-Heptanol
(c) : Pentanone
(d) : 3-Hexane-2-one

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time of isopropanol: 20 g.h/mol, contact time of propionaldehyde: 22 g.h/mol, flow rate of N_2 *carrier gas: 160 mL/min)*

4.3 Conversion of ethanol to higher alcohols

After preliminary study on MPV reaction, the catalytic activities in ethanol conversion of MgO and cLDH were investigated in a continuous fixed-bed reactor at 380°C, pressure 1 atm, contact time 20 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min.

4.3.1 Conversion of ethanol over MgO

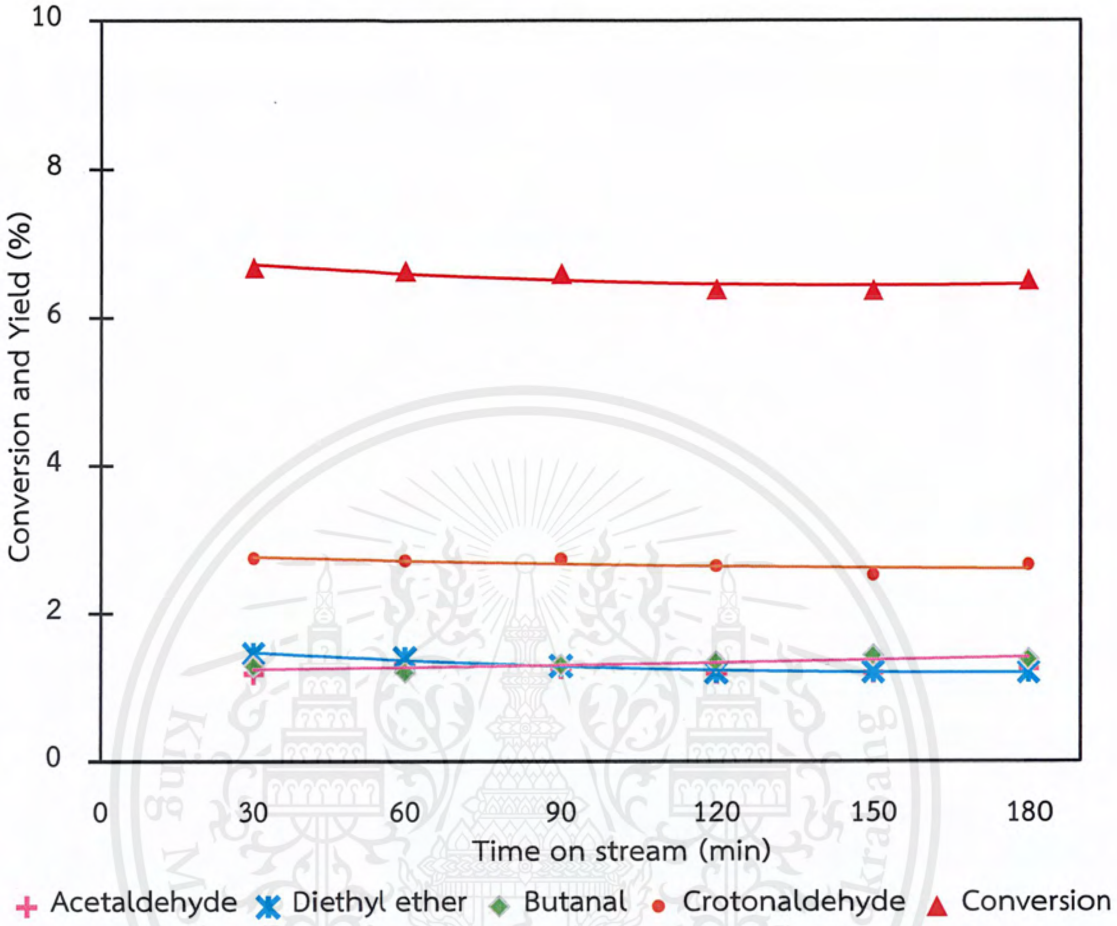
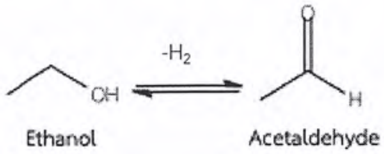


Figure 4.6 Conversion of ethanol and yields of products over MgO *(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of* N_2 *carrier gas: 160 mL/min)*

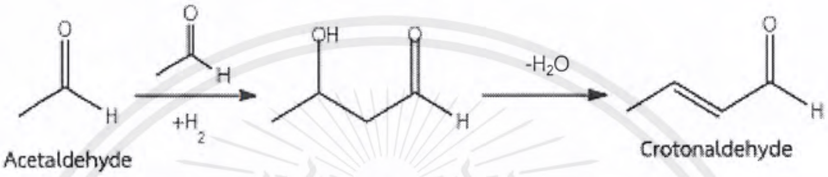
Figure 4.6 presents the conversion of ethanol and yields of products using MgO. It can be seen that the conversion of ethanol is steady (~7%) over 180 min on stream, suggesting a high stability of the MgO catalyst. It provides crotonaldehyde as a major product, while acetaldehyde, butanal, and diethyl ether are minor products.

According to Guerbet reaction, the conversion of ethanol to higher alcohols composes of three steps:

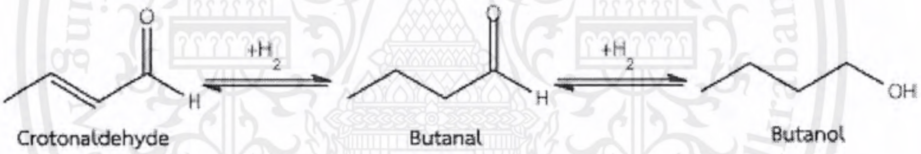
(i) Dehydrogenation of ethanol to acetaldehyde



(ii) Aldol condensation of two acetaldehyde molecules to crotonaldehyde



(iii) Hydrogenation of crotonaldehyde to butanal and butanol, sequentially

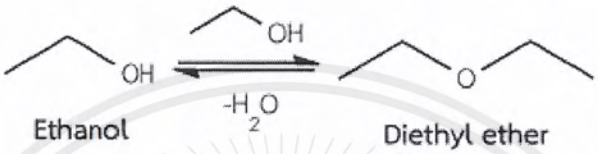


Scheme 4.4

From **Figure 4.6**, it can be observed that MgO has high activity in dehydrogenation of ethanol to acetaldehyde (i), presumably due to acid-base pair site of MgO (Mg-O) [41-43]. After that, the acetaldehyde intermediates can be converted to crotonaldehyde via aldol condensation, where basic property (Mg-O^{2-} pair) plays an important role [44]. However, those formed crotonaldehydes are not completely hydrogenated to butanol, only butanal was obtained. This is probably due to low hydrogen on MgO surface, resulting in partial hydrogenation of those unsaturated aldehydes. N.E. Fouad et al. suggested that the facilitation on aldol condensation of the acid-base catalysts is the result of the stabilization of a surface intermediates through a strong interaction between the oxygenated intermediates and the Lewis acid site. This interaction allows the formation of large aldol condensation products [44]. Thus, generation of new surface Lewis acid by incorporation of metal oxide on MgO could be an approach to increase the H_2-transfer ability of the catalyst.

However, MgO catalyst also gives diethyl ether as a minor product, which occurred from bimolecular dehydration of ethanol (iv).

(iv) Bimolecular dehydration of ethanol to diethyl ether.



Scheme 4.5

4.3.2 Conversion of ethanol over cLDH

Layered double hydroxides (LDH) are materials composed of a lamellar structure of magnesium and aluminum hydroxides. LDHs are presented by a general formula: $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$, where M^{2+} is a divalent cation such as Mg^{2+}, M^{3+} is a trivalent cation such as Al^{3+} and A^{n-} is an interlayer anion such as $CO_3{}^{2-}$ and OH^-. After calcined at 500°C (notified as cLDH), the layered structure of LDH was completely collapsed, only Mg-Al mixed oxides are presented [33].

The activity in ethanol conversion of cLDH, which possesses both acid and basic properties, was also investigated under the same reaction conditions at 380°C, pressure 1 atm, contact time 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min, as the result shown in **Figure 4.7**.

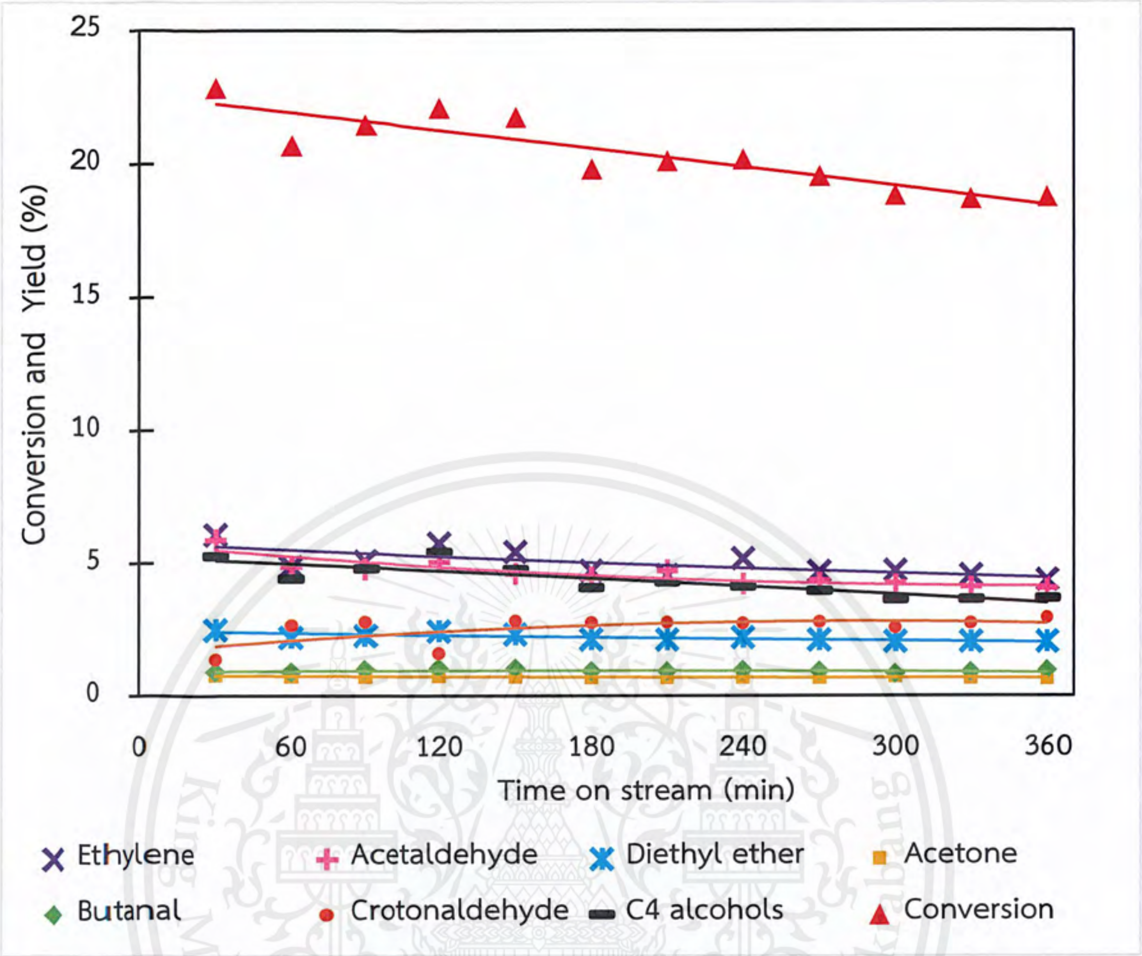
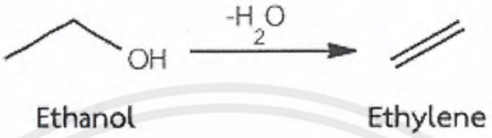


Figure 4.7 Conversion of ethanol and yields of products over cLDH *(Reaction condition; temperature: 380°C, pressure: 1 atm, flow rate of* N_2 *carrier gas: 160 mL/min)*

At the same reaction conditions, cLDH gives almost three times higher ethanol conversion compared with MgO, which can be explained from the presence of Mg-O^{2-} pair (Brønsted basic site) and Al^{3+} (stronger Lewis acid compared with Mg^{2+}) in the cLDH structure. The strong Lewis acid-base pair site promotes the formation of acetaldehyde, an important intermediate in Guerbet reaction and facilitates the aldol condensation [53-55, 57]. Thus, Al drastically increases the active acid-base pair site that enhances the formation of higher alcohols by promptly hydrogenates the formed higher aldehyde intermediate as evidence by higher yield of butanol compared with that of MgO.

As presented in **Table 4.3**, the conversion of ethanol over cLDH also provided an undesired product, diethyl ether, which is presumably due to the presence of Lewis acid as previously described in the case of MgO. In addition, cLDH also gives high yield of ethylene, while no ethylene was observed over MgO. This implies that the acidic sites in cLDH and MgO are not the same. Ethylene formation can occur via monomolecular dehydration of ethanol over Brønsted acid site (v).

(v) Dehydration of ethanol to ethylene



Scheme 4.6

Table 4.3 Comparison of ethanol conversion and product yields over MgO and cLDH

Catalysts	MgO	cLDH
Conversion (%)	6.5	19.0
Yield of Product (%)		
Ethylene	-	5.0
Acetaldehyde	1.2	4.6
Diethyl ether	1.3	2.2
Acetone	-	0.7
Crotonaldehyde	2.7	2.6
Butanal	1.3	0.9
C4 alcohols[(a)]	-	4.3

(a) : Butanol and 2-butenol

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min, average result from 6 h of time on stream)

According to the low selectivity towards undesired products (diethyl ether and ethylene) of MgO, the activity in ethanol conversion of MgO based catalysts were investigated further.

4.4 Conversion of ethanol over MgO based catalysts

From Section 4.3, it is clear that MgO has good activity in promoting dehydrogenation of ethanol to acetaldehyde and condensation of acetaldehydes to larger aldehyde molecules, but not readily active for hydrogenation of those aldehydes to corresponding higher alcohols. Thus, generation of new surface Lewis acid site by incorporation of metal oxides (RuO_2 and ZnO) on MgO was performed.

4.4.1 Effect of type of incorporated metal oxides on MgO

In order to study the effect of incorporated metal oxide on H_2-transfer and ethanol conversion activities, RuO_2 and ZnO incorporated MgO catalysts (5 wt.% RuO_2/MgO and 5 wt.% ZnO/MgO) were prepared by adsorption technique. The conversion of ethanol over MgO based catalysts with different basic and acid sites: MgO, 5 wt.% RuO_2/MgO and 5 wt.% ZnO/MgO were investigated under the same reaction conditions in fixed-bed reactor as presented in **Table 4.4.**

Table 4.4 Ethanol conversion and yield of products over MgO based catalysts

Catalysts	MgO	5 wt.% RuO_2/MgO	5 wt.% ZnO/MgO
Conversion (%)	6.5	16.9	20.6
Yield of Product (%)			
Ethylene	-	-	-
Acetaldehyde	1.2	1.0	1.6
Diethyl ether	1.3	7.4	5.8
Acetone	-	1.8	1.8
Diethyl acetal	-	-	0.5
Crotonaldehyde	2.7	2.2	2.9
Butanal	1.3	2.3	2.6
C4 alcohols[(a)]	-	2.1	3.9
C8 aldehydes[(b)]	-	0.3	0.7
$C8^+$ aromatic carbonyls	-	-	1.6

(a) : Butanol and 2-butenol

(b) : 2-Ethylhexanal

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min, average result from 6 h of time on stream)

The conversions of ethanol over 5 wt.% RuO_2/MgO and 5 wt.% ZnO/MgO were increased significantly, as compared to MgO. It is obvious that the yield of C4 alcohols is increased.

RuO_2/MgO provides approximately two times higher ethanol conversion, as compared to MgO. This is because of incorporation of RuO_2 on the MgO surface generated more strong Lewis acid sites as evidence by NH_3-TPD (**Figure 4.2**). These species could improve H_2-transfer activity in Guerbet reaction as can be observed by an increase in yield of C4 alcohols (butanol and 2-butenol). This implies that acid (Ru^{4+})-Brønsted base (Mg-O^{2-}) pair on RuO_2/MgO surface could enhance the formation of higher alcohols by promptly hydrogenates the formed C4 aldehyde intermediates (crotonaldehyde and butanal) to C4 alcohols.

However, high yield of undesired product diethyl ether was obtained over RuO_2/MgO. This is probably due to the high active Lewis-acid surface obtained from the agglomeration of RuO_2, which facilitated the bimolecular dehydration of ethanol. CO_2-TPD insists that basicity of RuO_2/MgO is decreased (**Figure 4.3**).

ZnO/MgO shows a remarkably higher ethanol conversion activity, as compared to RuO_2/MgO and the parent MgO. It can promote dehydrogenation of ethanol to acetaldehyde, and also condensation and readily hydrogenation to higher alcohol. Again, this is because of stronger Lewis acidity created by incorporated ZnO as confirmed by NH_3-TPD (**Figure 4.2**). These species are believed to increase ability in H_2-transfer, which promotes the dehydrogenation of ethanol and hydrogenation of higher aldehydes to higher alcohols. It is noteworthy that ZnO also facilitate the production of large carbonyl molecules (C8 and C10).

However, the reaction over ZnO/MgO also provided higher yield of undesired product, diethyl ether as compared to MgO. The yield of diethyl ether is in the following order: RuO_2/MgO > ZnO/MgO > MgO. This can be explained from the higher acidity obtained after incorporation of metal oxides on MgO. Highly dispersed ZnO on MgO surface (**Figure 4.4 (c)**), generated appropriate acid-base pair for H_2-tranfer and aldol condensation, while the agglomerated RuO_2 provided too much Lewis acidity.

It can be seen that no dehydration of ethanol to ethylene occurred over these catalysts, which confirmed that no Brønsted acid site presented on the MgO based catalysts.

4.4.2 Effect of percentage of ZnO loading

With high H_2-transfer activity, together with high aldol condensation activity, the ethanol conversion over ZnO/MgO catalysts was investigated further. The ethanol conversion and yield of products obtained from using different %loading of ZnO on MgO (3 wt.%, 5 wt.% and 10 wt.%) were investigated as shown in **Table 4.5**.

Table 4.5 Ethanol conversion and yield of products over different percent loading of ZnO on MgO

Catalysts	MgO	3 wt.% ZnO/MgO	5 wt.% ZnO/MgO	10 wt.% ZnO/MgO
Conversion (%)	6.5	15.2	20.6	21.2
Yield of Product (%)				
Acetaldehyde	1.2	0.9	1.6	1.3
Diethyl ether	1.3	3.1	5.8	4.9
Acetone	-	1.2	1.8	1.6
Diethyl acetal	-	0.3	0.5	0.4
Crotonaldehyde	2.7	3.1	2.9	2.8
Butanal	1.3	1.8	2.6	2.3
C4 alcohols[(a)]	-	4.3	3.9	4.1
C8 aldehydes[(b)]	-	0.5	0.7	0.8
$C8^+$ aromatic carbonyls	-	-	1.6	3.1

(a) : Butanol, 2-Butenol

(b) : 2-Ethylhexanal

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 *carrier gas: 160 mL/min, average result from 6 h of time on stream)*

The conversion of ethanol over 3 wt.% ZnO/MgO, 5 wt.% ZnO/MgO, and 10 wt.% ZnO/MgO were increased significantly as compared to MgO. This is because of adding ZnO increase amount of strong acid and basic site as shown by NH_3-TPD and CO_2-TPD (**Figure 4.2 and Figure 4.3**). These acid and basic sites would promote activity for H_2-transfer and aldol condensation, respectively. However, it is also seen that dehydration of ethanol to diethyl ether is significantly increased, with an increase of percentage of ZnO loading.

Increasing in loading of ZnO from 3 wt.% to 10 wt.% consequently increased the yield of large molecular weight products (C8 and C10 carbonyls).

Although, 5 wt.% and 10 wt.% ZnO/MgO shows the high activity for aldol condensation, low yield of higher alcohols was obtained. This may be due to a non-appropriate acid-base pair caused by the excessive acid sites, the formed large carbonyl molecules cannot be readily hydrogenated to higher alcohols. This is confirmed by the results of SEM-EDX as shown in **Figure 4.4 (c)** and **(d)**.

In addition, high loading ZnO catalysts also produced high yield of diethyl ether, compared with low ZnO loading, presumably due to the excess acid sites.

For more explanation on the role of acid and basic site, the Guerbet reaction over cLDH and 3 wt.% ZnO/MgO were further investigated. **Table 4.6** presents selectivity of products obtained from cLDH and 3 wt.% ZnO/MgO, compared at similar %conversion.

Table 4.6 Comparison of selectivity of products obtained from cLDH and 3 wt.% ZnO/MgO at similar conversion

Catalysts	cLDH	3 wt.% ZnO/MgO
Conversion (%)	20.4	18.7
Selectivity (%)		
Ethylene	24.5	0.0
Acetaldehyde	22.6	7.2
Diethyl ether	10.8	22.0
Acetone	3.5	6.7
Crotonaldehyde	12.7	16.3
Butanal	4.6	9.9
C4 alcohols$^{(a)}$	21.2	17.5
C8+ aromatic carbonyls	0.0	20.4

(a) : Butanol, 2-Butenol

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time over LDH: 16 g.h/mol, contact time over 3 wt.%ZnO/MgO: 20 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min, average result from 6 h of time on stream)

It can be observed that at similar conversion, cLDH provides significantly high selectivity towards ethylene by-product, while no ethylene was obtained from 3 wt.% ZnO/MgO. This implies that cLDH has active site for dehydration of ethanol to ethylene, but this site does not appear on 3 wt.% ZnO/MgO surface. It is well-known that the dehydration of alcohol to olefin is catalyzed by Brønsted acid site [39-40]. On the other hand, 3 wt.% ZnO/MgO gives higher selectivity towards higher molecular weight products. This can be explained from the higher amount of basic site of MgO and stronger basic site generated by incorporation of ZnO, compared with LDH (**Figure 4.3**). However, these aldol products are not readily hydrogenated to alcohols. As can be seen in **Table 4.6**, lower C4 alcohols selectivity was obtained over the 3 wt.% ZnO/MgO catalyst. As discussed earlier, the H_2-transfer activity is catalyzed by Lewis acid site. However, 3 wt.% ZnO/MgO catalyst gives higher selectivity towards diethyl ether, compared with LDH. The diethyl ether is occurred via biomolecular dehydration of ethanol where Lewis acid site plays an important role [58,59]. This means that 3 wt.% ZnO/MgO possesses Lewis acid sites but those sites were not well dispersed enough to generate appropriate acid-basic site proximity. Thus, promptly hydrogenation after aldol condensation was suppressed over 3 wt.% ZnO/MgO catalyst. Hence, it is important to balance the number of acid and basic site on catalyst to generate the appropriate acid-base pair.

4.4.3 Effect of contact time

In order to understand reaction pathway for the formation of products over ZnO/MgO catalyst, effect of contact time on the ethanol conversion was investigated as presented in **Figure 4.8**.

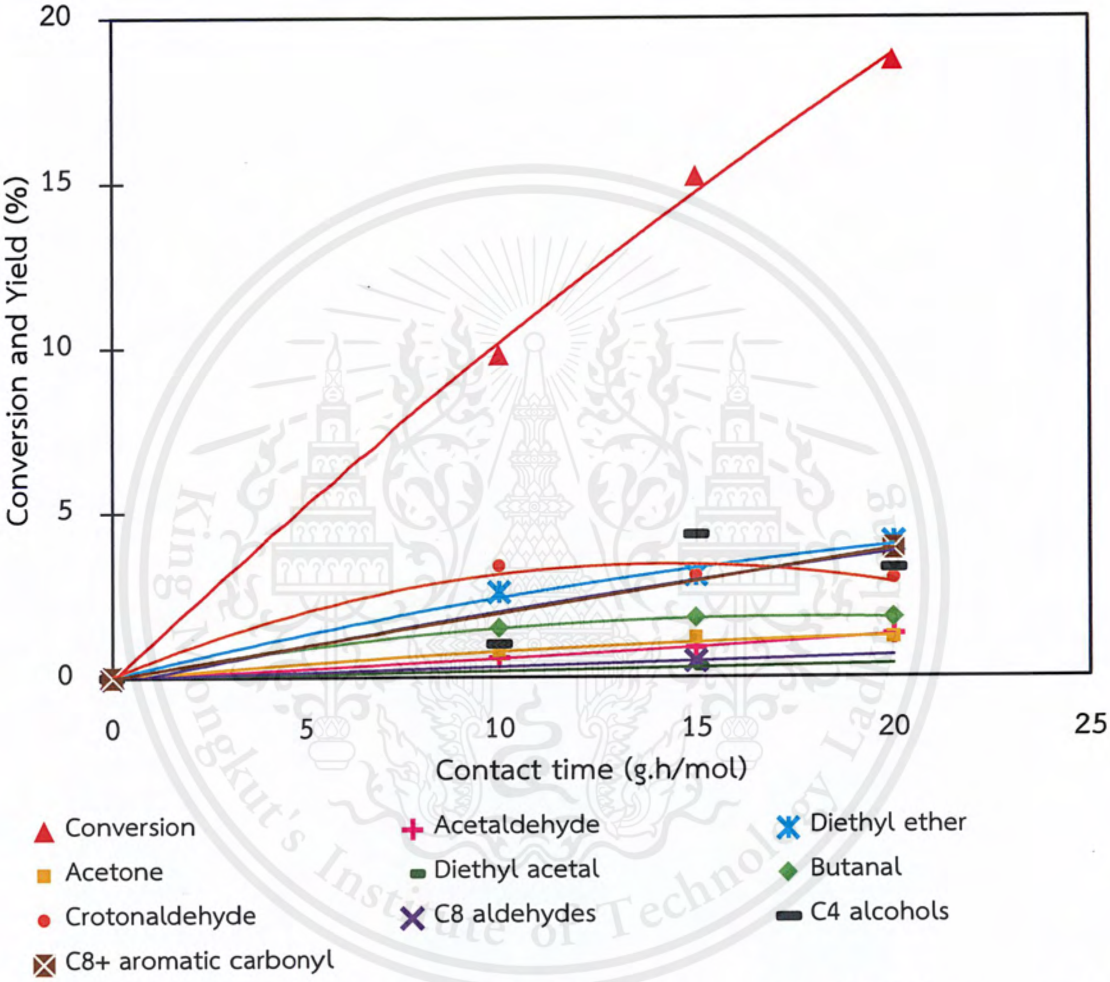


Figure 4.8. Conversion of ethanol and yield of products over 3 wt.% ZnO/MgO at various contact times *(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 10-20 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min, average result from 6 h of time on stream)*

It is shown that the conversion of ethanol was doubled with doubling contact time from 10 to 20 g.h/mol. This can be explained by increasing the amount of catalyst in the system, would consequently increase the number of active site for the reaction. In addition, the yield of diethyl ether was also increased with contact time, due to the bimolecular dehydration of ethanol.

However, no significant increase in yield of acetaldehyde was observed with increasing contact time. On the other hand, the yield of C4 alcohols were increased only at initial period, while the yields of other higher products ($C8^+$ carbonyls) were increased at high contact time as presented in **Table 4.7**.

Table 4.7 Conversion of ethanol and products yield over different contact times using 3 wt.% ZnO/MgO catalyst.

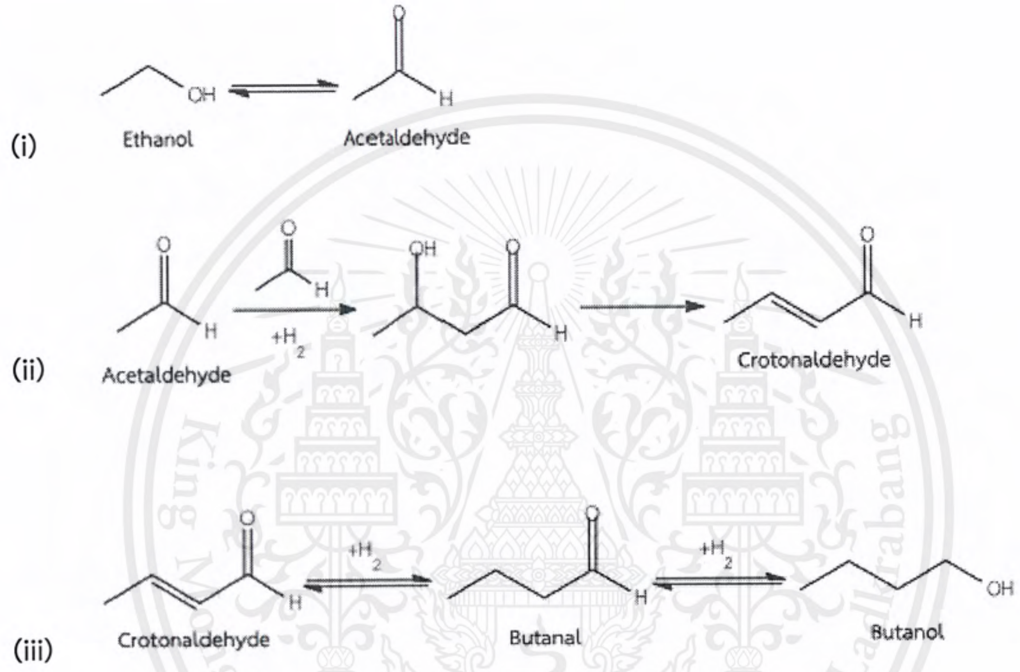
Contact time (g.h/mol)	**10**	**15**	**20**
Conversion (%)	9.8	15.2	20.0
Yield of Product (%)			
Acetaldehyde	0.6	0.9	1.3
Diethyl ether	2.6	3.1	4.1
Acetone	0.8	1.2	1.2
Diethyl acetal	-	0.3	-
Crotonaldehyde	3.6	3.1	3.0
Butanal	1.6	1.8	1.8
C4 alcohols(a)	1.4	4.3	3.3
C8 aldehydes(b)	-	0.5	-
$C8^+$ aromatic carbonyls	-	-	3.9

(a) : Butanol, 2-Butenol

(b) : 2-Ethylhexanal

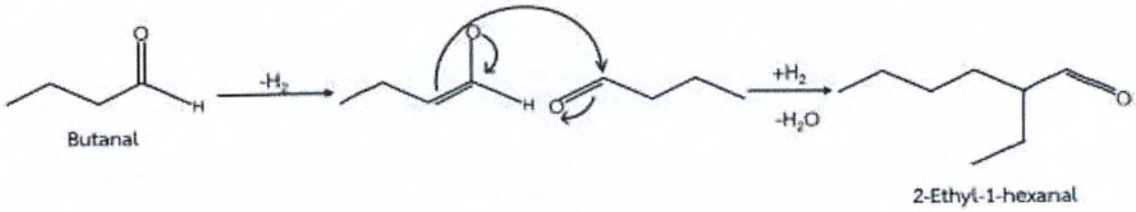
(Raction condition; temperature :380°C, pressure :1 atm, contact time :10-20 g.h/mol, flow rate of N_2 carrier gas :160 mL/min, average result from 6 h of time on stream)

According to Guerbet reaction, ethanol is primarily dehydrogenated to acetaldehyde (i). Then, the two acetaldehyde molecules undergo coupling via aldol condensation to crotonaldehyde (ii). The crotonaldehyde can be hydrogenated to butanal, an intermediate for butanol synthesis. Finally, butanal can be further hydrogenated to butanol (iii), as shown in **Scheme 4.7**.



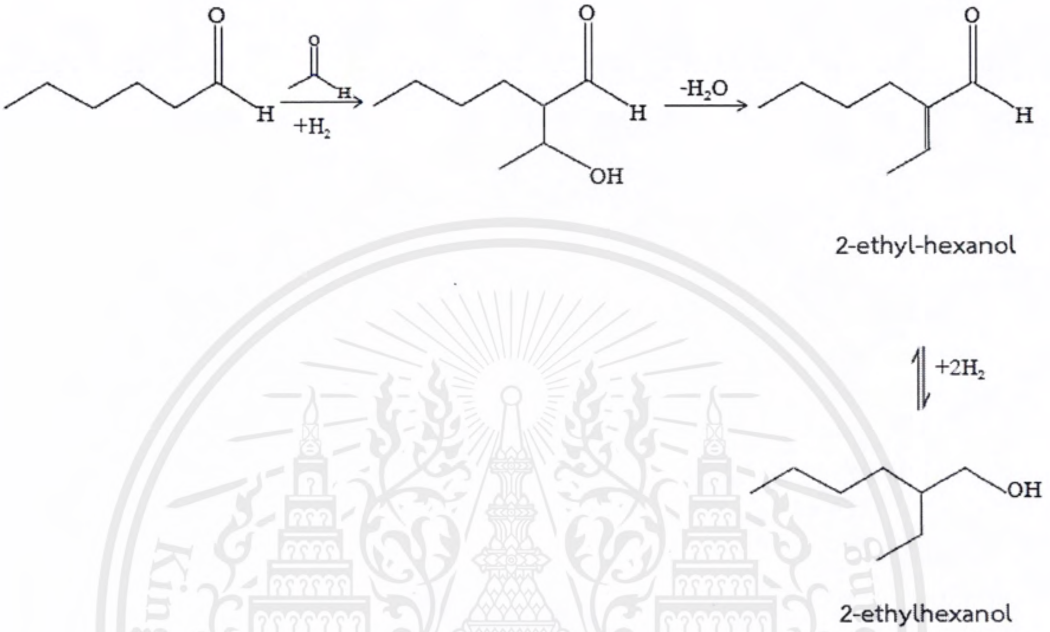
Scheme 4.7

Furthermore, butanal can be an intermediate for the production of C8 aldehydes (2-ethyl-hexanal) as shown in **Scheme 4.8**. These molecules desorbed and observed as carbonyl products.



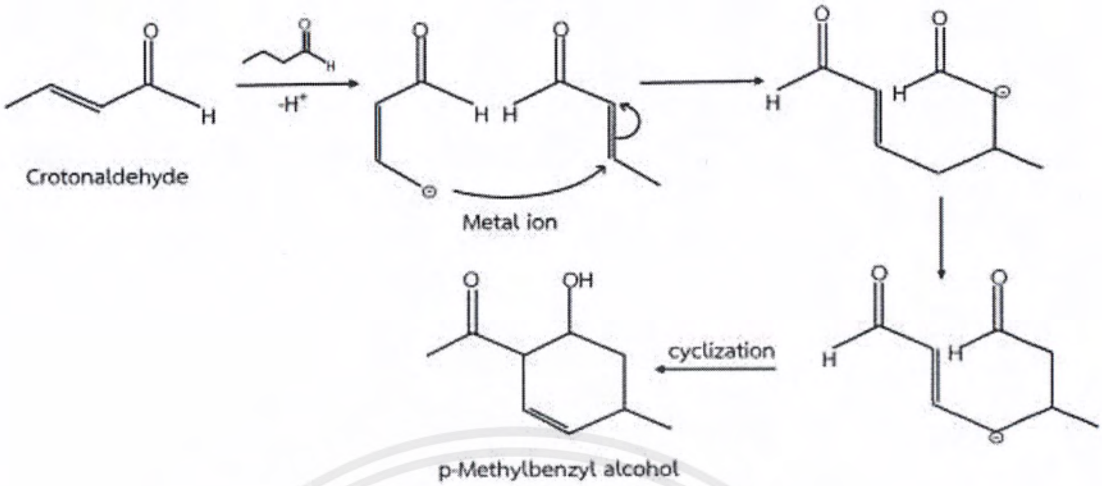
Scheme 4.8

In the case of C8 aldehydes, 2-ethylhexanal can be also obtained by the coupling of activated acetaldehyde with 1-hexanal. Then, it is further aldol condensed to 2-ethylhexanal as presented in **Scheme 4.9**.



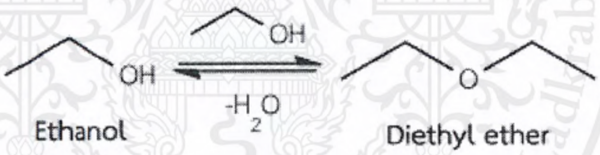
Scheme 4.9

C8 aromatic compounds can be obtained by coupling of crotonaldehydes. Then, it is further cyclized to 2-methylbenzaldehyde as presented in **Scheme 4.10**. It can be described that Zn^{2+} can stabilize the electron delocalization in the conjugated double bonds of crotonaldehyde.



Scheme 4.10

Moreover, over ZnO/MgO catalyst, ethanol can be also converted in parallel to diethyl ether. Diethyl ether is formed via bimolecular dehydration of ethanol, as seen in **Scheme 4.11**.



Scheme 4.11

This reaction does not give H_2 as products. Hence, increase in conversion of ethanol to diethyl ether limits the formation of higher alcohols.

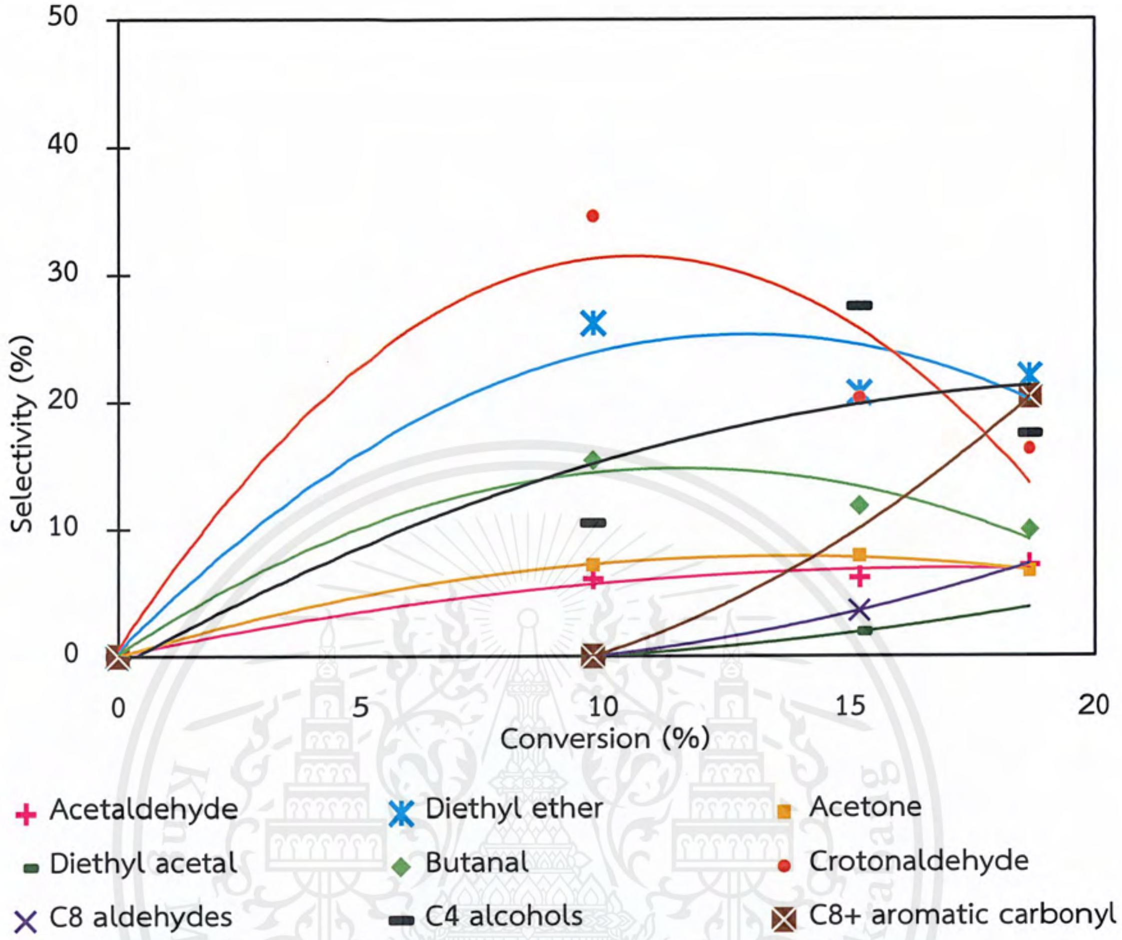
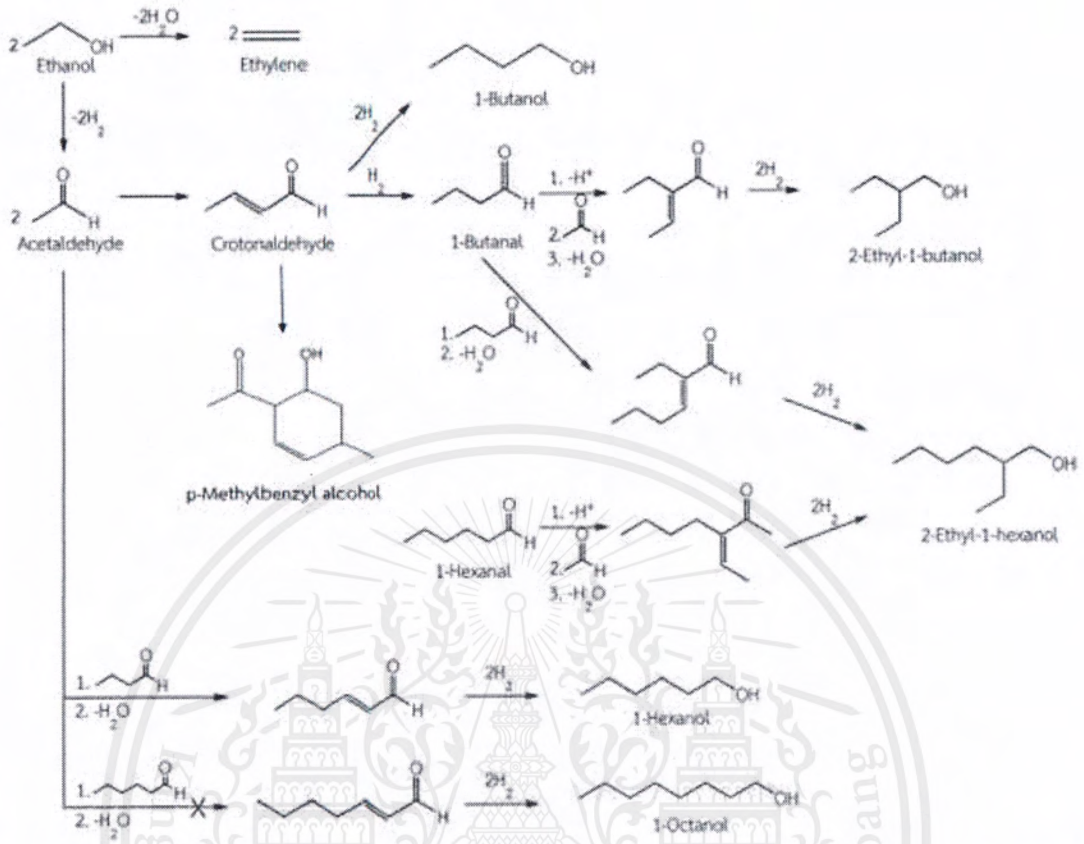


Figure 4.9 Selectivity of products at various conversions over 3 wt.% ZnO/MgO catalyst. *(Reaction condition; temperature :380°C, pressure :1 atm, contact time :10-20 g.h/mol, flow rate of N_2 carrier gas :160 mL/min, average result from 6 h of time on stream)*

It can be seen that the selectivity of acetaldehyde and C4 alcohols are decreased, while the selectivity of higher products as C8 and C10 carbonyls are increased. It is clear that Guerbet reaction is a series reaction and this reaction is controlled by dehydrogenation of ethanol. The overall reaction pathway can be proposed as shown in **Scheme 4.11**.



Scheme 4.12 The overall reaction pathway for ethanol conversion over ZnO/MgO catalyst.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The specific surface area of MgO synthesized by sol-gel method using citric acid is higher than the surface area of commercial MgO. It can be presumed that formation of porosity is contributed from citric acid combustion. TPD data show that acidity and basicity are increased when MgO was incorporated with ZnO, except RuO_2 and 10 wt.% ZnO where acidity is not significantly increased because of poor dispersion of metal oxides.

SEM-EDX results show that the dispersion of RuO_2 on MgO surface is worse than of ZnO. This is presumably due to non-polar solvent of ruthenium precursor solution, which leads to the agglomeration of ruthenium oxide on polar MgO surface. Accordingly, ethanol conversion activity of RuO_2/MgO is lower than of ZnO/MgO. The lower the percentage of ZnO loading, the better the dispersion of ZnO on MgO surface, and subsequently higher ethanol conversion.

H_2-transfer is an important step in Guerbet reaction to provide acetaldehyde intermediate and high yield of higher alcohols. MPV reaction of isopropanol-propionaldehyde shows that MgO has H_2-transfer activity, observed from yield of acetone and n-propanol. Moreover, MgO does not provide propylene, dehydration product of isopropanol. On the other side, calcined layered double hydroxide (cLDH) also has H_2-transfer activity but generates high yield of undesired product, propylene, presumably due to the Brønsted acid site presented on the surface.

In conversion of ethanol to higher alcohols, MgO has high activity in dehydrogenation due to Lewis acid property of Mg^{2+} and aldol condensation due to basic property of $Mg\text{-}O^{2-}$. However, MgO does not completely hydrogenate crotonaldehyde to butanol because of low hydrogen on MgO surface.

cLDH shows higher activity for higher alcohols production, as compared to MgO. Nevertheless, higher yield of undesired products, ethylene and diethyl ether, are obtained over cLDH.

Incorporated RuO_2/MgO provided higher ethanol conversion, as compared with MgO. This is because of generation of stronger Lewis acid sites, subsequently increases

H_2-transfer activity in Guerbet reaction, as observed by yield of higher alcohols. However, high yield of undesired product, diethyl ether was obtained because of agglomeration of RuO_2 on MgO surface.

ZnO/MgO shows a remarkably higher ethanol conversion activity, as compared to RuO_2/MgO and the parent MgO. It can promote activity of H_2-transfer and aldol condensation. This is because of stronger Lewis acidity created by incorporated ZnO. Furthermore, ZnO/MgO also facilitate the production for large carbonyl molecules (C8 and C10).

Increasing loading of ZnO (3 wt.% ZnO/MgO, 5 wt.% ZnO/MgO, and 10 wt.% ZnO/MgO), significantly increases the conversion of ethanol. This is because of adding zinc oxide increase amount of acid and basic site that would promote activity for H_2-transfer and aldol condensation, respectively. The higher percent loading of ZnO on MgO (5 wt.% and 10 wt.%) shows the higher activity for aldol condensation, as observed by high yield of large carbonyl molecules (C8 and C10). Nonetheless, these molecules are not hydrogenated to alcohols. Besides, it is also seen that dehydration of ethanol to diethyl ether is significantly increased, with an increase in percentage of ZnO loading. H_2-transfer may be inhibited by the excessive acid sites and the poor dispersion of zinc oxide on MgO surface. Thus, it is important to balance the number of acid and basic sites on catalysts surface, to provide the appropriate acid-base pair sites.

The study on effect of contact time can determine reaction pathway for ethanol conversion over ZnO/MgO catalyst. The higher alcohols occur via Guerbet reaction and diethyl ether occurs by dehydration of ethanol, as a parallel reaction.

5.2 Suggestions for future studies

5.2.1. Preparation of highly dispersed metal oxides on MgO catalysts by SEA (strong electrostatic adsorption) technique, to obtain appropriate acid-base pair sites.

5.2.2. The investigation of other metal oxides incorporated MgO should be attended, in order to improve the yield of higher alcohols.

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APPENDICES

APPENDIX A

CALCULATION

Contact time, W/F

Calculation of catalytic parameter

$$W/F = \frac{\text{Weight of catalyst (g)}}{\text{Molar feed rate (mol/h)}}$$

In the reaction using 0.7 mol/h of ethanol in feed and using 0.3 grams of catalyst, the W/F is calculated as follow:

$$W/F = \frac{[\ 0.28\ \text{g cat.}\ ]\,[\ 46\ \text{gEtOH/mol}\ ]}{[\ 1\ \text{mL/h}\ ]\,[\ 0.789\ \text{gEtOH/mL}\ ]}$$

$$= 16.3245\ \text{g.h/mol}$$

In similar manner; W/F of catalysts with different catalyst weight and different feed rate are calculated.

Calculation of % yield of products from gas chromatography

Table A1 The summation of the peak area of products.

Product	Peak area
Acetaldehyde	205.8
Diethyl ether	220.2
Butanal	189.5
Crotonaldehyde	427.6
Ethanol (Feed)	14675.5
Total	15718.6

*Information of ethanol conversion over MgO, contact time = 16 g.h/mol, time on stream = 60 minutes, flow rate of carrier gas: N_2 at 160 mL/min

In normalization method, the areas of all eluted peak were computed areas for differences in the detector response to different compound types. The concentration of the analyzed was found from the ratio of its area to the total area of all peaks.

Calculate the percent yield of each component in sample as follows:

$$\%\text{Yield of each product} = \frac{\text{Peak area of A} \times 100}{\text{Total area}}$$

Where A is each product.

For example;

$$\%\text{Yield of Acetaldehyde} = \frac{205.8 \times 100}{15718.6}$$

$$= 1.3$$

The percent yield of each product obtained from above calculation is shown in **Table A2**.

Table A2 Yield of product derived from normalization method.

Product	Yield (%)
Acetaldehyde	1.3
Diethyl ether	1.4
Butanal	1.2
Crotonaldehyde	2.7
Ethanol (Feed)	93.4
Total	100

Conversion

%Conversion can be calculated from the following equation:

$$\%\text{Conversion} = \frac{(\text{Total area} - \text{Area of feed}) \times 100}{\text{Total area}}$$

For example;

$$\%\text{Conversion} = \frac{(15718.6 - 14675.5) \times 100}{15718.6}$$

$$= 6.6$$

Selectivity

%Selectivity can be obtained from the following equation:

$$\%\text{Selectivity of each product} = \frac{\%\text{Yield of each product} \times 100}{\%\text{Conversion}}$$

For example;

$$\%\text{Selectivity of Acetaldehyde} = \frac{1.3 \times 100}{6.6}$$

$$= 19.7$$

APPENDIX B

GAS CHROMATOGRAM

Analysis of gas product from gas chromatography

Prior to analysis, the structure of each products in the sample is identified the by GC-MS (gas chromatography with mass spectrometer detector). Then, the quantitative analysis of each product was carried out by GC-FID (gas chromatography with flame ionization detector) with the condition expressed in **Table B1.**

Table B1 The GC condition for quantitative analysis

Column	CARBOWAX, 30 m x 0.32 mm x 0.25 μm
Temperature program	35°C (2 min hold) to 200°C at 15°C/min
Carrier gas	Nitrogen at 160 mL/min
Injection	200°C
Detector	FID

The chromatogram of gas products were identified using reference standard for comparison in **Table B2**.

Table B2 Chromatogram data of standard product distribution and feed

Feed and Products	Retention time (min)
Propylene	2.775
Ethylene	2.778
Acetaldehyde	2.788
Diethyl ether	2.908
Propanal	3.037
Acetone	3.114
Diethyl acetal	3.266
Butanal	3.389
Isopropanol	3.613
Ethanol	3.681
Pentanone	3.792
n-propanol	4.398
Crotonaldehyde	4.270
2-Heptanol	4.668
Butanol	5.429
2-Ethylhexanal	5.682
3-Hexane-2-one	6.184
2-Buten-1-ol	6.251
2-Methylpentanol	7.158
C9 aromatic alcohol	13.272/15.833
C8+ aromatic carbonyls	13.407/13.911/14.511

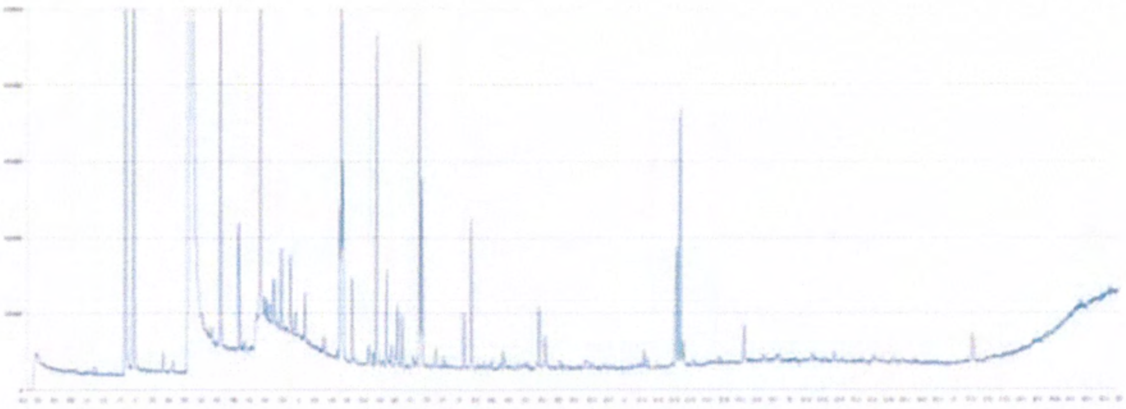


Figure B1 Chromatogram of product over MgO at contact time of isopropanol: 20 g.h/mol and, contact time of propionaldehyde: 22 g.h/mol at 380°C

APPENDIX C

CATALYTIC ACTIVITY DATA

1. MPV reaction

1.1 MPV reaction using 1:1 Isopropanol: Propionaldehyde feed ratio

1.1.1 Over MgO catalyst

Table C1 MPV (1:1) conversion and yield of products over MgO

Time on stream (min)	**60**	**120**	**180**	**240**	**300**	**360**
Conversion (%)						
Isopropanol	26	22	20	21	19	19
Propionaldehyde	26	0	0	0	0	0
Yield of product (%)						
Acetone	8.4	0.0	0.0	0.0	0.0	0.0
n-Propanol	6.9	0.6	0.0	0.0	0.0	0.0
C6 alcohols	3.0	0.0	0.0	0.0	0.0	0.0
C5 carbonyls	10.3	8.7	8.9	8.8	8.9	8.7
C6 carbonyls	1.0	0.0	0.0	0.0	0.0	0.0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time of isopropanol: 20 g.h/mol, contact time of propionaldehyde: 22 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

1.2 MPV reaction using 2:1 Isopropanol: Propionaldehyde feed ratio

1.2.1 Over MgO catalyst

Table C2 MPV (2:1) conversion and yield of products over MgO

Time on stream (min)	**30**	**60**	**90**	**120**	**150**	**180**
Conversion (%)						
Isopropanol	38.7	37.9	39.4	29.6	29.1	30.9
Propionaldehyde	79.4	63.8	54.5	62.4	58.8	53.7
Yield of product (%)						
Acetone	22.5	20.3	19.4	14.6	16.9	16.7
n-Propanol	24.9	22.0	20.8	18.8	17.7	17.4
C6 alcohols	0.7	0.0	0.0	0.0	0.0	0.0
C5 carbonyls	4.2	4.3	4.2	4.2	4.4	4.4

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time of isopropanol: 20 g.h/mol, contact time of propionaldehyde: 22 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

1.2.2 Over cLDH catalyst

Table C3 MPV (2:1) conversion and yield of products over cLDH

Time on stream (min)	**60**	**120**	**180**	**240**	**300**	**360**
Conversion (%)						
Isopropanol	60.5	37.9	36.9	32.7	33.3	22.4
Propionaldehyde	32.1	50.6	62.1	47.3	53.0	49.1
Yield of product (%)						
Propylene	12.6	17.5	15.7	14.4	13.3	15.5
Acetone	3.7	6.8	7.9	6.4	8.0	6.2
n-Propanol	10.6	16.7	17.2	15.6	17.5	16.2
C7 alcohols	0.5	0.7	0.7	0.5	0.7	0.5
C9 aromatic alcohol	34.1	0.0	0.0	0.0	0.0	0.0
C5 carbonyls	2.2	0.0	0.0	0.0	0.0	0.0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time of isopropanol: 20 g.h/mol, contact time of propionaldehyde: 22 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

3. Conversion of ethanol to higher alcohols

3.1 Ethanol conversion over MgO catalyst

Table C4 Ethanol conversion and yield of products over MgO

Time on stream (min)	30	60	90	120	150	180
Conversion (%)	6.7	6.6	6.6	6.4	6.4	6.5
Yield of product (%)						
Acetaldehyde	1.2	1.3	1.3	1.2	1.2	1.2
Diethyl ether	1.5	1.4	1.3	1.2	1.2	1.3
Crotonaldehyde	2.7	2.7	2.7	2.6	2.7	2.7
Butanal	1.3	1.2	1.3	1.3	1.4	1.3

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

3.2 Ethanol conversion over cLDH catalyst

Table C5 Ethanol conversion and yield of products over cLDH

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	20.7	21.5	19.8	20.2	19.5	18.8
Yield of product (%)						
Ethylene	4.9	5.1	4.7	5.2	4.7	4.4
Acetaldehyde	4.8	4.8	4.5	4.2	4.4	4.1
Diethyl ether	2.2	2.3	2.1	2.2	2.1	2.1
Acetone	0.7	0.7	0.7	0.7	0.7	0.7
Crotonaldehyde	2.7	2.8	2.8	2.7	2.8	2.9
Butanal	0.9	1.0	0.9	1.0	0.9	1.0
Butanol	4.4	4.8	4.1	4.1	4.0	3.7

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min

3.3 Ethanol conversion over 5 wt.% RuO_2/MgO catalyst

Table C6 Ethanol conversion and yield of products over RuO_2/MgO

Time on stream (min)	**60**	**120**	**180**	**240**	**300**	**360**
Conversion (%)	20.1	18.6	15.6	16.9	15.4	14.8
Yield of product (%)						
Acetaldehyde	1.5	1.2	0.8	0.9	0.7	0.7
Diethyl ether	8.2	7.8	7.1	7.6	7.0	6.7
Acetone	1.9	1.8	1.8	1.7	1.7	1.6
Crotonaldehyde	2.3	2.3	2.1	2.4	2.2	2.2
Butanal	2.5	2.5	2.0	2.4	2.1	2.2
C8 aldehydes	0.8	0.7	0.0	0.0	0.0	0.0
C4 alcohols	2.9	2.4	1.8	1.9	1.6	1.4

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

3.4 Ethanol conversion over 3 wt.% ZnO/MgO catalyst

Table C9 Ethanol conversion and yield of products over 3% ZnO/MgO

Time on stream (min)	**30**	**60**	**90**	**120**	**150**	**180**
Conversion (%)	13.9	15.5	13.9	14.7	13.5	13.4
Yield of product (%)						
Acetaldehyde	0.9	1.1	0.8	1.0	0.9	0.9
Diethyl ether	3.0	3.5	3.0	3.3	3.1	3.1
Acetone	1.2	1.2	1.1	1.2	1.2	1.1
Diethyl acetal	0.3	0.3	0.2	0.3	0.2	0.2
Butanal	1.6	2.0	1.6	1.8	1.6	1.6
Crotonaldehyde	2.7	2.9	2.7	2.9	2.7	2.8
C4 Alcohols	3.7	3.9	3.6	3.8	3.3	3.2
C8 Aldehydes	0.5	0.6	0.7	0.4	0.4	0.5

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 *carrier gas: 160 mL/min)*

3.5 Ethanol conversion over 5 wt.% ZnO/MgO catalyst

Table C7 Ethanol conversion and yield of products over 5% ZnO/MgO

Time on stream (min)	**30**	**60**	**90**	**120**	**150**	**180**
Conversion (%)	25.6	20.5	21.3	20.2	20.6	20.7
Yield of product (%)						
Acetaldehyde	2.4	1.4	1.4	1.5	1.4	1.6
Diethyl ether	0.4	6.8	7.0	6.9	7.0	7.0
Acetone	2.2	1.7	1.7	1.7	1.7	1.7
Diethyl acetal	1.0	0.5	0.5	0.5	0.5	0.5
Crotonaldehyde	3.2	2.8	2.8	2.8	2.8	2.8
Butanal	2.8	2.5	2.6	2.5	2.6	2.6
C8 Aldehydes	1.0	0.7	0.7	0.6	0.6	0.6
C4 Alcohols	6.5	3.4	4.0	3.2	3.2	3.1
C8+ aromatic carbonyls	6.0	0.8	0.8	0.7	0.8	0.8

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

3.6 Ethanol conversion over 10 wt.% ZnO/MgO catalysts

Table C10 Ethanol conversion and yield of products over 10% ZnO/MgO

Time on stream (min)	30	60	90	120	150	180
Conversion (%)	23.5	20.5	22.3	20.5	19.1	20.1
Yield of product (%)						
Acetaldehyde	1.2	1.5	1.5	1.4	1.2	1.1
Diethyl ether	4.7	4.8	4.7	4.6	5.0	4.8
Acetone	1.5	1.5	1.4	1.2	2.4	1.4
Diethyl acetal	0.4	0.4	0.4	0.4	0.2	0.3
Crotonaldehyde	2.8	2.2	2.8	2.0	4.0	2.7
Butanal	2.3	2.2	2.5	2.3	2.4	2.1
C4 Alcohols	5.3	4.5	4.3	4.1	2.6	3.7
C8 Aldehydes	0.9	0.8	0.8	0.7	0.7	1.0
C8+ aromatic carbonyls	4.5	2.7	3.9	3.8	0.6	3.0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 16 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

4. Conversion of ethanol to higher alcohols over 3 wt.% ZnO/MgO catalysts

4.1 Effect of contact time over 3 wt.% ZnO/MgO catalysts

Table C11 Ethanol conversion and yield of products at contact time 10 g.h/mol

Time on stream (min)	**60**	**120**	**180**	**240**	**300**	**360**
Conversion (%)	11.1	10.7	9.5	9.9	9.3	9.9
Yield of product (%)						
Acetaldehyde	0.6	0.6	0.5	0.7	0.7	0.6
Diethyl ether	2.6	2.5	2.5	2.8	2.8	2.6
Acetone	0.8	0.7	0.7	0.7	0.7	0.7
Crotonaldehyde	3.8	4.0	3.6	2.8	2.7	3.6
C4 Alcohols	1.6	1.3	0.8	1.2	0.9	0.8

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 10 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

Table C12 Ethanol conversion and yield of products at contact time 20 g.h/mol

Time on stream (min)	**30**	**60**	**90**	**120**	**150**	**180**
Conversion (%)	2.7	19.8	20.8	18.4	16.7	18.7
Yield of product (%)						
Acetaldehyde	1.5	0.9	1.4	1.1	1.3	1.2
Diethyl ether	4.2	4.2	4.0	4.1	4.2	4.0
Acetone	1.3	1.3	1.2	1.3	1.3	1.2
Crotonaldehyde	2.9	3.2	2.9	3.0	3.0	3.0
Butanal	1.8	2.0	1.9	1.7	1.8	1.8
C4 Alcohols	3.8	3.5	3.2	3.1	3.1	2.9
C8+ aromatic carbonyls	5.2	4.7	6.2	4.1	2.0	4.6

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 20 g.h/mol, flow rate of N_2 carrier gas: 160 mL/min)

APEENDIX D

CATALYST CHARACTERIZATION

X-ray diffraction pattern of catalysts

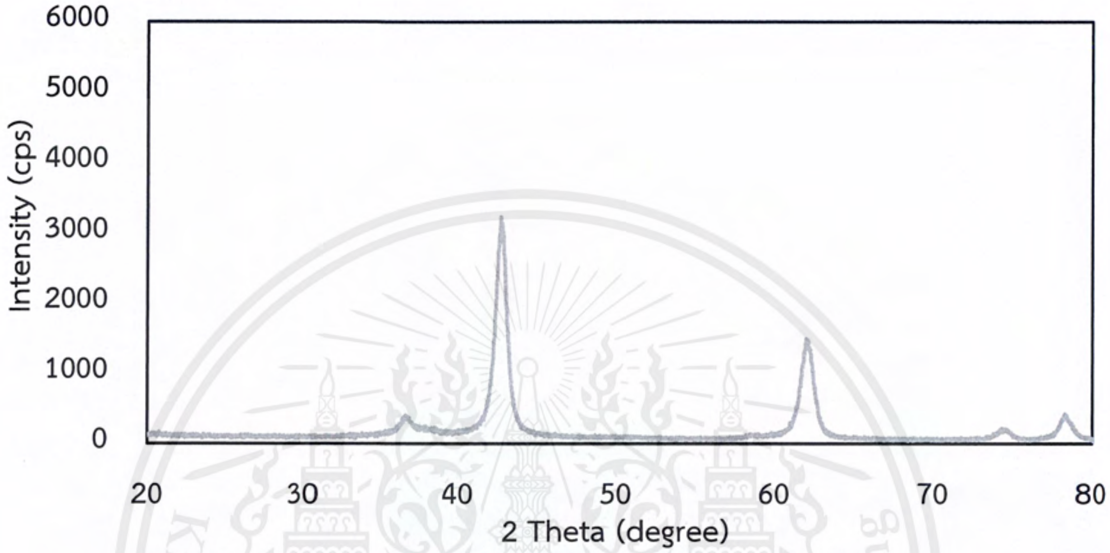


Figure D1 X-ray diffraction pattern of MgO

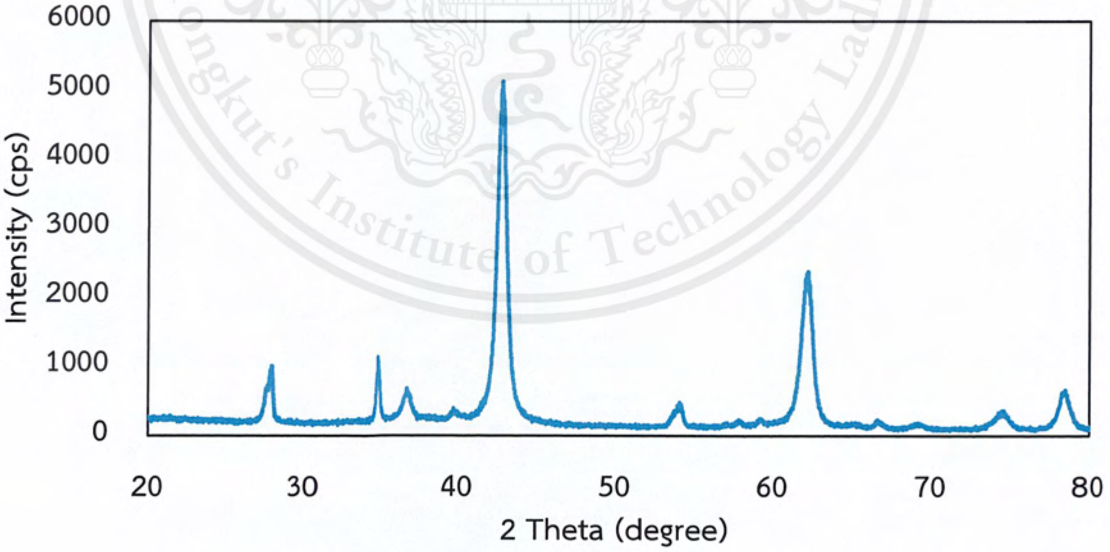


Figure D2 X-ray diffraction pattern of 5 wt.% RuO_2/MgO

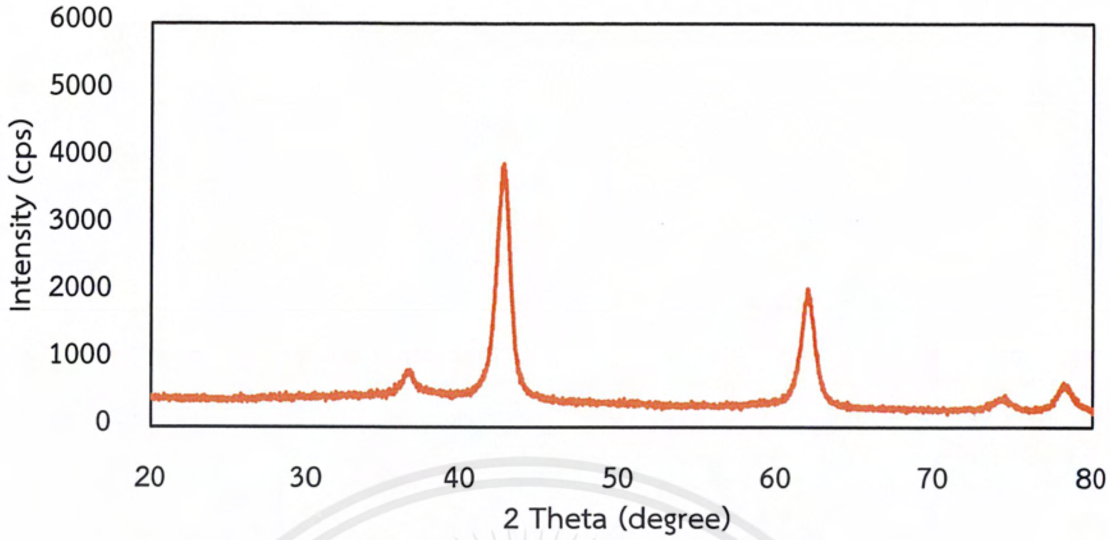


Figure D3 X-ray diffraction pattern of 5 wt.% ZnO/MgO

Apsorption-desorption isotherm

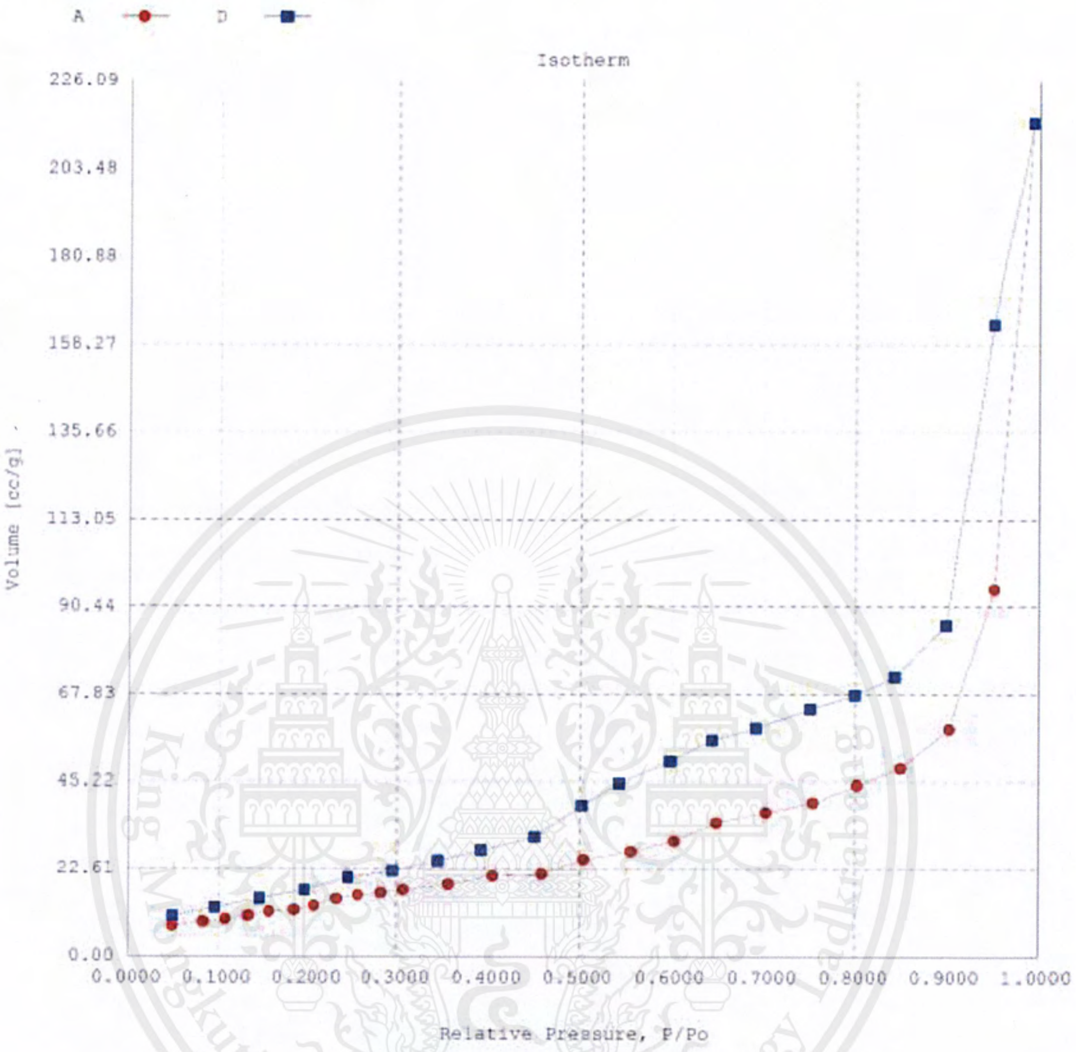


Figure D4 N_2 adsorption-desorption isotherm of MgO comerrcial.

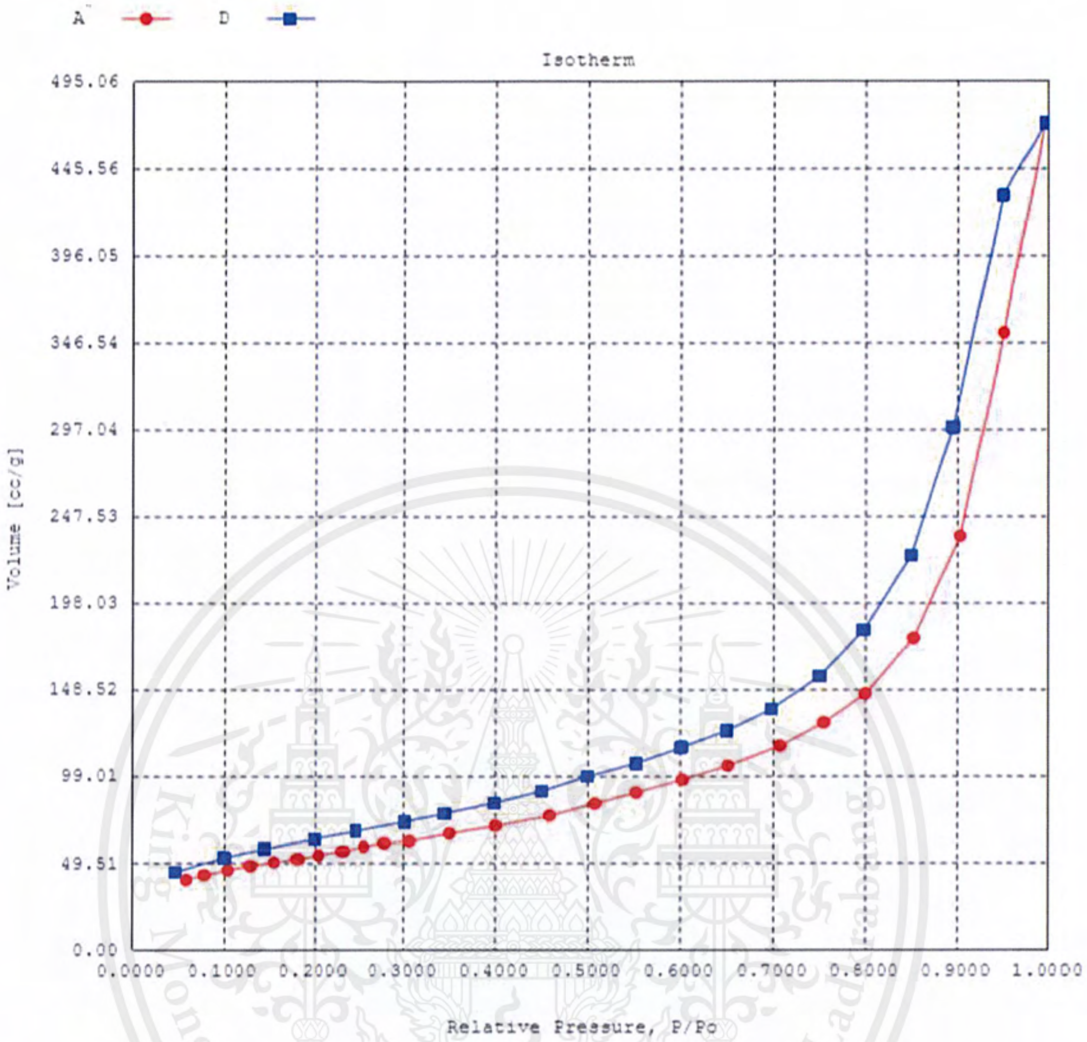
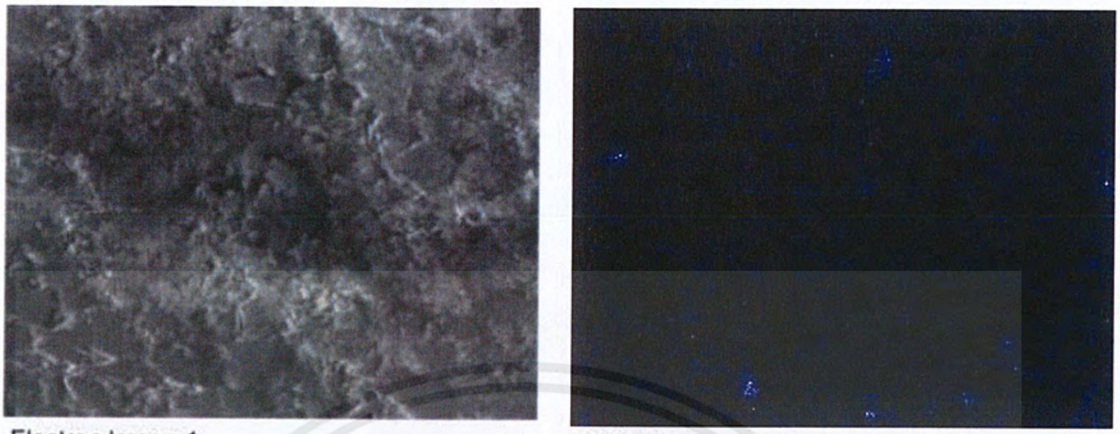


Figure D5 Adsorption-desorption isotherm of MgO synthesized by sol-gel method

Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX)



Electron Image 1

Ru La1

Figure D5 5 wt.% RuO/MgO

Electron Image 1

Zn Ka1

Figure D6 3 wt.% ZnO/MgO

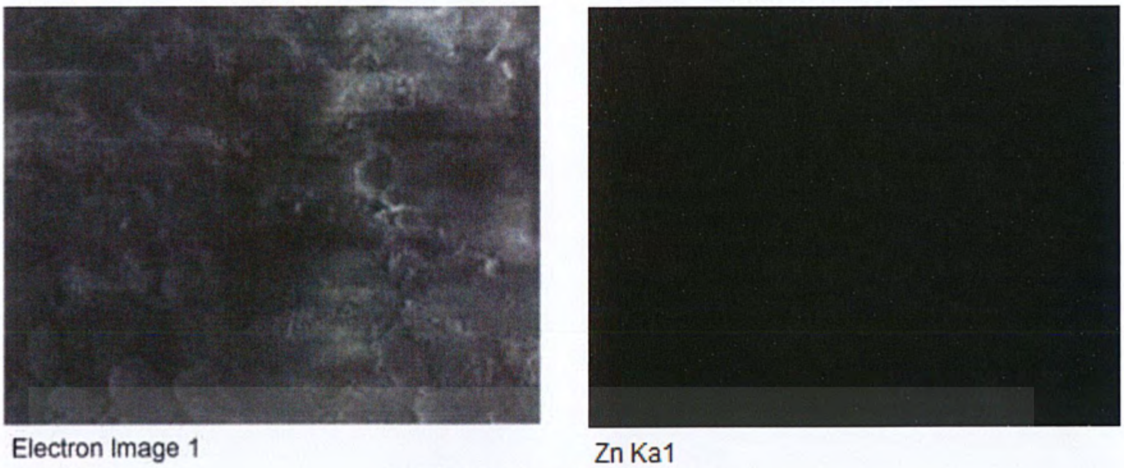
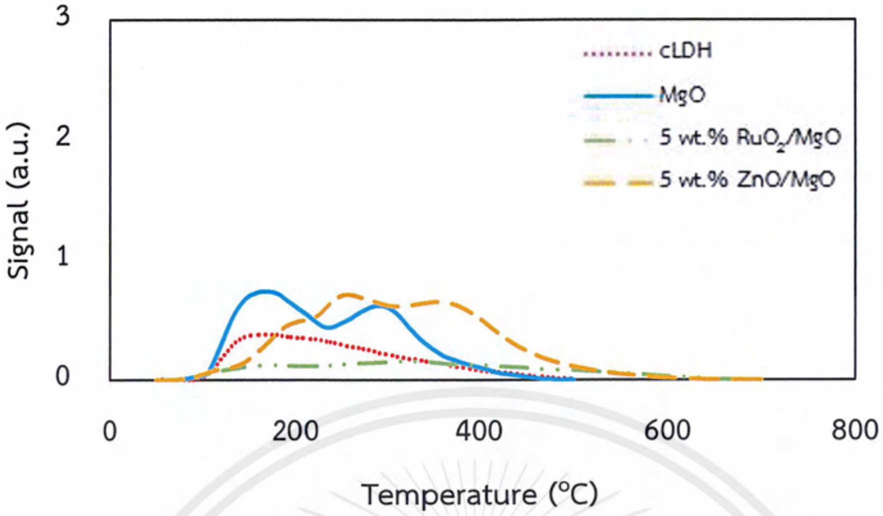


Figure D7 5 wt.% ZnO/MgO

Figure D8 10 wt.% ZnO/MgO

Temperature programed desorption



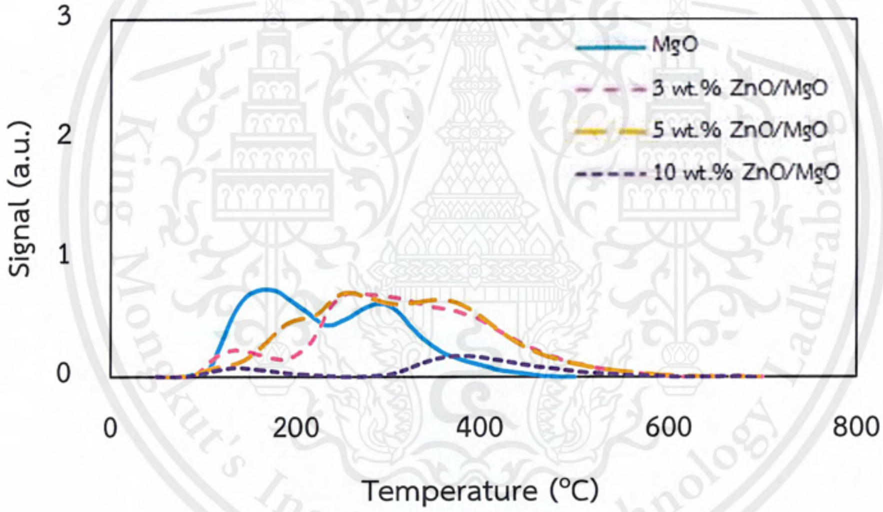


Figure D7 NH$_3$-temperature programmed desorption profile of catalysts

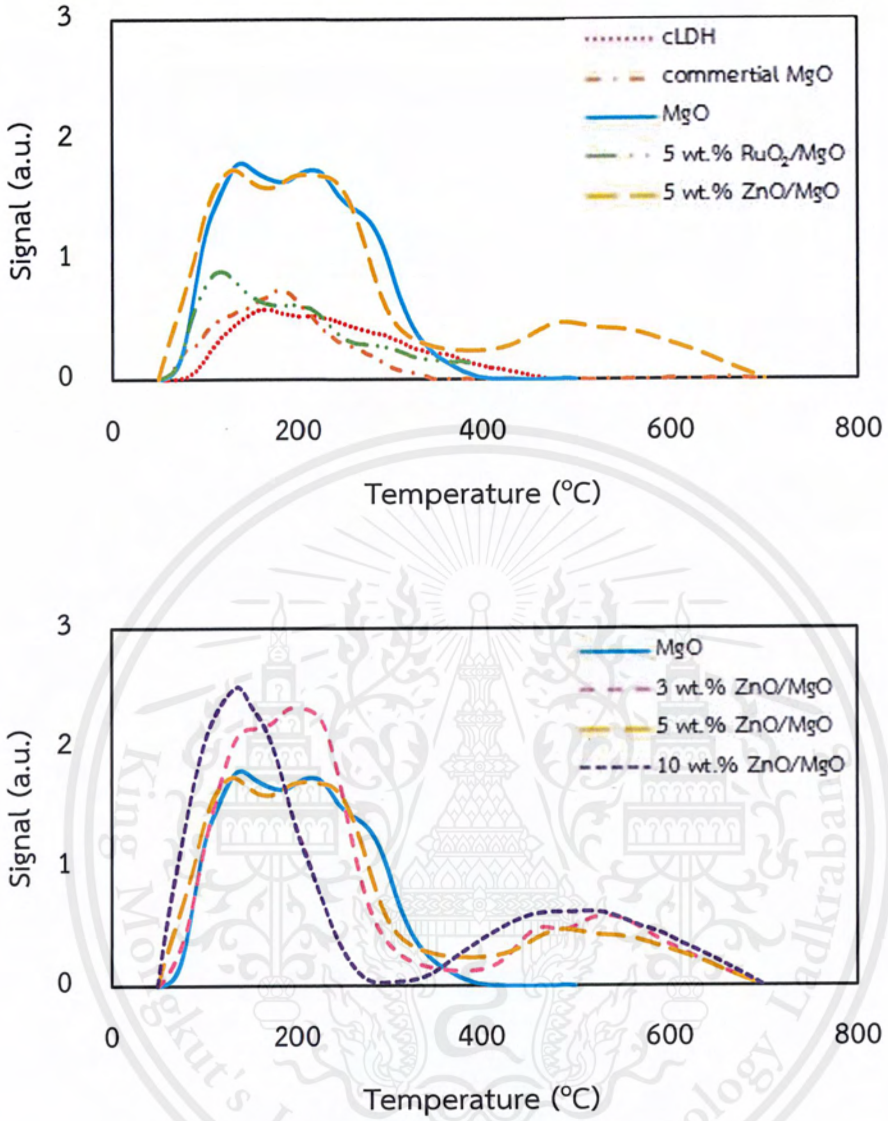


Figure D8 CO_2-temperature programmed desorption profile of catalysts