การผลิตแอลกอฮอล์โมเลกุลใหญ่จากเอทานอล โดยใช้ตัวเร่งปฏิกิริยาเลเยอร์ดับเบิลไฮดรอกไซด์

PRODUCTION OF HIGHER ALCOHOLS FROM ETHANOL USING LAYERED DOUBLE HYDROXIDES CATALYST

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ABSTRACT

In this special project, the conversion of ethanol to higher alcohols via Guerbet reaction (C4, C6 and C8 long chain alcohols) over basic catalysts such as MgO and catalysts with both acid and basic sites on the surface such as hydroxyapatite (HAp), and calcined layered double hydroxide (cLDH) were investigated. It was found that the cLDH catalyst provides higher activity to higher alcohol products, as compared to MgO and HAp. Modification of cLDH by washing with base solutions (KOH and $KMnO_4$) can readily neutralize the acid sites of cLDH as lower yield of ethylene, the dehydration product is obtained. However, the dehydrogenation products and higher alcohols were not enhanced, due to suppression of dehydrogenation and H_2 transfer sites by base washing. In addition, the metal oxides (La_2O_3, K_2O, ZnO, and Cs_2O) impregnated on cLDH were studied to improve the dehydrogenation activity. It was found that ZnO/cLDH gives higher activity, as compared to other metal oxides and the parent cLDH. It can promote dehydrogenation of ethanol to acetaldehyde, and also gives C8 aromatic compounds. Finally, the effect of reaction temperature on H_2 transfer over ZnO/cLDH was investigated. It was found that the yield of ethylene is increased with temperature, while the yield of higher alcohols is relatively high at low temperature (350°C). This is because at low temperature H_2 transfer can be promoted.

Keywords : aldol condensation, ethanol, guerbet reaction, layered double hydroxides , metal oxides

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Natsuda Toesier

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CONTENTS

Page

ABSTRACT I

ACKNOWEDGEMENT II

CONTENTS III

LIST OF TABLES VI

LIST OF SCHEMES VII

LIST OF FIGURES VIII

CHAPTER 1 INTRODUCTION 1

- 1.1 Motivation 1
- 1.2 Objectives 2
- 1.3 Scopes of study 2
- 1.4 Expected results 2

CHAPTER 2 THEORY AND LITURATURE REVIEWS 3

- 2.1 Alcohol 3
- 2.2 Ethanol 4
- 2.3 Higher alcohol 4
  - 2.1.1 Butanol 4
  - 2.1.2 Hexanol 5
  - 2.1.3 Octanol 5
  - 2.1.3 Benzyl alcohol 5
- 2.4 Aldehyde 6
  - 2.4.1 Acetaldehyde 6
  - 2.4.2 Butanal 6
  - 2.4.3 Hexanal 7
  - 2.4.4 Benzaldehyde 7
- 2.5 Guerbet reaction 7
- 2.6 Catalyst 8
  - 2.6.1 Magnesium oxide 9
  - 2.6.2 Hydroxyapatite 9
  - 2.6.3 Layered Double Hydroxides (LDH) 10

CONTENTS (CONTINUED)

2.7 Literature reviews ... 11

CHAPTER 3 EXPERIMENTAL DETAILS ... 14

3.1 Reagents ... 14

3.2 Apparatus ... 14

3.3 Experimental procedure ... 15

3.3.1 Catalyst preparation ... 15

3.3.1.1 Preparation of LDH, MgO, and HAp ... 15

3.3.1.2 Preparation of Metal Oxide loaded on LDH ... 16

3.3.2 Catalyst characterization ... 16

3.3.2.1 Structural analysis using X-ray diffraction ... 16

3.3.2.2 Quantitative elemental composition analysis by X-ray fluorescence ... 17

3.3.2.3 Determination of specific surface area by nitrogen adsorption ... 17

3.3.2.4 Determination of basicity of the catalyst by CO_2-temperature programmed desorption ... 18

3.3.2.5 Determination of acidity of the catalyst by NH_3-temperature programmed desorption ... 18

3.3.2.6 Determination of coke deposition on the catalysts by thermogravimetric analysis ... 18

3.3.2.7 Scanning electron microscope ... 18

3.3.3 Catalytic activity testing ... 19

3.3.4 Products analysis ... 20

CHAPTER 4 RESULTS AND DISCUSSION ... 21

4.1 Catalyst characterization ... 21

4.1.1 X-Ray Powder Diffraction ... 21

4.1.1.1 Hydroxyapatite (HAp) ... 21

4.1.1.2 Layered double hydroxides (LDH) ... 22

4.1.2 Surface area, acid, and basic characteristics of catalysts ... 22

4.1.3 Thermogravimetric Analysis (TGA) ... 23

CONTENTS (CONTINUED)

4.1.4 Scanning Electron Microscopy (SEM) 25
4.2 Study on the conversion of ethanol to higher alcohols 25
4.2.1 Effect of catalyst 25
4.2.2 Conversion of ethanol to higher alcohols over cLDH catalyst 27
4.2.3 Conversion of ethanol to higher alcohols over metal incorporated cLDH catalysts 32
4.2.3.1 The base modified cLDH 32
4.2.3.2 Influence of metal oxides impregnated cLDH 33
4.2.3.3 Effect of reaction temperature on activity of ZnO/cLDH catalyst 35
4.2.3.4 Effect of contact time for ZnO/cLDH catalyst 37
CHAPTER 5 CONCLUSIONS AND SUGGESTIONS 41
5.1 Conclusions 41
5.2 Suggestions for future studies 42
REFERENCE 43
APPENDIX A 47
APPENDIX B 50
APPENDIX C 53
APPENDIX D 69

LIST OF TABLES

Table Page
4.1 Surface area, acid, and basic characteristics of catalysts 23
4.2 Conversion of ethanol and yield towards each product over different types of catalyst 26
4.3 Ethanol conversion and selectivity of products over base modified cLDH catalysts 33
4.4 Ethanol conversion and selectivity of products over metal oxide incorporated cLDH catalysts 34

LIST OF SCHEMES

Schemes Page

4.1 The C4 alcohol formation mechanism 29

4.2 The C6 alcohols formation mechanism 29

4.3 The C8 alcohols formation mechanism 30

4.4 The ethylene and diethyl ether formation mechanism 30

4.5 The overall reaction pathway over cLDH catalyst 32

4.6 The C8 aromatic compounds formation mechanism 35

4.7 The overall reaction pathway over ZnO/cLDH catalyst 40

LIST OF FIGURES

Figure Page
1.1 Guerbet reaction 1
2.1 The structure of alcohols 3
2.2 Acetaldehyde formations from ethanol 8
2.3 Aldol condensation 8
2.4 Dehydration of the aldol, and hydrogenation of crotonaldehyde 8
2.5 The structure of magnesium oxide 9
2.6 Unit cell of hydroxyapatite (HAp) crystal 10
2.7 The structure of Layered Double Hydroxides 11
3.1 Catalytic testing rig 20
4.1 XRD patterns of hydroxyapatite (HAp) 21
4.2 XRD patterns of non-calcined LDH and calcined LDH 22
4.3 TGA analysis of non calcined LDH and calcined LDH at 450°C for 8 h 24
4.4 SEM images of non-calcined LDH and calcined LDH at 450°C for 8 h 25
4.5 Ethanol conversion over MgO 26
4.6 Selectivity of ethanol over various support catalysts 27
4.7 Converison of ethanol and yields of products at various contact times 28
4.8 Selectivity of products at various contact times 31
4.9 Conversion of ethanol and yield of products at various reaction temperatures 36
4.10 Selectivity of ethanol at various reaction temperatures 37
4.11 Conversion of ethanol and yield of products at various contact times over ZnO/cLDH 38
4.12 Conversion versus products selectivity over ZnO/cLDH 39

CHAPTER 1
INTRODUCTION

1.1 Motivation

In present, the investigation of alternative renewable energy resources is increasing because of reduction of the remaining petroleum resources. One of the most popular renewable feedstock is ethanol, which is obtained from agricultural products or by-products of petrochemical process. The catalytic transformation of ethanol to the more valuable products such as higher alcohols is interesting. These larger alcohol molecules are useful for the manufacturing of polymer, surfactant, and solvent.

Basic catalysts such as MgO or catalysts with both acid and basic sites on the surface can be used for the conversion of ethanol to higher alcohols. Hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$) is one of the catalyst remarked by many researchers. It presents high selectivity for the catalytic reaction of ethanol to higher alcohols. Another interesting one is Mg-Al oxides, which is a group of Layered Double Hydroxide (LDH) materials. The layered double hydroxide is an anionic clay in which divalent cations within brucite-like layers are replaced by trivalent cations. The resulting positive charge is compensated by hydrated anions located in the interlayer space between two brucite sheets [1]. It has received increasing attention in the search for environmentally benign catalysts due to its high surface area, acid–base properties, phase purity, and structural stability [2]. It also shows high activity in the production of higher alcohols from ethanol via Guerbet reaction.

In Guerbet reaction, ethanol will be converted into higher alcohol over the catalyst surface as shown in Figure 1.1. First, ethanol is adsorbed on the catalyst surface and dehydrogenated to acetaldehyde. Then, an aldol condensation of acetaldehydes to larger unsaturated aldehyde molecule. Finally, the hydrogen transfer to that unsaturated aldehyde to higher alcohol.

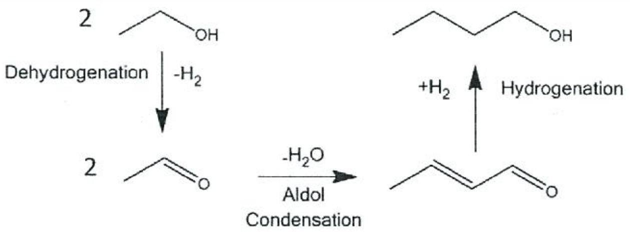


Figure1.1 Guerbet reaction [3]

In this special project, MgO, a basic catalyst, and acid-basic catalysts like hydroxyapatite and LDH are interested to be used as a catalyst for ethanol conversion. Previous study shows that metal incorporated hydroxyapatite can improve ethanol conversion activity of the catalyst due to the strong hydrogen transfer function [4]. Hence, the effect of incorporated metal oxide on catalytic activity was investigated in this study. In addition, the effect contact time and reaction temperature in fixed-bed reactor were also the scope of this research.

1.2 Objectives

1) To obtain higher alcohols from the ethanol over MgO, hydroxyapatite, Layered double hydroxide (LDH), and metal oxide supported on LDH catalysts via Guerbet reaction.

2) To understand the reaction pathway of the ethanol conversion over LDH catalysts.

3) To understand the effect of catalyst structure, and type of metal oxide on the conversion of ethanol to higher alcohols.

1.3 Scopes of study

1) Study the effect of catalyst structure, and type of metal oxide on the conversion of ethanol.

2) Study the effect of contact time, and reaction temperature in fixed-bed reactor.

3) Characterize the catalysts by X-ray Diffraction (XRD), BET surface area analysis, Thermogravimetric Analysis (TGA) and Temperature-Programmed Desorption (TPD).

4) Analyze liquid products by online Gas Chromatography with Flame Ionization Detector (GC-FID).

1.4 Expected results

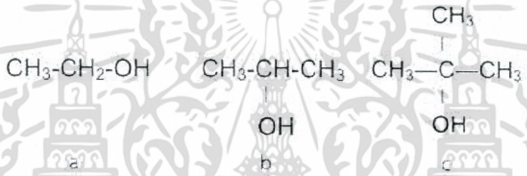
We expected that this study could improve the catalyst with high activity, selectivity, and stability for the conversion of ethanol to higher alcohols. The knowledge from this study will be an alternative way to convert ethanol to higher value products in chemical industry.

CHAPTER 2

THEORY AND LITERITURE REVIEWS

2.1 Alcohol

Alcohols are hydroxyl (-OH) derivatives of hydrocarbons formed by replacing a hydrogen with the hydroxyl group, and general form is R-OH where R represents the hydrocarbon. There are three classes of alcohols: primary, secondary, and tertiary. A primary alcohol is an alcohol which has the hydroxyl group connected to a primary carbon atom. A secondary alcohol, the hydroxyl group connected to a secondary carbon atom. A tertiary alcohol the hydroxyl group connected to a tertiary carbon atom. Alcohols that contain two or more hydroxyl groups are referred to as polyhydroxy alcohols [5].



$CH_3\text{-}CH_2\text{-}OH \quad CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_3 \quad CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}\text{—}CH_3$

Figure 2.1 The structure of alcohols: primary alcohol (a), secondary alcohol (b), and tertiary alcohol (c) [5]

The low molecular weight alcohols are volatile liquids, and the high molecular weight alcohols (more than 13 carbons) are solids. The first three alcohols (C1 to C3) are completely miscible (mix in any proportion) with water. The water solubility decreases as the number of carbons increases, and the large molecular weight alcohols are insoluble in water [5].

Alcohol has a long history of several uses worldwide. It is found in alcoholic beverages sold to adults, as fuel, and also has many scientific, medical, and industrial uses. Some alcohols, mainly ethanol and methanol, can be used as an alcohol fuel. Alcohols can use for solvent in industry because hydroxyl groups (-OH) are polar, therefore hydrophilic (water loving) but their carbon chain portion is non-polar, which make them hydrophobic, and low toxicity compared [6].

Several reactions of alcohols involve only the oxygen-hydrogen bond and leave the carbon-oxygen bond interact [7]. Alcohol can undergo oxidation to give aldehydes and carboxylic acid, or they are dehydrated to alkenes. Reduction of alcohols can give ketones [8]. Alcohols can undergo dehydration to give ethers, and they can combine with many kinds of acids to form esters [1]. Moreover, alcohols can undergo Guerbet Reaction give higher alcohol.

2.2 Ethanol

Ethanol (ethyl alcohol, grain alcohol) is an alcohol, a group of chemical compounds whose molecules contain a hydroxyl group, –OH, bonded to a carbon atom. It is a clear, colorless liquid with a characteristic agreeable odor [9].

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 [9].

Ethanol has been produced since prehistoric times, mostly through the fermentation of fruit juices. The fermented juice could be stored in a sealed container, and this primitive wine remained safe to drink throughout the winter. Many different sources can provide the sugars and starches that are broken down to simpler compounds during fermentation [1].

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 [9].

2.3 Higher alcohol

2.3.1 Butanol

Butanol (butyl alcohol) refers to a four-carbons alcohol with a formula of C_4H_9OH. There are four possible isomeric structures for butanol, from a straight-chain primary alcohol to a branched-chain tertiary alcohol [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 manufactured by the catalyzed hydrogenation of butyraldehyde in enclosed systems, followed by distillation. They can be used predominately as an industrial intermediate. For example, it is used to make butyl acetate and other butyl esters; butyl ethers, such as ethylene glycol monobutyl ether, di- and triethylene glycol monobutyl ether, and the corresponding butyl ether acetates. It is used to manufacture dibutyl phthalate, pharmaceuticals, polymers, pyroxylin plastics, butyl xanthate and other butyl compounds.

In addition, butanol is used as a diluent/reactant in the manufacture of urea/formaldehyde and melamine/formaldehyde resins. When used as an industrial intermediate, butanol is consumed by chemical conversion to the desired product [11].

2.3.2 Hexanol

1-Hexanol is an organic alcohol with a six carbons chain and a condensed structural formula of $CH_3(CH_2)_5OH$. It has colorless liquid and slightly soluble in water, but miscible with ether and ethanol. Two additional straight chain isomers of 1-hexanol exist, 2-hexanol and 3-hexanol, both of which differ by the location of the hydroxyl group. Many isomeric alcohols have the formula $C_6H_{13}OH$. 1-hexanol is believed to be a component of the odor of freshly mowed grass. It is used in the perfume industry [12].

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 [13].

2.3.4 Benzyl alcohols

Benzyl alcohol is an aromatic alcohol with the formula $C_6H_5CH_2OH$. It is a colorless liquid with a mild pleasant aromatic odor [14].

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 [13].

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 surfaces. 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 [14].

2.4 Aldehyde

Aldehydes result from the first oxidation of alcohols. Since aldehydes cannot form hydrogen bonds between themselves, they have lower boiling points than corresponding alcohols or acids. The lower-molecular-weight aldehydes (up to five carbons) are soluble in water. Aldehydes are neutral in pH and undergo both oxidation and reduction reactions. They are easily oxidized to acids and reduced to alcohols. Some aldehydes, such as vanillin and benzaldehyde, are frequently used in the pharmacy as flavoring agents [15].

2.4.1 Acetaldehyde

Acetaldehyde (ethanal) is an organic chemical compound with the formula CH_3CHO [16]. Acetaldehyde is a natural product from combustion and photo-oxidation of hydrocarbons commonly found in the atmosphere. It is an important industrial chemical, and may be released into the air or in wastewater during its production and use.

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.

Other uses of acetaldehyde include: in the silvering of mirrors; in leather tanning; as a denaturant for alcohol; in fuel mixtures; as a hardener for gelatin fibers; in glue and casein products; as a preservative for fish and fruit; in the paper industry; as a synthetic flavouring agent; and in the manufacture of cosmetics, aniline dyes, plastics and synthetic rubber [17].

2.4.2 Butanal

Butyraldehyde, also known as butanal, is an organic compound with the formula $CH_3(CH_2)_2CHO$. This compound is the aldehyde derivative of butane. It is a colourless flammable liquid with an acrid smell. [18] It is miscible with most organic solvents, biomarker for oxidative damage to lipids, proteins and DNA [19].

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 [18]

2.4.3 Hexanal

Hexanal or hexanaldehyde ($C_6H_{12}O$) is an alkyl aldehyde used in the flavor industry to produce fruity flavors. Its scent resembles freshly cut grass, like cis-3-hexenal [20].

Hexanal is oxidized to the corresponding caboxylic acid by aldehyde dehydrogenase mainly in the liver, but also in other tissues and cells. The acid can serve as a substrate for the Krebs cycle or is excreted as a salt. Alternatively, it can conjugate with glutathione or the sulfhydryl group of other proteins [21].

2.4.4 Benzaldehyde

Benzaldehyde (C_6H_5CHO) 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

Guerbet reaction of alcohols is the oldest and best understood material in the class of compounds first synthesized by Marcel Guerbet [24]. The reaction related to the dehydrogenation of alcohols, aldol condensation, and hydrogenation of alcohols.

The reaction proceeds by: (i) dehydrogenation of alcohol to aldehyde, (ii) aldol condensation after proton extraction, (iii) dehydration of the aldol product, and (iv) hydrogenation of the allylic aldehyde [24].

Many catalysts have been described in the literature as effective for the preparation of Guerbet alcohols including, nickel, lead salts (U.S. Patent 3,119,880), and oxides of copper, lead, zinc, chromium, molybdenum, tungsten, and manganese (U.S. Patent 3,558,716). Later U.S. patents have included palladium compounds (U.S. Patent 3,979,466) and silver compounds (U.S. Patent 3,864,407). There are advantages and disadvantages for each type of catalyst [24].

J. I. Di Cosimo, *et.al* [1] reported that Guerbet reactions of alcohol over Mg-Al mixed oxides, acid-strong base pair site. First, ethanol is adsorbed and dehydrogenated to ethoxy intermediate over acid-strong base pair site. Then, α-hydrogen in the ethoxy group is abstracted by another strong basic site, forming to acetaldehyde.

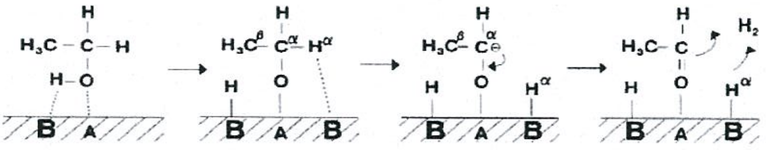


Figure 2.2 Acetaldehyde formations from ethanol [1]

Then, the α-hydrogen is abstracted by basic site, α-hydrogen loss electron to carbon atom. Carbanion intermediate reacts with neighboring acetaldehyde, aldol condensation.

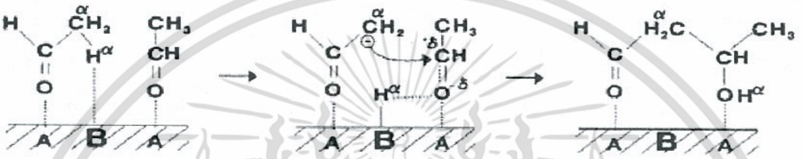


Figure 2.3 Aldol condensation [1]

After aldol condensation, the product of aldol condensation will be dehydrated to crotonaldehyde. Finally, crotonaldehyde will be hydrogenated to 1-butanol and released from surface.

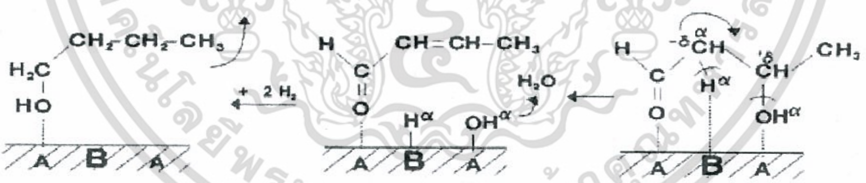


Figure 2.4 Dehydration of the aldol, and hydrogenation of crotonaldehyde [1]

2.6 Catalyst

Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst [25].

Almost of industrial chemical processes are catalytic, the importance and economic significance of catalysis is enormous. More than 80% of the present industrial processes established since 1980 in the chemical, petrochemical, and biochemical industries, and in the production of polymers and in environmental protection [26].

Acid-catalyzed reactions are among the industrially most important hydrocarbon conversions. Acid sites can be classified as Lewis acidic sites, such as coordinatively unsaturated cations, e.g., Al^{3+} on the surface of partially dehydroxylated alumina, and Brønsted acidic sites, which are typically surface OH groups, e.g., in H^{+} forms of zeolites. A typical solid base is MgO [26].

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.

The application of MgO is largely. It can be used in agricultural, chemical, construction, environmental, and other industrial applications [27].

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 [28].

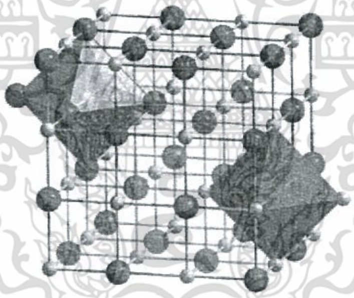


Figure 2.5 The structure of magnesium oxide [27]

2.6.2 Hydroxyapatite

Hydroxyapatite (HAp) can be found in teeth and bones of the human body. Bone is the structural component of our body and can be considered as a natural bio composite comprising of biopolymers (collagen and non-collagenous proteins) and minerals (HAp) [29].

The application of HAp materials is not limited as coating materials. It also use as a catalyst, they have the unusual property of containing both acid sites and basic sites in a single crystal lattice. The stoichiometric form of HAP is shown as $Ca_{10}(PO_4)_6(OH)_2$, and its molar ratio is 1.67. The cell structure of HAp is shown is Figure 2.5.

It is known that at a Ca/P ratio of 1.50, highly crystalline HAP acts as an acid catalyst, catalyzing chiefly ethylene synthesis from ethanol by dehydration; however, at a Ca/P ratio of 1.67, it acts as a basic catalyst, catalyzing chiefly acetaldehyde synthesis from ethanol by dehydrogenation [30].

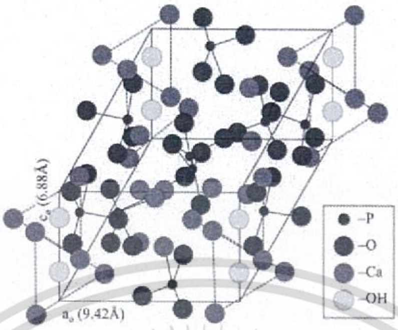


Figure 2.6 Unit cell of hydroxyapatite (HA) crystal. [31]

2.6.3 Layered Double Hydroxides (LDH)

Layered double hydroxides (LDH) are a broad class of inorganic lamellar compounds of basic character with high capacity for anion intercalation. The LDH are also widely known as hydrotalcite-like compounds due to their structural similarities to hydrotalcite, a mineral with the formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ [32].

The hydrotalcite structure results from the stacking of brucite-like layers $[Mg(OH)_2]$ containing a positive residual charge arising from the partial isomorphous substitution of Mg^{2+} cations by Al^{3+} cations. This positive excess charge is balanced by the carbonate anions, which reside in the interlamellar spaces [32].

They are represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$ $(A^{n-}_{x/n}).mH_2O$, where M^{2+} and M^{3+} can be any divalent and trivalent metal ions (whose ionic radius is not too different from that of Mg^{2+}), which can be accommodated in the octahedral holes in the brucite-like layers and x is the metal ratio $M^{3+}/(M^{2+}+M^{3+})$. The species A^{n-} in the interlamellar region can be any charge compensating anion (organic or inorganic) and m is the amount of water present in the same region [32]. The structure of LDH is shown is Figure 2.6.

It is known that LDH can collapse to Mg-Al mixed oxides. They have received increasing attention in the search for environmentally benign catalysts due to their high surface area, acid–base properties, and structural stability, as well as because they can be easily and cheaply synthesized [33], which can be used in Guerbet reaction for the synthesis higher alcohols.

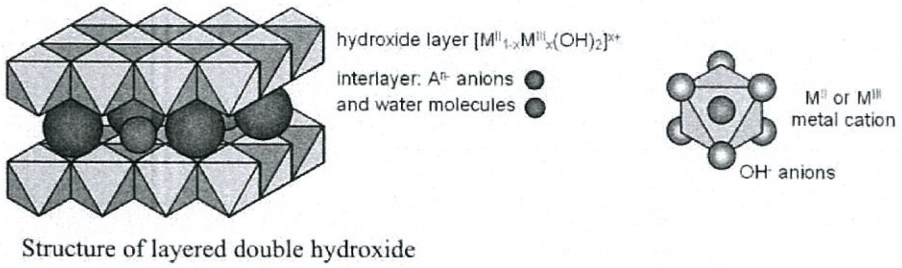


Figure 2.7 The structure of Layered Double Hydroxides [34]

2.7 Literature reviews

One of the most popular renewable feedstock is ethanol, which is obtained from agricultural products or by-products of petrochemical process. Ethanol can be converted to higher molecular weight alcohols, so-called Guerbet alcohols, to be used, for instance, in the production of high-added value solvents and surfactants [2]. Therefore, a conversion of ethanol to higher alcohols is an interesting reaction to be studied.

Many researchers have studied the ethanol conversion under various reaction conditions and over several catalysts. Metal oxides, metal phosphates, and supported transition metals, such as copper, are important components of heterogeneous catalysts for this reaction [35]. A.S. Ndou, et al. [36] studied the conversion of ethanol to 1-butanol over alkali earth metal oxides and modified MgO catalysts. Reaction of various intermediates (acetaldehyde, crotonaldehyde, crotylalcohol, butanal) and butanol over MgO, CaO, BaO, Al_2O_3, and modified Al_2O_3 supported with alkali metal, such as Na, K, Cs, and Mg was also studied. The results showed that the highest yield of butanol occur over basic MgO catalyst, while Al_2O_3 did not give butanol product. Moreover, the results showed that the modification of Al_2O_3 catalyst by alkaline metal impregnation can give butanol product. Thus, formation of butanol occurs on basic site. Moreover, they modified MgO with transition metal: Zn, Ce, Zr, Pb, and Sn. Modification can increase basic nature of catalyst, but did not increase yield of butanol because the basicity of MgO is increased by the addition of metal ions when the ionic radius was greater than that of Mg^{2+}.

J. I. Di Cosimo, et al. [1] investigated structure, surface, and catalytic properties of Mg-Al basic oxides. Mg-Al mixed oxides with Mg/Al molar ratios of 0.5–9.0 were obtained by thermal decomposition of precipitated hydrotalcite precursors. They studied the effect of incorporation of Al with different Mg/Al molar ratio on aldol condensation of acetaldehyde to 1-butanol. The Mg-Al mixed oxide with Mg/Al 0.47 gives the highest n-butanol product due to acid-based properties on the catalyst surface. They reported the initial adsorption of ethanol on Lewis acid site, and dehydrogenation to ethoxy intermediate, which require acid-strong based pair. In the case of MgO, the isolated O^{2-} ion on MgO surface would be unable to form ethoxide intermediates. Thus, the incorporation of small amounts of Al^{3+} cations to MgO drastically increased the acetaldehyde formation rate because of the generation of new surface Lewis acid–strong base pair sites.

M. León, et al. [33] studied the effect of partial and total substitution of aluminium by iron on the performance of different hydrotalcite-derived mixed oxides for the condensation of ethanol to valuable C4 products. The substitution of Al^{3+} by Fe^{3+} in the structure of the resulting mixed oxide leads to a slight decrease of the basic sites and a more marked decrease of the concentration of acid sites. Nevertheless, the Al^{3+} cation is completely replaced by Fe^{3+}, no acid site in the catalyst. Almost total abatement of the acid sites of the catalyst largely decrease the selectivity for ethanol dehydration, resulting in an increase of the formation of the dehydrogenation product (acetaldehyde), key reactant for condensation reactions.

T. Tsuchida, et.al [30] studied the effect of Ca/P molar ratios of hydroxyapatite on the conversion of ethanol to higher alcohols. This hydroxyapatite was prepared by controlling the pH of the solution during precipitation synthesis. Hydroxyapatite is a highly nonstoichiometric calcium phosphate compound with a Ca/P molar ratio ranging from 1.50 to 1.67. At a Ca/P ratio of 1.67, it acts as a basic catalyst, catalyzing chiefly acetaldehyde synthesis from ethanol by dehydrogenation. The results showed that hydroxyapatite with high Ca/P molar ratios had high selectivity to C4-C8 alcohols more than lower Ca/P ratios because of acid-base site over the catalyst

R. Shi, et al. [37] used a highly efficient Cu/La_2O_3 catalyst for transfer dehydrogenation of primary aliphatic alcohols. A Cu/La_2O_3 catalyst affords fairly high activity for the transfer dehydrogenation of primary aliphatic alcohols through a synergistic effect between the basicity of the support and the fast hydrogen spillover of Cu nanoparticles. They used 1-octanol as a hydrogen donor, and styrene as a hydrogen acceptor. The basic sites of La_2O_3 are mainly responsible for proton abstraction from alcohol, while the Cu particles promote the hydrogenation of styrene.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

Chemicals	Grade of purity	Manufactures
1. Ethanol	99.99%	Carlo Erba
2. Nitrogen gas	High purity (99.99%)	Praxair
3. Air	High purity (99.99%)	Praxair
4. Distilled water	-	
5. Layered Double Hydroxides (LDH)	-	SCG pcl.
[Mg_3Al-CO_3]	99%	Fluka
6. Lanthanumnitrate hexahydrate		
[$La(NO_3)_3 \cdot 6H_2O$]	99.5%	Carlo Erba
7. Potassium nitrate [KNO_3]	99%	Fluka
8. Zinc acetate dihydrate		
[$Zn(O_2CCH_3)_2(H_2O)_2$]	95%	Fluka
9. Caesium acetate [CH_3CO_2Cs]	99%	Carlo Erba
10. Calciumnitrate tetrahydrate	99%	Carlo Erba
[$Ca(NO_3)_2 \cdot 4H_2O$]		
11. Diammonium hydrogen phosphate	30%	Carlo Erba
[$(NH_4)_2HPO_4$]	87.4%	Baker Analyed
	99%	Univar
12. Ammonia solution [NH_3]	99%	Sigma Aldrich
13. Potassium hydroxide [KOH]	87.4%	Baker Analyed
14. Potassium permanganate [$KMnO_4$]	99%	Univar
15. Magnesium oxide [MgO]	99%	Sigma Aldrich

3.2 Apparatus

1. Syringe (10 mL, 50 mL)
2. Syringe pump
3. Magnetic stirrer
4. pH meter
5. Laboratory glassware

6. Laboratory plastic ware
7. Oven
1. Furnace
2. Sieve
3. Catalytic testing rig
4. Mass flow controller
5. Temperature programmed reduction (TPR) system
6. Temperature programmed desorption (TPD) system
7. X-ray fluorescence spectrometer (Wavelength Dispersive, Philips, PW2400, Scientific and Technological Research Equipment Centre 2-3 Building, Chulalongkorn University and Energy Dispersive, Oxford, ED-2000, Scientific and Technological Research Equipment Centre 2-3 Building, Chulalongkorn University)
8. X-ray powder diffractometer (Rigaku, DMAX 2200/Ultima+, National Metal and Materials Technology Center)
9. Thermogravimetric analyzer (Perkin-Elmer, Scientific Instrument Service Centre, KMITL)
10. Gas Chromatography with Flame Ionization detector (GC-FID)
11. Gas Chromatography-mass spectrometry (GC-MS) (Agilent Technologies, 6890N Network GC system)
12. Scanning electron microscope (EVO®MA10, College of Data Storage Innovation, KMITL)

3.3 Experimental procedure

3.3.1 Catalyst preparation

3.3.1.1 Preparation of LDH, MgO, and HAp

Layered double hydroxides (LDH) with Mg/Al ratio of 3 were obtained from Siam Cement Group Pcl., Bangkok, Thailand. Mixed oxides were derived from the resulting LDH by heat treatment at 400°C in air flow. The temperature was raised at 5°C/min up to 450°C and maintained for 8 h [2].

Base modified LDH: KOH-LDH and KMnO4-cLDH were prepared by base washing method. cLDH were washed by 0.1 M KOH and 0.1 M KMnO4. After that, the resultants were stirred at room temperature, dried, and treated under air flow at 450°C.

Magnesium oxide (MgO) was treated under air flow at 450°C for 8 h with a heating rate of 5°C/min before used as a catalyst.

Hydroxyapatite (HAp) was prepared using co-precipitation method. First, a solution containing 35 mL of 0.50 M calcium nitrate and 35 mL of 0.30 M $(NH_4)_2HPO_4$ was added into 30 mL of ammonia solution with the rate of 8 mL/min at room temperature. During the co-precipitation, the pH was continuously controlled at 10.5 all time. The resultant was heated to 80°C with stirring rate of 800 rpm for 5 h. After that, the precipitates were washed by centrifugal separation at 5,000 rpm for 10 minutes with distilled water and then dried at 100°C. Finally, it was calcined under atmosphere at 600°C for 2 h [30].

3.3.1.2 Preparation of Metal Oxide loaded on cLDH

The 2 wt.% metal oxides (La_2O_3, Cs_2O, K_2O, and ZnO) loaded on cLDH catalysts were prepared by impregnation method using lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$), caesium acetate (CH_3CO_2Cs), potassium nitrate (KNO_3), and zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$) as metal oxide precursors. The impregnated catalyst was dried in an oven at 100°C for 24 hours and calcined in a horizontal tube furnace under a flow of air zero (60 mL/min) at 450°C for 8 hours with a heating rate of 5°C/min.

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 is packed on the sample holder. Analysis was done employing Rigaku diffractometer (Cu-K[redacted] radiation, 40 kV, 30 mA), covering the range of 2θ = 10-70°, at the rate of 0.02°/step, and a scanning rate of 1 s/step.

3.3.2.2 Quantitative elemental composition analysis by X-ray fluorescence (XRF)

X-ray fluorescence is a surface composition determination that results from bombarding the sample with high-energy X-rays to releases characteristic secondary X-ray. This technique can be performed according to the procedure: the 0.5 g of catalyst sample and 4.5 g of boric acid were mixed, ground together, and compressed into an alumina pan before bring into the XRF sample holder in XRF instrument.

3.3.2.3 Determination of specific surface area by nitrogen adsorption

The specific surface areas of the samples were measured by nitrogen physisorption using the BET method (Autosorb-1C, Quantachrome). Approximately 0.05 g of the sample was loaded into the cell, which is attached to the outgassing station equipped with a heating mantle. The temperature was raised to 350°C during outgassing process. 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 the corresponding surface area was analyzed using BET equation as shown in **Equation 3.1**.

$$\frac{1}{v\left[(p_0/p)-1\right]}=\frac{c-1}{v_{\mathrm{m}}c}\left(\frac{p}{p_0}\right)+\frac{1}{v_m c} \qquad \text{Equation 3.1}$$

Where p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, V is the adsorbed gas quantity, and V_m is the monolayer adsorbed gas quantity. 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 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. Samples (0.1 g) were preheated in the flowing of He at 450°C for 2 h and evacuated and then exposed to 20 kPa of pure CO_2 gas at room temperature 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 700°C under vacuum. The TPD spectra were normalized based on the specific surface area.

3.3.2.5 Determination of acidity of the catalyst by NH_3-temperature programmed desorption (NH_3-TPD)

The acid function of the catalyst was identified using NH_3-TPD measurement. Samples (0.1 g) were preheated in flowing He at 450°C for 2 h and evacuated and then exposed to 20 kPa of 1% NH_3/He gas at room temperature until saturation coverage was reached. After 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 700°C under vacuum. The TPD spectra were normalized based on the specific surface area.

3.3.2.6 Determination of coke deposition on the catalysts by thermogravimetric analysis (TGA)

Phase transformation upon the heating treatment is a convenient method to study the coke deposit of the samples. The samples were manually ground in mortar to homogeneous fine particles for a while, and then approximately 10 mg of the samples was weighed into a platinum pan to perform thermogravimetric analysis (Pyris) under 20 mL/min of nitrogen atmosphere. The temperature was scanned form 50 to 900°C with a heating rate of 5°C/min. The data was collected corresponding to mass loss during the temperature range.

3.3.2.7 Scanning electron microscope (SEM)

The catalyst surface morphology was determined by SEM technique. 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.

3.3.3 Catalytic activity testing

Catalytic conversion of ethanol was carried out at 380°C using 2.0 g of catalyst in a fixed-bed continuous-flow glass reactor (8 mm). 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 checked by a bubble flow meter. The scheme of catalytic testing rig is shown in **Figure 3.1**. Before the catalytic reaction, the as-prepared catalysts were pretreated at 400°C for 1 h in air zero flow (30 mL/min). Ethanol was introduced into the reactor using a syringe pump at 0.7 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.

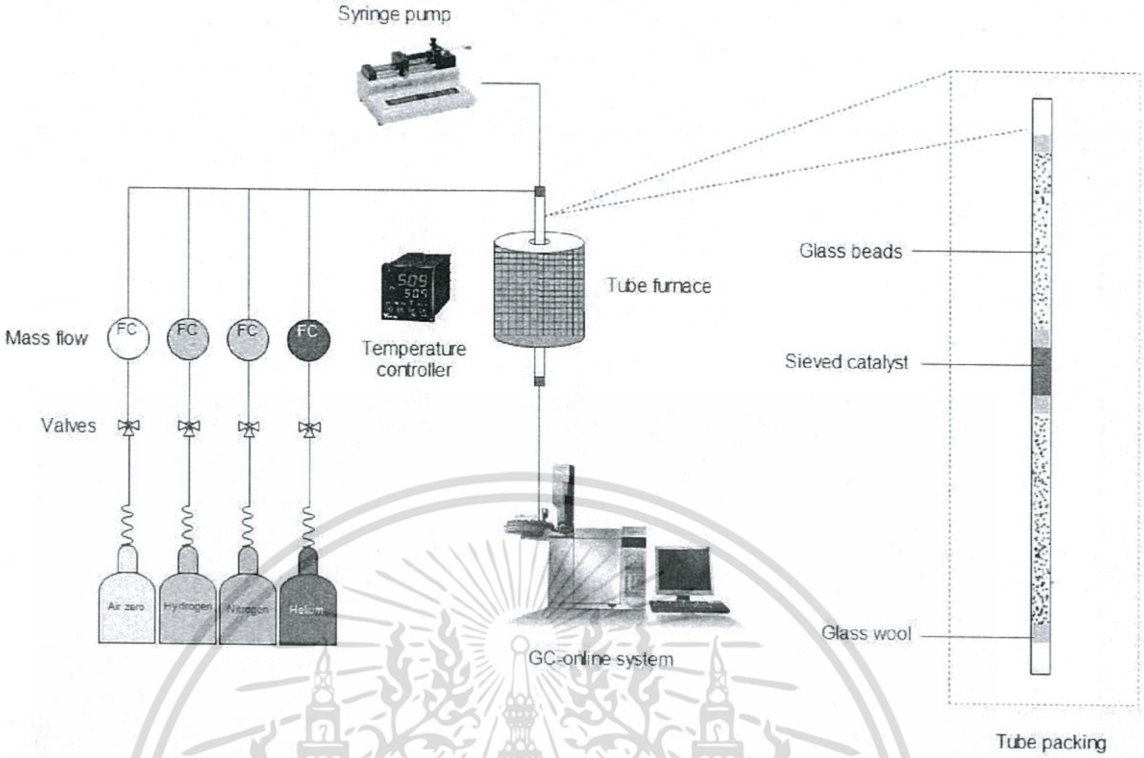


Figure 3.1 Catalytic testing rig

3.3.4 Products analysis

The products identification was confirmed by online gas chromatograph equipped with a flame ionized detector (GC–FID, CP-3800). The products was 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, 40°C for column oven, and 250°C for FID detector. The GC temperature condition was started at 40°C, hold for 2 min and heated up to 120°C, hold for 2 min. Then, heated up to 200°C and hold for 2 min. Pressure of the carrier gas was fixed to 4 psi all time. The products were recorded as a chromatogram. Each peak areas from the chromatogram was measured and calculated. Compared with standard peak areas, the species and composition of each product were determined.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 X-Ray Powder Diffraction (XRD)

4.1.1.1 Hydroxyapatite (HAp)

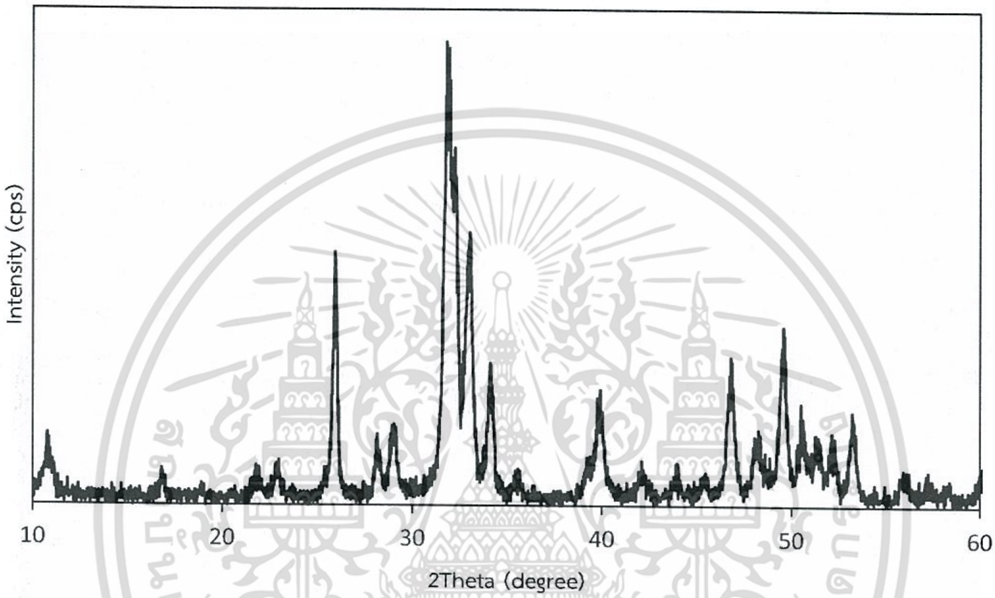


Figure 4.1 XRD patterns of HAp.

Figure 4.1 shows the XRD patterns of HAp. Two diffraction peaks at 2theta of 28° and 33° can be detected, which can be assigned to crystalline phase of HAp. This result confirmed that the synthesized HAp is composed of crystalline HAp with no presence of other impurities [38].

4.1.1.2 Layered double hydroxides (LDH)

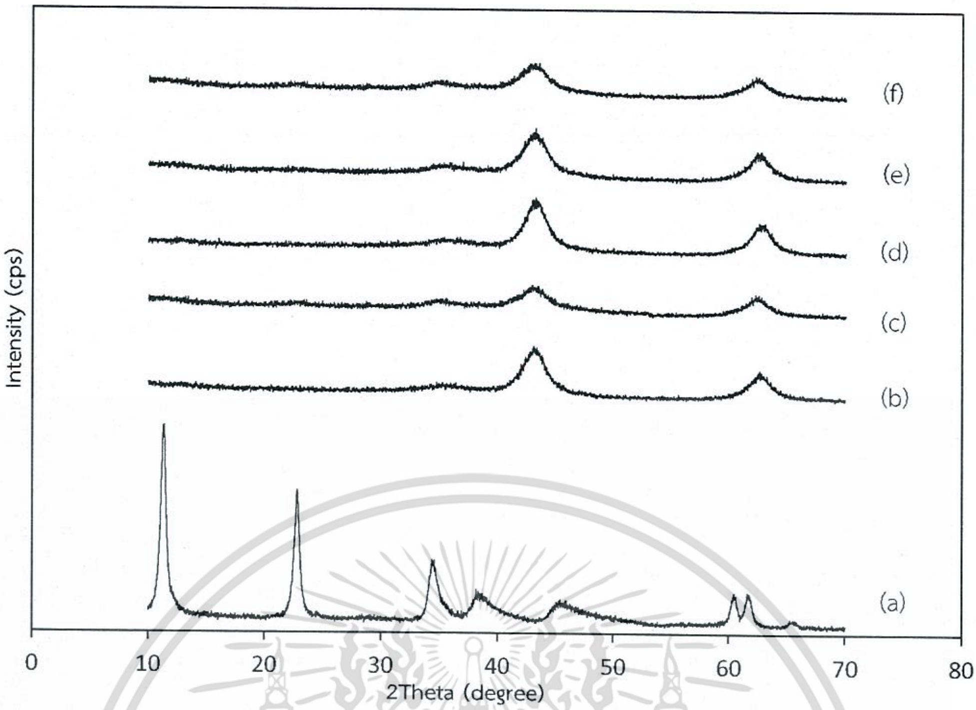


Figure 4.2 XRD patterns of (a) non-calcined LDH, (b) calcined LDH (under a flow of air zero at 450°C for 8 h), (c) La_2O_3/cLDH, (d) K_2O/cLDH, (e) ZnO/cLDH, and (f) Cs_2O/cLDH

Figure 4.2 shows the XRD patterns of LDH before and after calcination. Regarding to the XRD pattern of calcined LDH, it revealed that the peak at 12°, 23° and 34° are characteristic of a lamellar material and 61° is the distance of the cations within the layers of the structure [39]. In addition, the peaks at 37°, 45° and 65° are the peak of $MgAl_2O_4$ [40] and 63° corresponds to the MgO phase [41]. After calcined at 450°C, the layered structure of LDH was completely collapsed. Only broad peaks of MgO phases were observed at 2θ of 37°, 43° and 62°. No aluminium oxides was detected, suggesting that aluminium oxide are either well dispersed or forming an amorphous phase.

There are no significant changes in XRD patterns after the calcined LDH (cLDH) was incorporated with metal oxides (Figure 4.1 (c-f)). Again, only broad peaks at 2θ of 37°, 43° and 62° were observed for MgO phase. No significant peak of metal oxides were detected, suggesting that metal oxides are well dispersed over cLDH.

4.1.2 Surface area, acid, and basic characteristics of catalysts

The surface area, acidity, and basicity of the catalysts were determined by BET measurement and temperature programmed desorption (TPD) as shown in **Table 4.1**.

Table 4.1 Surface area, acid, and basic characteristics of catalysts

Catalyst	nLDH	cLDH	MgO	HAp	La_2O_3/cLDH	ZnO/cLDH	Cs_2O/cLDH	K_2O/cLDH
Surface area (m^2/g)	92.6	171.1	156.4	53.4	-	-	-	-
Pore volume (mL/g)	0.8	0.6	0.2	0.6	-	-	-	-
Pore diameter (nm)	34	15	6	41	-	-	-	-
Acid sites (μmol/g)	-	1,146	-	515	724	1,029	908	412
Acid sites (μmol/m^2)	-	6.7	-	9.6	-	-	-	-
Basic sites (μmol/g)	-	973	1,087	451	287	590	747	285
Basic sites (μmol/m^2)	-	5.7	7.0	8.4	-	-	-	-

* LDH = non-calcined LDH
cLDH = calcined LDHs at 450°C for 8 h
HAp = Hydroxyapatite

A decrease in pore volume and pore diameter as well as an increase in surface area of LDH can be observed after calcination at 450°C for 8 h. This is due to the decomposition of interlayer carbonate and hydroxyl groups of the lamellae, in consistence with the XRD results (**Figure 4.2**). In addition, cLDH possesses both acid and basic properties, due to the presence of Mg-O pair (basic site) and Al^{3+} (acid site) in the structure. However, the acid and basic sites are decreased when cLDH was incorporated with metal oxides. This may be because these acid and basic sites are obscured by the incorporated metal oxides.

4.1.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the catalysts are shown in **Figure 4.3**.

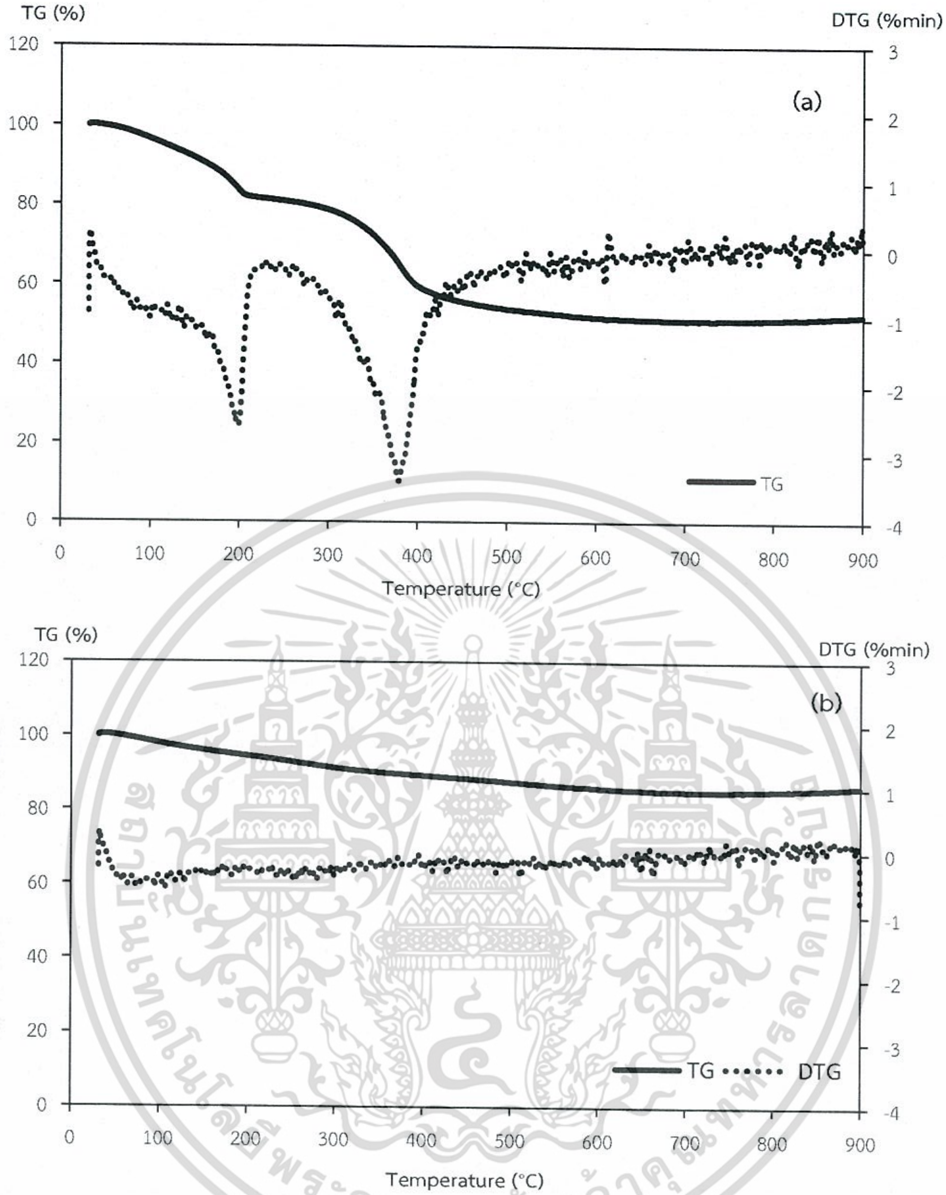


Figure 4.3 TGA analysis (under air) of (a) non calcined LDH and (b) calcined LDH at 450°C for 8 h.

Figure 4.3(a) shows TGA result of the original LDH. The first weight loss below 200°C, is associated with the evaporation of adsorbed and intercalated water molecules. The other steps, between 200°C and 400°C, is referred to the decomposition of interlayer carbonate and hydroxyl groups of the lamellae [39]. On the other hand, there are no significant changes in the weight loss of the calcined LDH at 50°C to 900°C. This reveals the stable structure of LDH after removal of carbonate and hydroxyl groups by calcination at 450°C.

4.1.4 Scanning Electron Microscopy (SEM)

The morphology of non-calcined LDH and calcined LDH are presented by images of scanning electron microscopy as shown in **Figure 4.4**.

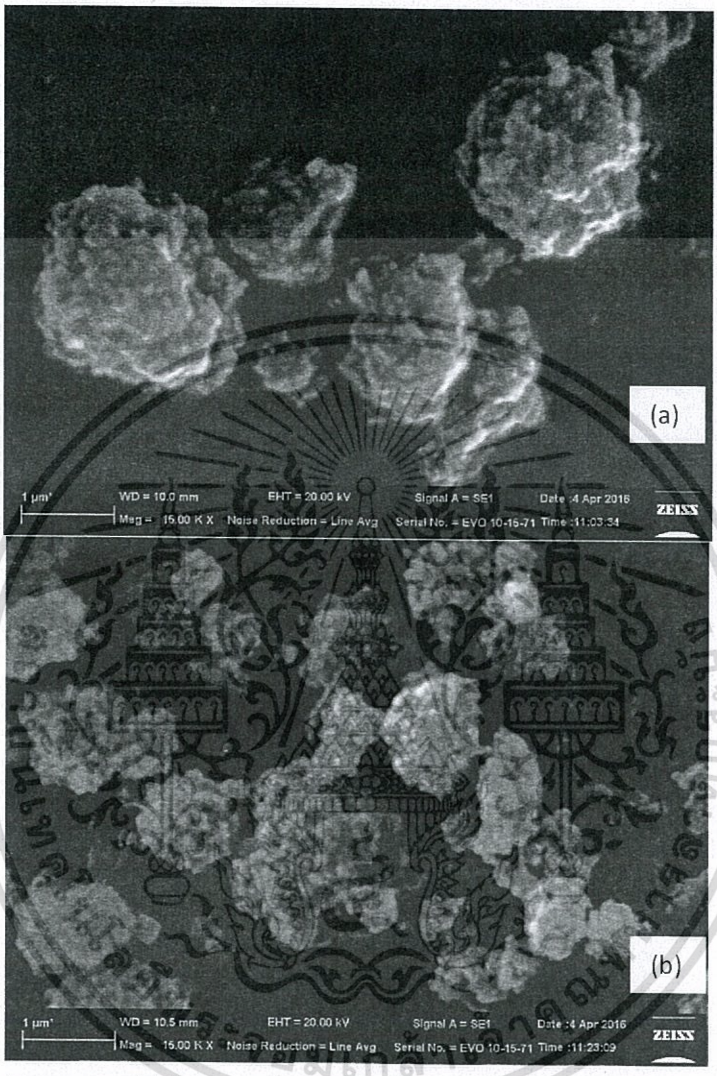


Figure 4.4 SEM images of (a) non-calcined LDH, and (b) calcined LDH at 450°C for 8 h

Figure 4.4(a) shows the morphology of the non-calcined LDH, which is accumulated spherical particles. After calcination (**Figure 4.4(b)**), there are no significant changes in the morphology of the LDH, except the accumulated particles becomes smaller.

4.2 Study on the conversion of ethanol to higher alcohols

4.2.1 Effect of catalyst

In order to study the effect of basic and acid sites of catalyst, the conversion of ethanol over three catalysts with different basic and acid sites: MgO, cLDH, and HAp, were investigated under the same reaction conditions in fixed-bed reactor at a condition of: temperature 380°C, pressure: 1 atm, flow rate of N_2 carrier gas: 60 mL/min, contact time: 25 g·h/mol. **Table 4.2** shows the performance of various catalysts in promoting higher alcohols (C4 and C6 alcohols) from ethanol.

Table 4.2 Conversion of ethanol and yield towards each product over different types of catalysts (results at 60 minutes of time on stream).

Catalyst	MgO	HAp	cLDH
Conversion (%)	8.9	49.7	32.7
Yield of products (%)			
Ethylene	1.9	35.0	12.3
Diethyl ether	-	-	4.8
Acetaldehyde	2.2	1.8	3.9
Butanal	0.1	1.8	0.8
Crotonaldehyde	0.1	0.2	0.1
Hexanal	0.1	0.04	0.1
C4 alcohols	4.6	9.8	9.6
C6 alcohols	0.1	1.0	1.0

(C4 alcohols: 1-Butanol and 2-Butenol, C6 alcohols: 2-Ethyl-1-butanol and 1-Hexanol)

It can be seen that MgO gives lower activity, as compared to other catalysts. This is due to low amount of active site, and only small yields of higher alcohols were obtained. T. Tsuchida et al. [30] reported that low higher alcohols production of MgO is due to the short distance of Mg-O bond. That was suggested that the ethanol dissociatively adsorbed as ethoxide species, proton-like hydrogen was released on the surface. Then, the ethoxide species is dissociated to acetaldehyde baring hydride-like hydrogen on the surface. However, the short distance between proton-like hydrogen on O and hydride-like hydrogen on Mg lead to their migration to form H_2 (**Figure 4.5**). Accordingly, H_2 transfer cannot readily facilitate over MgO.

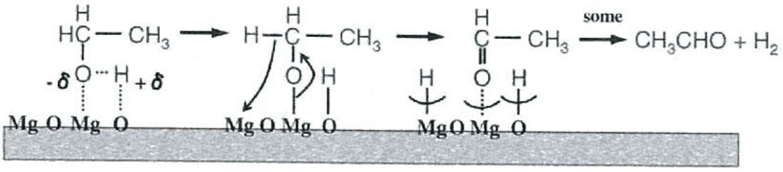


Figure 4.5 Ethanol conversion over MgO [30]

In contrast, the proton-like hydrogen was stabilized on O of phosphate in HAp. Hence, the recombination between proton-like hydrogen and hydride-like hydrogen can be limited. As a result, HAp gives higher yields of higher alcohols. Nevertheless, HAp also gives high yield of ethylene presumably due to high acidity (9.6 μmol/m^2).

Although, cLDH gives a lower activity, as compared to HAp. It provides higher selectivity to higher alcohol products as shown in **Figure 4.6**.

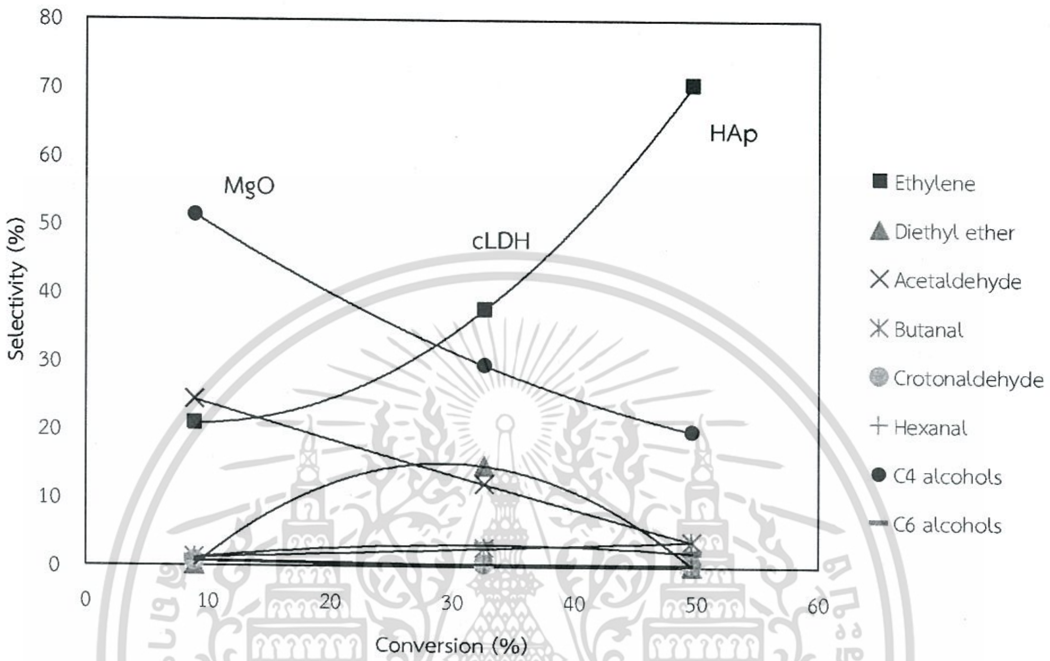


Figure 4.6 Selectivity of ethanol over various catalysts (Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

J. I. Di Cosimo et al. [1] reported that incorporation of small amounts of Al^{3+} cations to MgO drastically increased the acetaldehyde formation due to the generation of new surface Lewis acid-strong base pair sited. Consequently, cLDH are selected for further investigation.

4.2.2 Conversion of ethanol to higher alcohols over cLDH catalyst

In order to understand the reaction pathway for the product formation on cLDH catalyst, effect of contact time on the ethanol conversion was studied as shown in **Figure 4.7**.

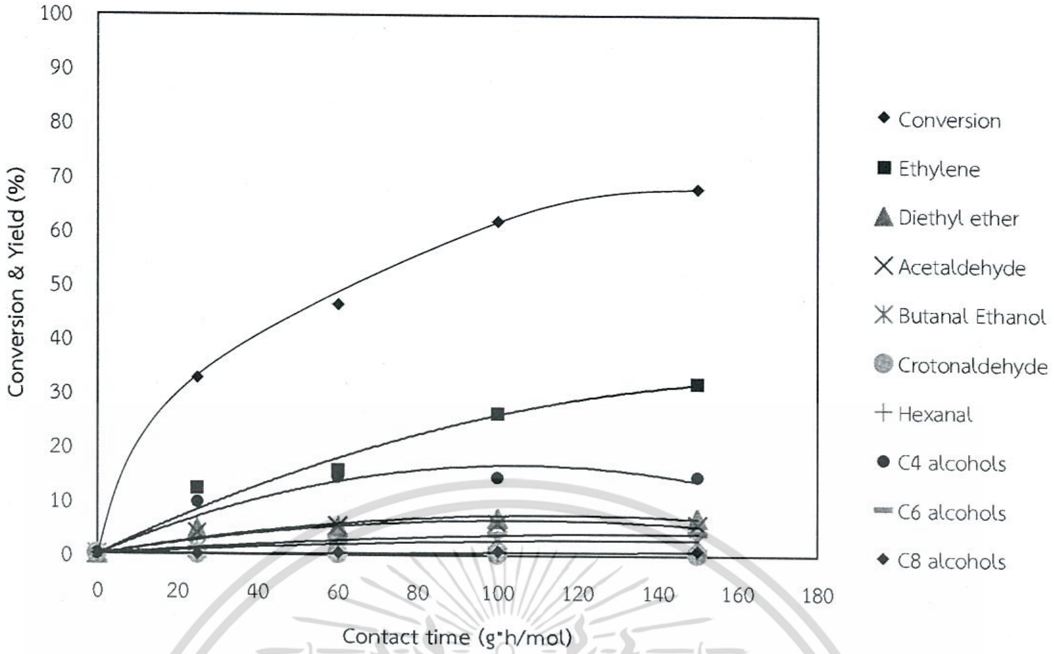
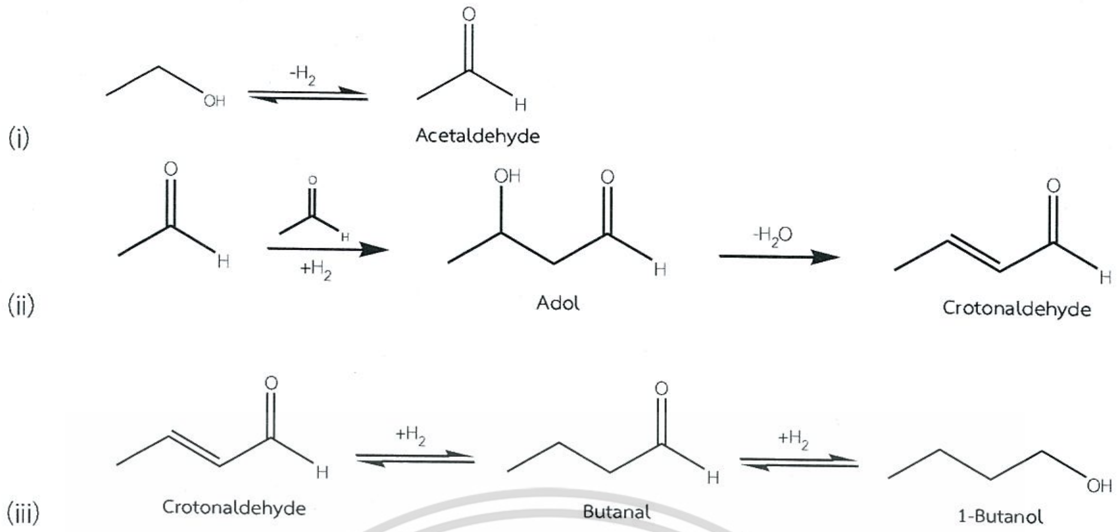


Figure 4.7 Converison of ethanol and yields of products at various contact times (Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25-150 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

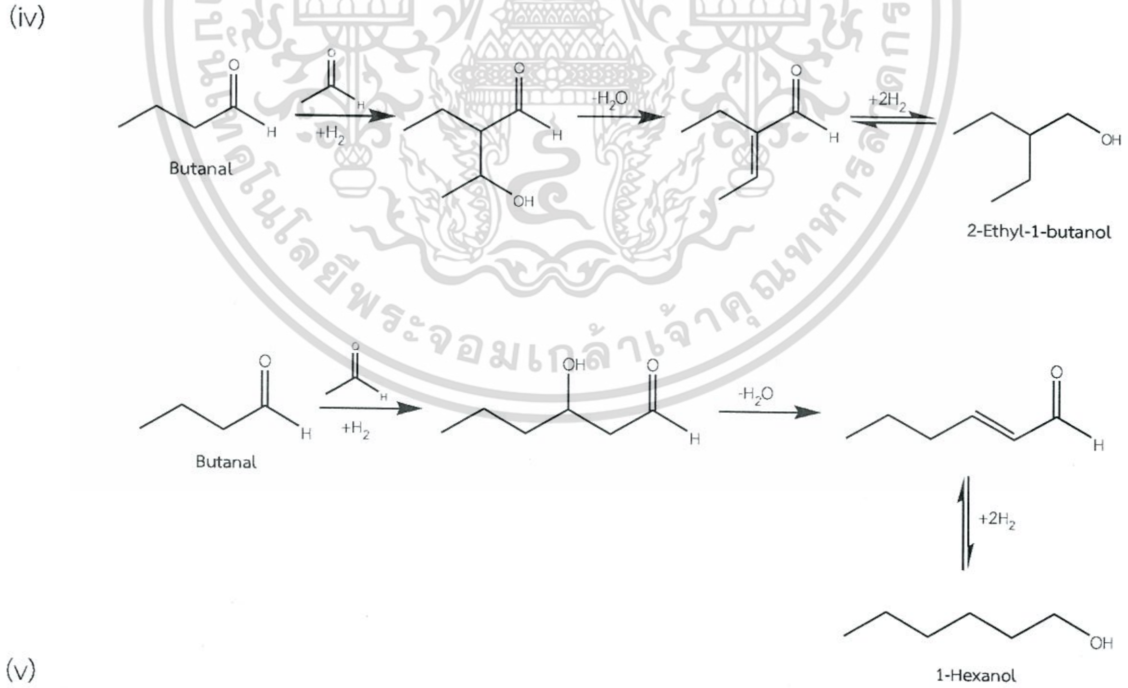
It is shown that the conversion of ethanol was increased with contact time up to about 70% conversion. This can be explained by an increasing of the amount of catalyst in the system and consequently higher number of active site for the reaction. Furthermore, the yield of ethylene was increased with contact time, due to dehydration of ethanol. However, the yield of acetaldehyde and higher alcohols were increased only at initial period and no significant increase in yield of higher alcohol can be observed at high contact time. This is because the Guerbet reaction is reversible. 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. Butanal can be further hydrogenated to butanol (iii), as shown in **Scheme 4.1**.



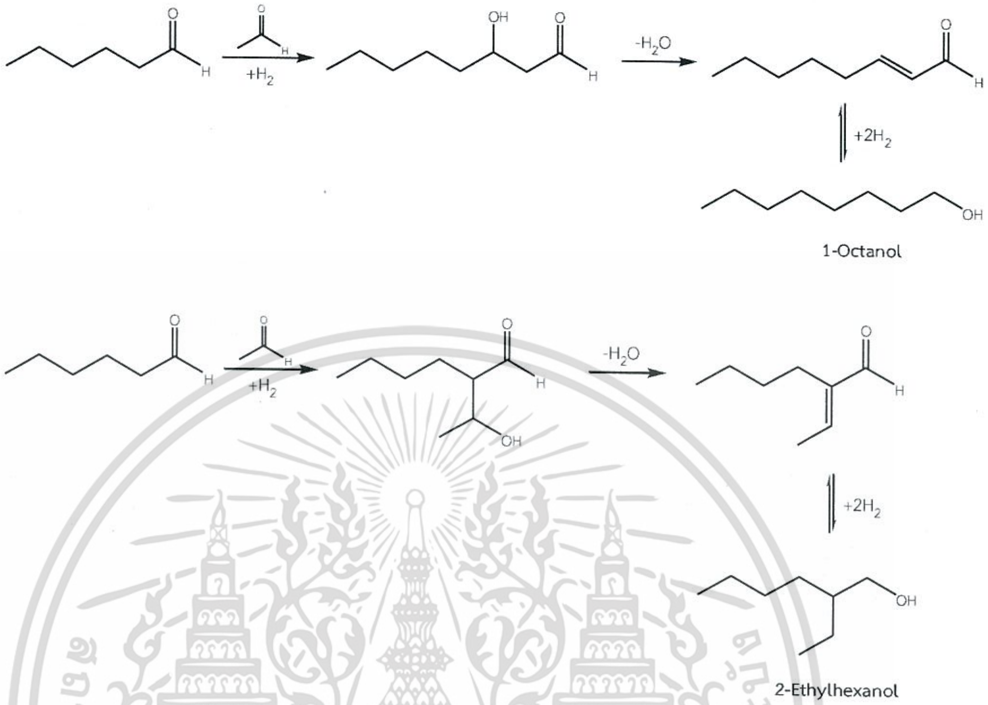
Scheme 4.1

Butanal can be also an intermediate for production of 2-ethyl-1-butnol (iv) and 1-hexanol (v) via aldol condensation and hydrogenation process, as shown in **Scheme 4.2**.



Scheme 4.2

In the case of C8 alcohols, 1-octanol and 2-ethylhexanol can be obtained by the coupling of activated acetaldehyde with 1-hexanal. Then, it is further aldol condensed and hydrogenated to 1-octanol (vi) and 2-ethylhexanol (vii), as presented in **Scheme 4.3**.

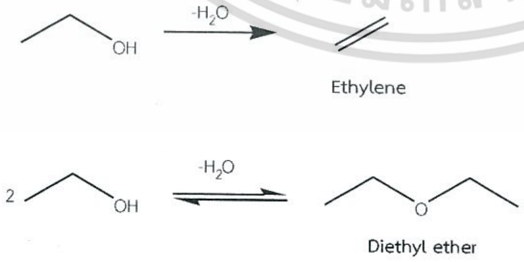


(vi)

(vii)

Scheme 4.3

Moreover, ethanol can be also converted in parallel to ethylene and diethyl ether. The ethylene formation can occur via mono molecular dehydration of ethanol over acid site (viii), while diethyl ether is formed via bimolecular dehydration of ethanol (ix), as seen in **Scheme 4.4**.



(viii)

(ix)

Scheme 4.4

These reactions do not give H_2 as products. Hence, increase in conversion of ethanol to ethylene and diethyl ether limit the formation of higher alcohols as seen by a drop in selectivity of higher alcohols with an increase in selectivity of ethylene (**Figure 4.8**).

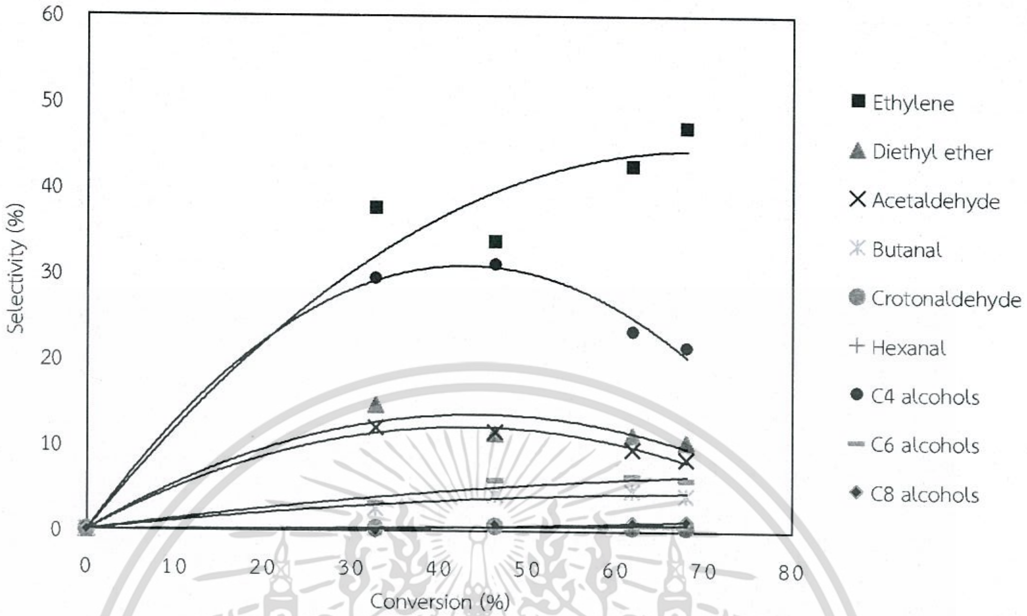
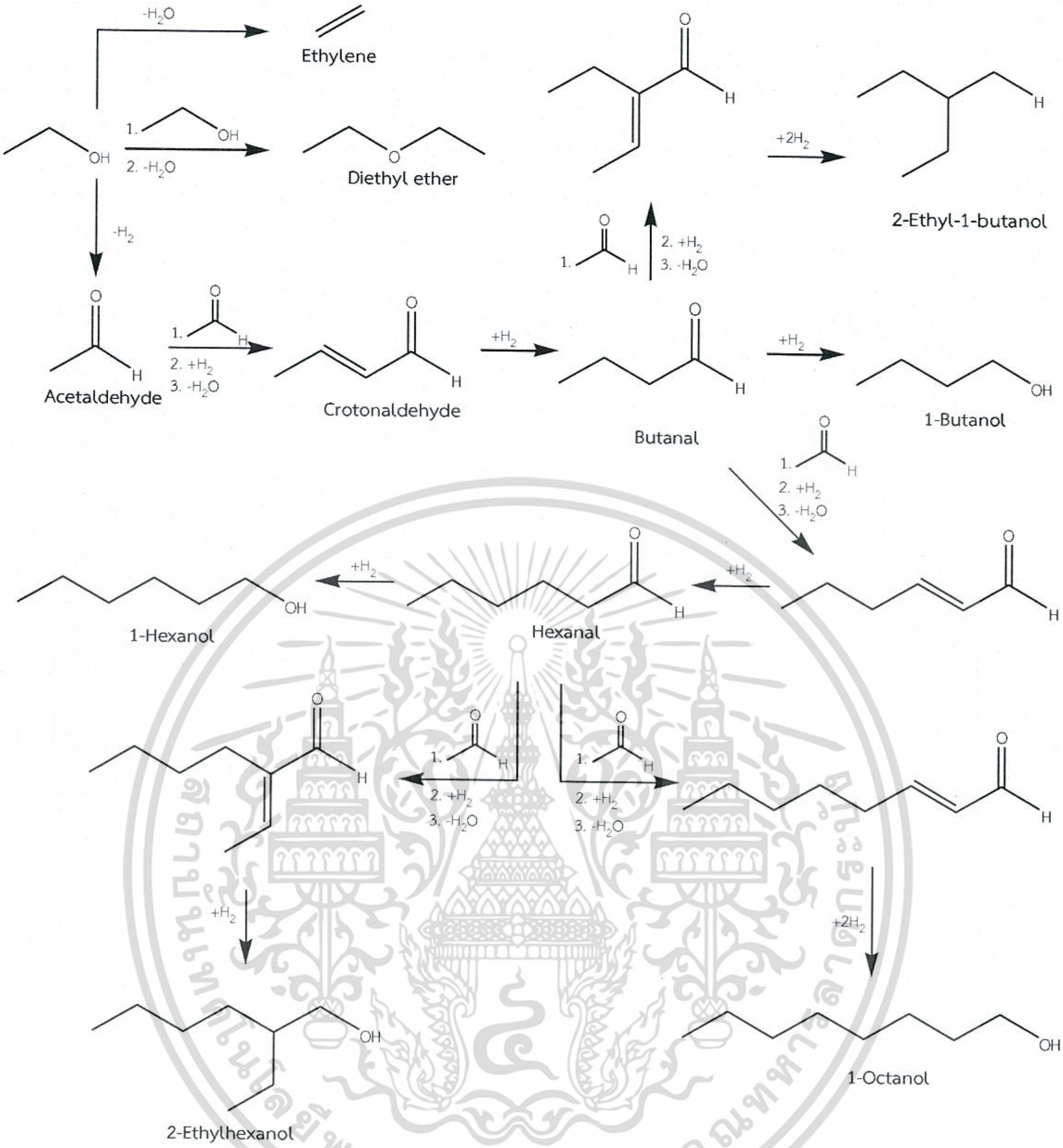


Figure 4.8 Selectivity of products at various contact times

It can be seen that, the selectivity of ethylene is clearly increased. However, the selectivity of acetaldehyde and C4 alcohols are clearly decreased, while the selectivity of some products as C6 alcohols and butanal are slightly increased. It is clear that the dehydration of ethanol to ethylene, and the dehydrogenation of ethanol to acetaldehyde are parallel reaction. In the case of Guerbet reaction, it is series reactions and control by H_2 production from ethanol as discussed earlier. Hence, the increase in ethylene production leads to decrease higher alcohols. The overall reaction pathway can propose as in **Scheme 4.5**.



Scheme 4.5 The overall reaction pathway.

In order to increase higher alcohol and decrease ethylene yield, cLDH modification by washing with base solutions were studied.

4.2.3 Conversion of ethanol to higher alcohols over metal incorporated cLDH catalysts

4.2.3.1 The base modified cLDH

In order to neutralize the acid sites, cLDH was washed with two types of base solution: 0.1 M KOH and 0.1 M $KMnO_4$. The conversion of ethanol and selectivity of product over base modified cLDH are shown in **Table 4.3**.

Table 4.3 Ethanol conversion and selectivity of products over base modified cLDH catalysts.

Catalyst	cLDH	KOH/cLDH	$KMnO_4$/cLDH
Conversion (%)	32.7	23.4	25.2
Yield of products (%)			
Ethylene	12.29	13.33	12.59
Diethyl ether	4.79	0	2.3
Acetaldehyde	3.92	3.22	5.3
Butanal	0.84	0.3	1.07
Crotonaldehyde	0.08	0.25	0.3
Hexanal	0.09	0	0
C4 alcohols	9.62	5.67	3.2
C6 alcohols	1.02	0.6	0.45

*C4 alcohols: 1-Butanol and 2-Butenol, C6 alcohols: 2-Ethyl-1-butanol and 1-Hexanol (Reaction condition; Temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

As seen from **Table 4.3**, the base modified cLDH can readily neutralize the acid sites as seen by a decrease in dehydration product, namely ethylene and diethyl ether. Especially, the diethyl ether was not found after washing LDH by KOH. However, the dehydrogenation product (acetaldehyde) and higher alcohols were not enhanced. This may be because the active sites for dehydrogenation and hydrogen transfer may also be suppressed by base washing.

Hence, the modification of cLDH by washing base is not the best way to produce the higher alcohols. The influence of metal loaded on cLDH was investigated further.

4.2.3.2 Influence of metal oxides impregnated cLDH

In order to increase the active site for dehydrogenation, metal oxides (K_2O, La_2O_3, ZnO, Cs_2O) were incorporated and tested for the conversion of ethanol as shown in **Table 4.4**.

Table 4.4 Ethanol conversion and selectivity of products over metal oxide incorporated cLDH catalysts

Catalysts	cLDH	La_2O_3/cLDH	K_2O/cLDH	Cs_2O/cLDH	ZnO/cLDH
Conversion (%)	32.6	30.9	15.6	28.3	51.4
Yield of products (%)					
Ethylene	12.3	11.5	7.9	18.4	13.3
Diethyl ether	4.8	5.4	-	-	1.4
Acetaldehyde	3.9	4.5	3.9	3.0	21.2
Butanal	0.8	0.8	0.3	0.4	4.4
Crotonaldehyde	0.1	0.1	0.2	0.2	1.6
Hexanal	0.1	0.1	0.01	-	0.7
C4 alcohols	9.6	7.6	3.0	5.2	7.0
C6 alcohols	1.0	0.9	0.2	0.9	1.4
C8 alcohols	-	-	-	0.1	0.2
2-Methylbenzaldehyde	-	-	-	-	0.2
2-Methylbenzyl alcohol	-	-	-	-	0.1

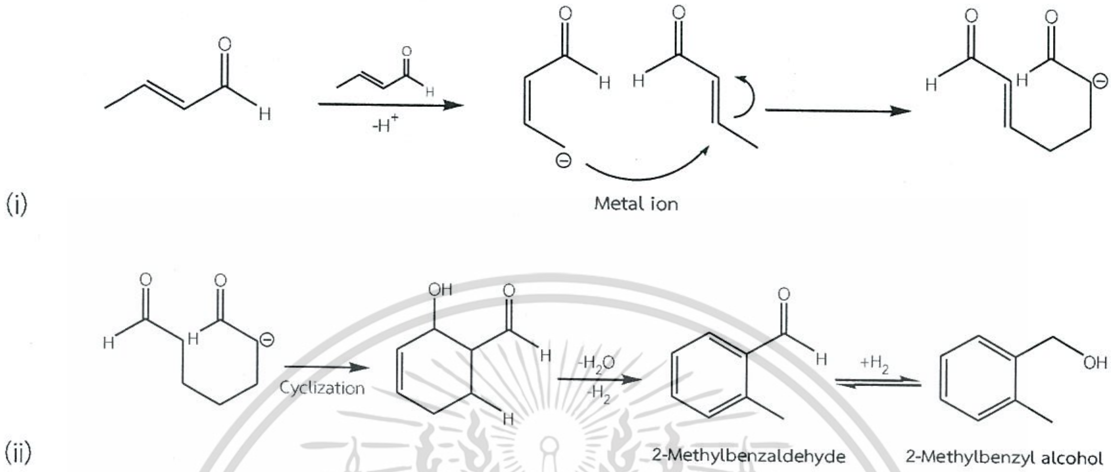
*C4 alcohols: 1-Butanol and 2-Butenol, C6 alcohols: 2-Ethyl-1-butanol and 1-Hexanol, C8 alcohols: 2-Ethylhexanol and 1-Octanol.

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

K_2O/cLDH and Cs_2O/cLDH give lower activity, as compared to the parent cLDH because the metal oxide may block the active site for dehydrogenation. For La_2O_3/cLDH, the conversion is slightly decreased, and the yield of C4 alcohols is also decreased. This may be due to the low surface area of La_2O_3, leading to lower active surface for aldol condensation. This is consistent with the work done by Xin et al. [42]. They have reported that La_2O_3 could be used as a basic catalyst, but it exhibited low specific surface, which is a disadvantage in heterogeneous catalysis.

Nevertheless, ZnO/cLDH shows a remarkably higher activity, as compared to other metal oxides and the parent cLDH. It can promote dehydrogenation of ethanol to acetaldehyde. However, the reaction over ZnO/cLDH gives mainly C8 aromatic compounds (2-methylbenzaldehyde and 2-methylbezyl alcohol).

This can be described that Zn ion can stabilize the electron delocalization in the conjugated double bounds of crotonaldehyde [4]. It is suggest that crotonaldehyde can be deprotonated at γ-hydrogen, with the help of metal complex. Then, this crotonaldehyde will be coupled with another crotonaldehyde forming a higher molecular weight unsaturated aldehyde intermediate (i). The intermediate can undergo cyclization to cyclic compound and dehydration to 2-methylbezaldehyde that can be hydrogenated to 2-methylbenzyl alcohols (ii), as shown in **Scheme 4.6**.



Scheme 4.6

Although, ZnO/cLDH shows high activity for dehydrogenation, low yield of higher alcohols were obtained. This is because H_2 transfer may be inhibited by the high reaction temperature. Therefore, ethanol conversion over ZnO/cLDH was further studied at various temperatures.

4.2.3.3 Effect of reaction temperature on activity of ZnO/cLDH catalyst

In order to understand the effect of reaction temperature on H_2 transfer, ethanol conversion was tested at 350-400°C as shown in **Figure 4.9**.

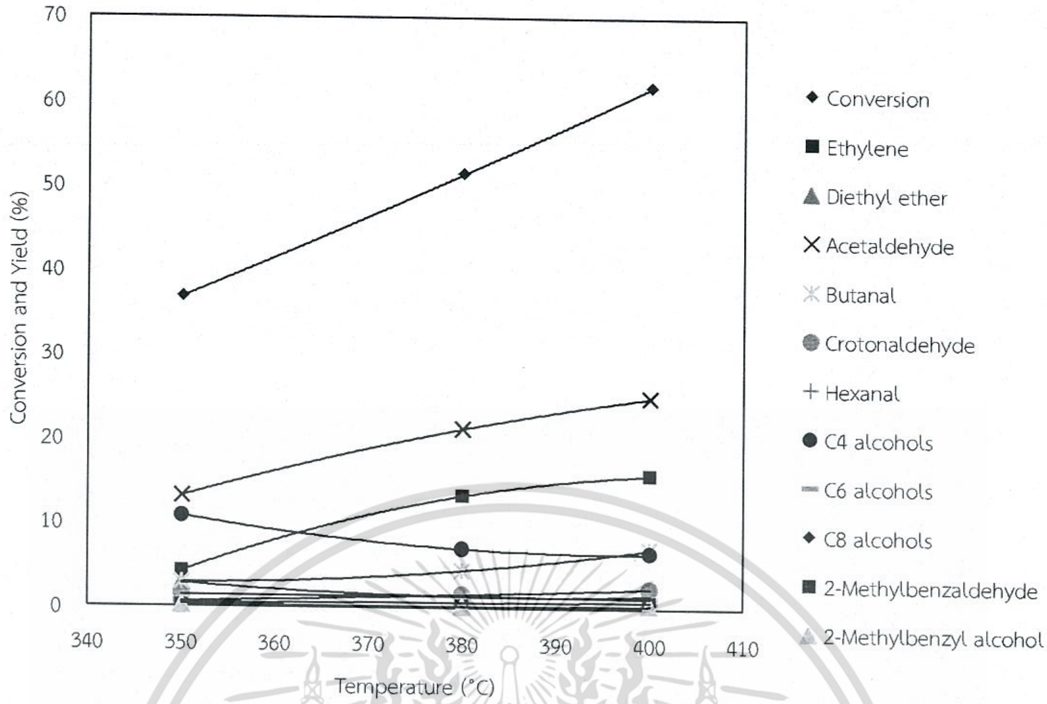


Figure 4.9 Conversion of ethanol and yield of products at various reaction temperatures
(Reaction condition; temperature: 350-400°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

It can be seen that the conversion of ethanol and yield of primary products, acetaldehyde and ethylene are increased with temperature. On the other hand, higher alcohols are noticeably decreased. This is because at low temperature, H_2 transfer can be promoted. At high temperature, the dehydration reaction is promoted as seen by ethylene yield. Hence, decreasing reaction temperature would increase higher alcohol selectivity as shown **in Figure 4.10**.

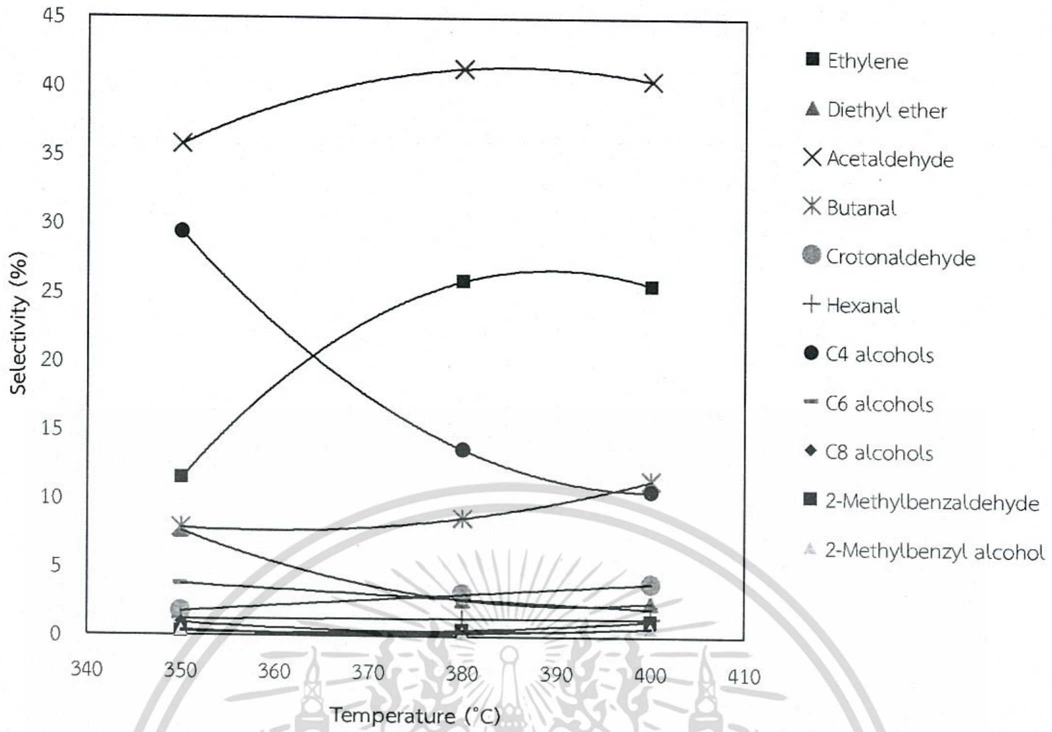


Figure 4.10 Selectivity of ethanol at various reaction temperatures (Reaction condition; temperature: 350-400°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

It is clear that at low temperature the selectivity of higher alcohols is increased. Moreover, the selectivity of butanal and crotonaldehyde are slightly increased with temperature. This is because C4 alcohols can be dehydrogenated to butanal and crotonaldehyde.

Considering **Figure 4.9**, the selectivity of butanol is relatively high at 350°C. Thus, the effect of contact time over ZnO/cLDH was investigated again at this temperature.

4.2.3.4 Effect of contact time for ZnO/cLDH catalyst

In order to understand the reaction pathway of the products formation over ZnO/cLDH, the effect of contact time on products distribution is studied as shown in **Figure 4.11**.

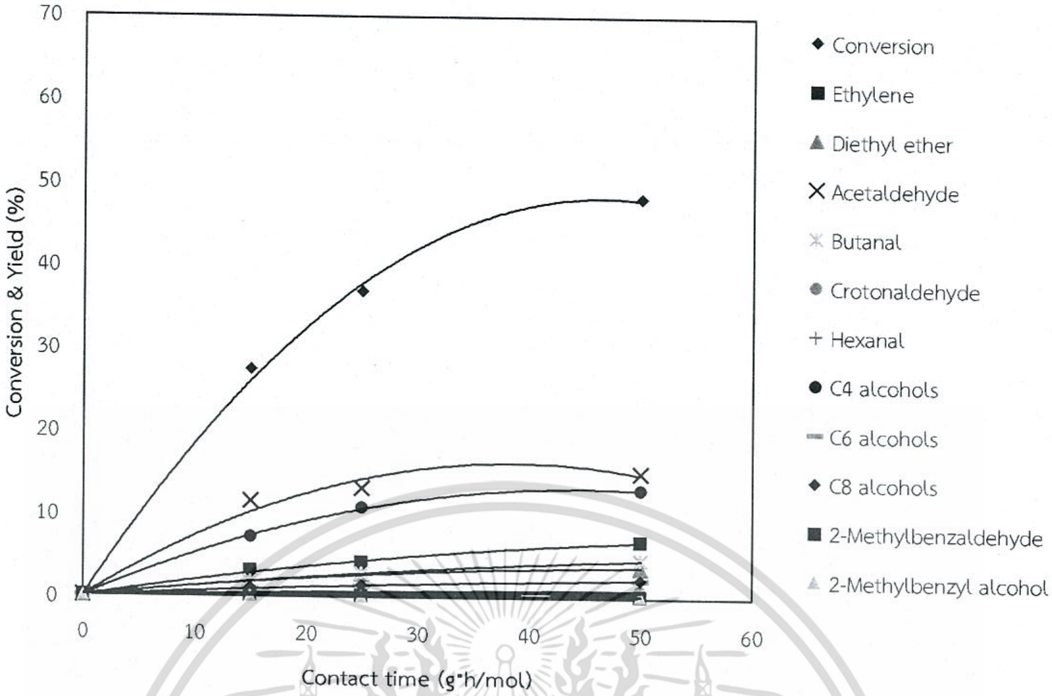


Figure 4.11 Conversion of ethanol and yield of products at various contact times over ZnO/cLDH (Reaction condition; temperature: 350 °C, pressure: 1 atm, contact time: 15-50 g•h/mol, flow rate of N_2 carrier gas: 60 mL/min, results at 60 minutes of time on stream)

It can be seen that the conversion is increased with contact time. The yield of Guerbet reaction products and dehydration products are also increased with contact time. Hence, increasing contact time, the selectivity of higher alcohols and ethylene are increased as seen in **Figure 4.12**.

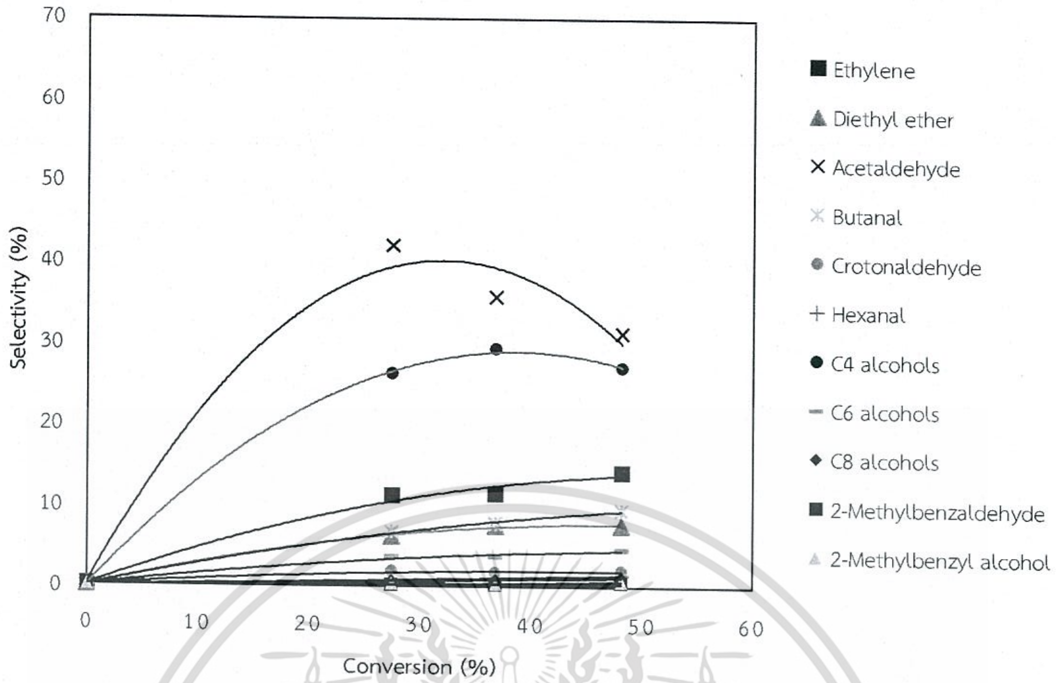
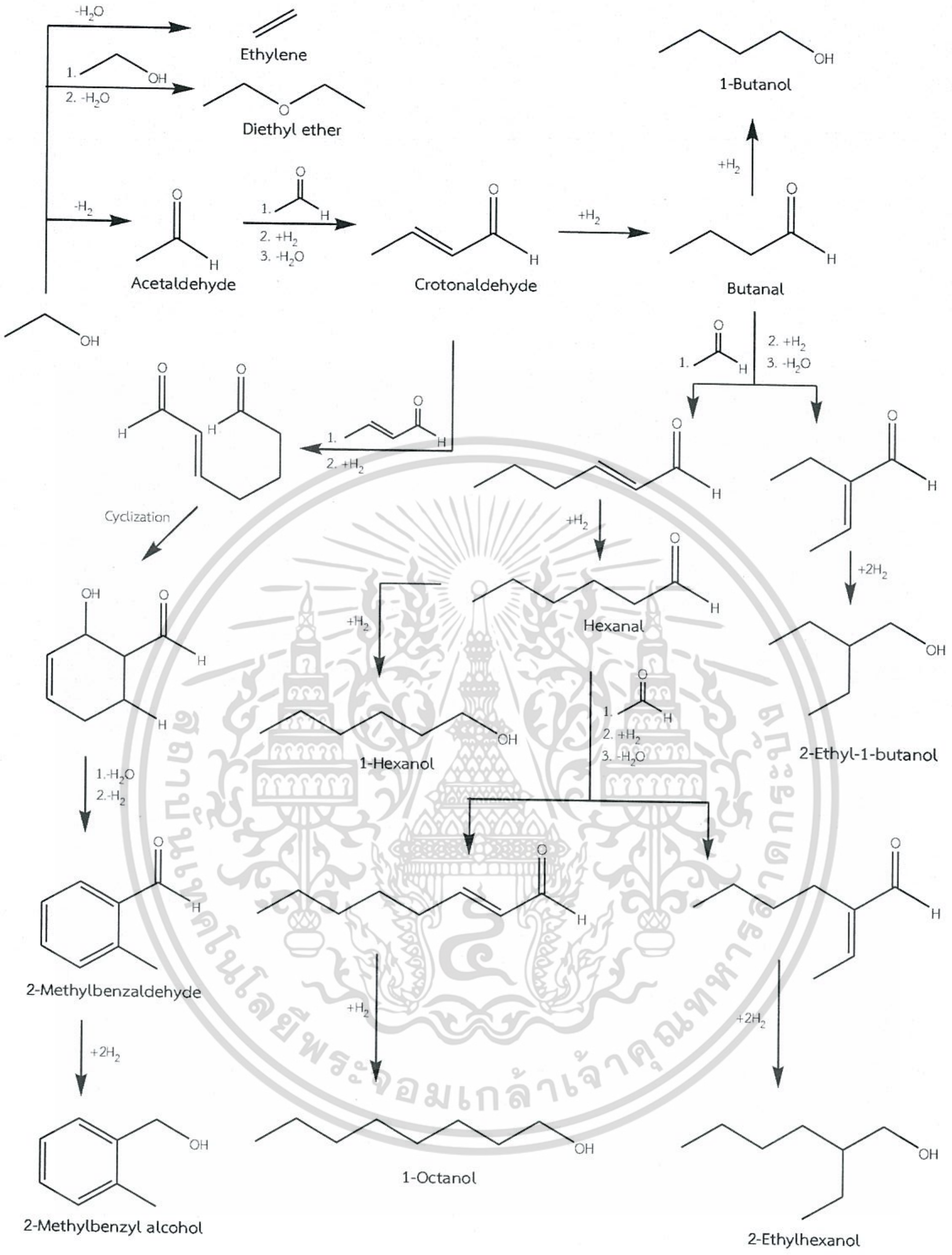


Figure 4.12 Conversion versus products selectivity over ZnO/cLDH (Reaction condition; Temperature: 350°C, Pressure: 1 atm, Contact time: 15-50 g•h/mol, Flow rate of N_2 carrier gas: 60 mL/min, Results at 60 minutes of time on stream)
C4 alcohols: 1-Butanol, 2-Butenol; C6 alcohols: 2-Ethyl-1-butanol, 1-Hexanol; C8 alcohols: 2-Ethylhexanol, 1-Octanol

However, at the high contact time the selectivity to higher alcohols and crotonaldehyde are slightly decreased, while C8 aromatic compounds (2-Methylbezaldehyde and 2-Methylbenzyl alcohol) are increased because crotonaldehyde can be converted to C8 aromatic compounds via aldol condensation and cyclization processes.

The overall reaction pathway over ZnO/cLDH can be proposed as presented in **Scheme 4.7**.


-H_2O
Ethylene
1. OH
2. -H_2O
Diethyl ether
-H_2
Acetaldehyde
1. H
2. +H_2
3. -H_2O
Crotonaldehyde
+H_2
Butanal
+H_2
1-Butanol
OH
1. H
2. +H_2
3. -H_2O
1.
2. +H_2
Cyclization
+H_2
Hexanal
+H_2
+$2H_2$
1-Hexanol
2-Ethyl-1-butanol
1. H
2. +H_2
3. -H_2O
1.-H_2O
2.-H_2
2-Methylbenzaldehyde
+$2H_2$
+H_2
+$2H_2$
2-Methylbenzyl alcohol
1-Octanol
2-Ethylhexanol

Scheme 4.7

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

Calcined LDH (cLDH) is the best catalyst for higher alcohols production from ethanol, as compared to MgO and HAp. The reaction involves dehydrogenation of ethanol to acetaldehyde, follows by an adol condensation and hydrogenation of high molecular weight aldehyde to higher alcohols.

XRD and SEM show that before calcination, LDH is a lamella material with accumulated spherical particles. After calcination at 450°C, the layered structure of LDH was completely collapsed and those accumulated particles become smaller. This can be confirmed by TGA result, there are no significant changes in the weight loss of the calcined LDH at 50°C to 900°C. This reveals the stable structure of LDH after removal of carbonate and hydroxyl groups by calcination at 450°C. No significant XRD diffraction peaks of metal oxides were detected in metal oxide supported on cLDH, suggesting that metal oxides are well dispersed over cLDH. A decrease in pore volume and pore diameter as well as an increase in surface area of LDH can be observed after calcination. TPD data shows that acid and basic sites are decreased when cLDH was incorporated with metal oxides. This may be because these acid and basic sites are obscured by the incorporated metal oxides.

The study on the effect of contact time can determine reaction pathway for higher alcohols and ethylene production. The higher alcohols occur via Guerbet reaction and the ethylene production occurs by dehydration, as a parallel reaction. The yield of ethylene increased with contact time, but the yield of acetaldehyde and higher alcohols increased only at initial period and no significant increase in yield of higher alcohols can be observed at high contact time. Thus, the dehydration of ethanol to ethylene limits the formation of higher alcohols.

The base modified cLDH can readily neutralize the acid sites as seen by a decrease in dehydration products. However, the dehydrogenation products and higher alcohols were not enhanced. This may be because the active sites for dehydrogenation and hydrogen transfer may be suppressed by base washing.

The activities over K_2O/cLDH and Cs_2O/cLDH are lower than the parent cLDH because the incoporated metal oxides may block the active site for dehydrogenation. For La_2O_3/cLDH, the conversion is slightly increased but the yield of higher alcohols is decreased. This may be due to the low surface area of La_2O_3, leading to lower active surface for aldol condensation. However, ZnO/cLDH shows a remarkably higher activity, as compared to other metal oxides and the parent cLDH.

It can promote dehydrogenation of ethanol to acetaldehyde, and also gives C8 aromatic compounds (2-methylbenzaldehyde and 2-methylbezyl alcohol). This is because Zn ion can stabilize the electron delocalization in the conjugated double bounds of crotonaldehyde, an intermediate for C8 aromatic compounds production.

The reaction temperature has an important effect on H_2 transfer ability of ZnO/cLDH catalyst. At high temperature (400°C), the dehydrogenation and dehydration reactions can be promoted, as higher yield of acetaldehyde and ethylene can be obtained. On the other hand, the yield of higher alcohols is relatively high at low temperature (350°C) because H_2 transfer can be promoted.

5.2 Suggestions for future studies

5.2.1 The synthesis of hydroxyapatite (HAp) by co-precipitation method is difficult to control, especially, the pH of the preparation solution and environment gases (CO_2) strongly affect the structure and surface area of the prepared HAp.

5.2.2 The effect of Mg/Al of LDH on reaction pathway of ethanol conversion should be studied further.

5.2.3 The investigation of other metal oxides incorporated cLDH should be attended, in order to improve the yield of higher alcohols especially aromatic alcohol compounds.

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

$$W/F = \frac{[0.3\ (g)][46\ (gEtOH/mol)]}{[0.7\ (mL/h)][0.789\ (gEtOH/mL)]}$$

$$= 24.98\ g.h/mol$$

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 for products

Product	Peak area
Ethylene	241993
Diethyl ether	24786
Acetaldehyde	386504
Acetone	10811
Butanal	80492
2-Pentanone	18779
Crotonaldehyde	28512
Hexanal	11791
4-Nonanone	4905
C4 alcohols	127412
C6 alcohols	25276
C7 ketones	12849
C8 alcohols	2912
2-methylbenzaldehyde	4056
Acetophenone	4316
2-methylbenzyl alcohol	2009
Ethanol (Feed)	883941
Total	1871344

*Information of the reaction of ethanol to higher alcohols over ZnO/LDH, contact time = 25 g.h/mol, time on stream = 60 minutes, flow rate of carrier gas: N_2 at 60 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:

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

Where A is each product.

For example;

$$\%\text{yield of C4 alcohols} = \frac{127412 \times 100}{1871344} = 6.80$$

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

Table A2 Yield of product derived by normalization method.

Product	Yield(%)
Ethylene	12.93
Diethyl ether	1.32
Acetaldehyde	20.65
Acetone	0.57
Butanal	4.30
2-Pentanone	1.00
Crotonaldehyde	1.52
Hexanal	0.63
4-Nonanone	0.26
C4 alcohols	6.80
C6 alcohols	1.35
C7 ketones	0.68
C8 alcohols	0.15
2-methylbenzaldehyde	0.21
Acetophenone	0.23
2-methylbenzyl alcohol	0.10
Ethanol (Feed)	47.23
Total	100

Conversion

%Conversion can be calculated from the following equation:

$$\%\text{Conversion} = \text{Total yield} - \text{yield of ethanol (Feed)}$$

For example;

$$\%\text{Conversion} = 100 - 47.23$$

$$= 52.77$$

Selectivity

%Selectivity can be obtained from the following equation:

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

For example;

$$\%\text{Selectivity of C4 alcohols} = \frac{6.80 \times 100}{52.77}$$

$$= 12.88$$

APPENDIX B

GAS CHROMATOGRAM

Prior to analysis, the structure of each product in the sample is identified 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 conditions for quantitative analysis

Column	FFAP,
Temperature program	35°C (2 min hold) to 120°C at 10°C/min 120°C (2 min hold) to 200°C (2 min hold) at 10°C/min
Carrier gas	Helium
Column flow rates	1.0
Column velocity	28 cm/s
Injection	250°C
Detector	Flame ionization 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 or Products	Retention time (min)
Ethylene	2.602
Diethyl ether	2.745
Acetaldehyde	2.957
Acetone	3.513
Butanal	3.974
Ethanol	4.739
2-Pentanone	5.129
Crotonaldehyde	6.115
Hexanal	6.622
4-Heptanone	7.273
1-Butanol	7.646
2-Heptanone	8.275
2-Butenol	8.816
2-Ethyl-1-butanol	10.141
4-Nonanone	10.685
1-Hexanol	10.871
2-Ethylhexanol	13.498
1-Octanol	14.623
2-Methylbenzaldehyde	16.064
Acetophenone	16.59
2-Methylbenzyl alcohol	21.209

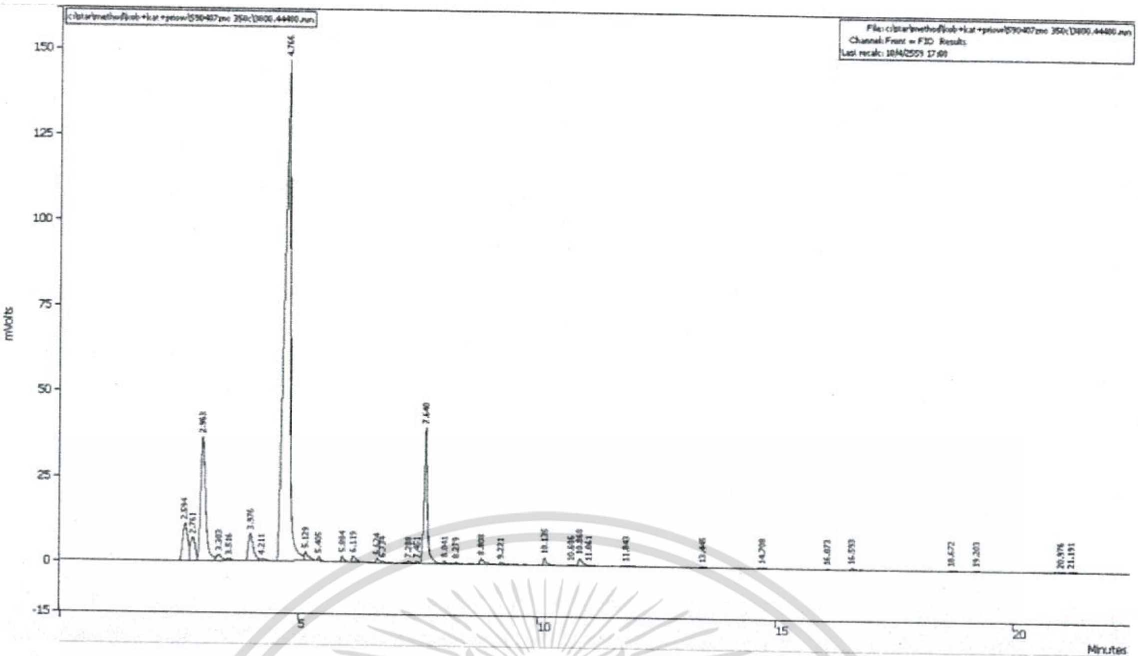

Figure B1 Chromatogram of products over ZnO/LDH at W/F = 25 g.h/mol at 350°C

APPENDIX C

REACTION DATA

1. Conversion of ethanol to higher alcohols over various catalysts

1.1 Ethanol conversion over MgO catalyst

Table C1 The ethanol conversion and yield of products over MgO catalyst

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	8.9	10.4	6.7	6.6	7.1	7.5
Yield of products (%)						
Ethylene	1.9	2.8	1.8	1.9	1.8	2.0
Diethyl ether	0	0	0	0	0	0
Acetaldehyde	2.2	2.4	1.8	1.8	2.2	2.0
Butanal	0.1	0.1	0.1	0.1	0.1	0.1
Crotonaldehyde	0.1	0.1	0	0	0	0
Hexanal	0.1	0.1	0.1	0.1	0.1	0.1
C4 alcohols	4.6	4.8	2.9	2.6	2.9	3.3
C6 alcohols	0.1	0.1	0.1	0.1	0.1	0.1
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

1.2 Ethanol conversion over cLDH catalyst

Table C2 The ethanol conversion and yield of products over Layered double hydroxides (cLDH) catalyst

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	32.7	30.3	30.2	30.6	27.1	25.7
Yield of products(%)						
Ethylene	12.3	11.7	11.4	11.9	9.7	9.0
Diethyl ether	4.8	4.6	4.4	4.2	4.2	4.1
Acetaldehyde	3.9	3.8	3.9	4.0	3.7	3.6
Butanal	0.8	0.7	0.7	0.8	0.6	0.6
Crotonaldehyde	0.1	0.1	0.1	0.1	0.1	0.1
Hexanal	0.1	0.1	0.1	0.1	0.1	0
C4 alcohols	9.6	8.5	8.7	8.7	8.0	7.6
C6 alcohols	1.0	0.9	0.9	0.9	0.8	0.7
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

1.3 Ethanol conversion over HAp catalyst

Table C3 The ethanol conversion and yield of products over Hydroxyapatite (HAp) catalyst

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	49.7	39.5	30.9	30.6	30	28.2
Yield of products(%)						
Ethylene	35.0	29.1	22.1	22.6	22.5	20.8
Diethyl ether	0	0	0	0	0	0
Acetaldehyde	1.8	2.8	2.6	1.9	1.6	1.6
Butanal	1.8	1.1	0.7	0.7	0.7	0.6
Crotonaldehyde	0.2	0.1	0.1	0.1	0.1	0.1
Hexanal	0	0.1	0.1	0.1	0.1	0.1
C4 alcohols	9.8	6.0	5.0	4.9	4.8	4.8
C6 alcohols	1.0	0.4	0.2	0.2	0.3	0.2
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

2. Conversion of ethanol to higher alcohols over cLDH catalyst

2.1 Effect of contact time over cLDH catalyst

Table C4 The ethanol conversion and yield of products at contact time of 60 g.h/mol

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	46.3	45.2	46.1	44.4	41	43.9
Yield of products (%)						
Ethylene	15.6	15.9	16.3	14.8	13.3	15.9
Diethyl ether	5.3	5.2	5.1	5.6	5.3	4.9
Acetaldehyde	5.3	5.4	5.4	5.4	5.0	5.0
Butanal	2.0	2.0	2.0	1.7	1.5	1.8
Crotonaldehyde	0.3	0.3	0.2	0.3	0.2	0.1
Hexanal	0.3	0.2	0.2	0.2	0.2	0.2
C4 alcohols	14.4	13.4	14.2	13.8	13.1	13.9
C6 alcohols	2.7	2.3	2.3	2.2	2.1	2.1
C8 alcohols	0.4	0.3	0.3	0.3	0.3	0.1
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 60 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C5 The ethanol conversion and yield of products at contact time of 100 g.h/mol

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	61.8	57.2	58	59.2	57.8	56.3
Yield of products (%)						
Ethylene	26.3	22.9	22.7	23	23.9	21.0
Diethyl ether	6.9	6.4	7.8	7.3	7.8	7.6
Acetaldehyde	5.9	5.6	5.7	5.6	5.8	5.4
Butanal	2.9	2.5	2.6	2.4	2.5	2.2
Crotonaldehyde	0.3	0.3	0.3	0.3	0.3	0
Hexanal	0.5	0.4	0.4	0.4	0.3	0.3
C4 alcohols	14.4	14.9	14.7	15.9	14.0	15.9
C6 alcohols	4.0	3.4	3.3	3.7	2.9	3.3
C8 alcohols	0.6	0.8	0.6	0.6	0.3	0.6
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 100 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C6 The ethanol conversion and yield of products at contact time of 150 g.h/mol

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	67.9	64.3	66	62.7	61.2	58.5
Yield of products (%)						
Ethylene	31.9	27.7	30.3	28.3	26.8	24.9
Diethyl ether	7.1	6.3	6.2	6.7	6.0	6.7
Acetaldehyde	5.7	5.4	5.7	5.6	5.4	5.4
Butanal	2.8	2.7	2.8	2.7	2.5	2.4
Crotonaldehyde	0.3	0.3	0.3	0.3	0.3	0.3
Hexanal	0.5	0.4	0.4	0.4	0.4	0.3
C4 alcohols	14.6	15.6	14.8	14.4	15.1	14.7
C6 alcohols	4.1	4.9	4.6	3.6	3.8	3.4
C8 alcohols	0.8	0.9	0.8	0.6	0.7	0.4
2-Methylbenzaldehyde	0.1	0.1	0	0	0	0
2-Methylbenzyl alcohol	0.1	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 150 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

3. Conversion of ethanol to higher alcohols over metal incorporated cLDH catalysts

3.1 Effect of washing method

Table C7 The ethanol conversion and product yield of KOH/cLDH

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	23.4	19	18.2	18.4	18.7	18.3
Yield of products (%)						
Ethylene	13.3	10.5	10.0	10.2	10.6	9.9
Diethyl ether	0	0	0	0	0	0
Acetaldehyde	3.2	3.3	3.2	3.2	3.3	3.1
Butanal	0.3	0.3	0.4	0.3	0.3	0.3
Crotonaldehyde	0.2	0.2	0.2	0.2	0.2	0.2
Hexanal	0	0	0	0	0	0
C4 alcohols	5.7	4.2	4.0	4.1	4.0	4.3
C6 alcohols	0.6	0.5	0.4	0.4	0.4	0.5
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C8 The ethanol conversion and product yield of $KMnO_4$/cLDH

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	25.2	35.4	27.9	32.7	32.3	31
Yield of products (%)						
Ethylene	12.6	19.4	14.5	17.5	16.8	16.9
Diethyl ether	2.3	2.1	2	2.1	2.1	2
Acetaldehyde	5.3	6.9	5.9	7.0	7.1	6.4
Butanal	1.1	1.3	1.1	1.2	1.2	1.2
Crotonaldehyde	0.3	0.4	0.4	0.4	0.4	0.4
Hexanal	0	0	0	0	0	0
C4 alcohols	3.2	4.6	3.7	4.0	4.1	3.7
C6 alcohols	0.5	0.5	0.5	0.4	0.5	0.4
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

3.2 Effect of incorporated metal oxides

Table C9 The ethanol conversion and product yield of La_2O_3/cLDH

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	30.7	28.7	26.5	31.2	28.2	28.8
Yield of products (%)						
Ethylene	11.5	10.3	10.7	14.7	11.8	12.7
Diethyl ether	5.4	5.9	4.1	4.2	4.0	4.2
Acetaldehyde	4.5	4.4	3.6	3.4	3.6	0.5
Butanal	0.7	0.7	0.6	0.6	0.5	0.5
Crotonaldehyde	0.1	0.1	0.1	0.1	0.1	0.1
Hexanal	0.1	0	0	0	0	0
C4 alcohols	7.6	6.7	6.8	7.5	7.3	6.8
C6 alcohols	0.9	0.7	0.7	0.8	0.8	0.8
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C10 The ethanol conversion and product yield of ZnO/cLDH

Time on stream(min)	60	120	180	240	300	360
Conversion (%)	51.4	44.3	44.5	41.7	44.7	41.3
Yield of products (%)						
Ethylene	13.3	10.7	11.4	8.9	10.9	7.8
Diethyl ether	1.4	1.2	0.8	1.4	1.4	2.0
Acetaldehyde	21.2	17.6	17	17.7	16.7	18.5
Butanal	4.4	4.2	4.2	3.6	3.9	3.3
Crotonaldehyde	1.6	1.4	1.6	1.4	1.9	1.3
Hexanal	0.6	0.5	0.6	0.6	0.8	0.4
C4 alcohols	7.0	6.9	7.1	6.4	7.2	6.4
C6 alcohols	1.4	1.2	1.2	1.2	1.3	1.1
C8 alcohols	0.2	0.2	0.2	0.2	0.2	0.2
2-Methylbenzaldehyde	0.2	0.2	0.2	0.2	0.2	0.2
2-Methylbenzyl alcohol	0.1	0.1	0.2	0.1	0.2	0.1

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C11 The ethanol conversion and product yield of Cs_2O/cLDH

Time on stream (min)	60	120	180	240	300	360
conversion (%)	28.3	28.7	24.8	27.8	24.9	26.9
Yield of products (%)						
Ethylene	18.4	17.9	15.5	17.3	14.4	16.4
Diethyl ether	0	0	0	0	0	0
Acetaldehyde	3.0	3.0	3.5	3.2	3.6	2.9
Butanal	0.4	0.5	0.5	0.5	0.4	0.4
Crotonaldehyde	0.2	0.2	0.1	0.2	0.1	0.1
Hexanal	0	0	0	0	0	0
C4 alcohols	5.2	6.1	4.5	5.6	5.6	6.1
C6 alcohols	0.9	1.0	0.7	1.0	0.8	0.9
C8 alcohols	0.1	0.1	0	0.1	0.1	0.1
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 380°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C12 The ethanol conversion and product yield of K_2O/cLDH

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	15.6	15.8	13.3	16.5	12.6	13.7
Yield of products (%)						
Ethylene	7.9	8	6.7	8.8	6.3	7.3
Diethyl ether	0	0	0	0	0	0
Acetaldehyde	3.9	3.9	3.3	2.9	3.2	3.3
Butanal	0.3	0.3	0.3	0.3	0.2	0.3
Crotonaldehyde	0.2	0.2	0.2	0.2	0.1	0.1
Hexanal	0	0	0	0	0	0
C4 alcohols	3.0	3.1	2.6	3.9	2.4	2.5
C6 alcohols	0.2	0.3	0.3	0.4	0.3	0.3
C8 alcohols	0	0	0	0	0	0
2-Methylbenzaldehyde	0	0	0	0	0	0
2-Methylbenzyl alcohol	0	0	0	0	0	0

(Reaction condition; temperature: 350°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

4. Conversion of ethanol to higher alcohols over ZnO/cLDH catalysts

4.1 Effect of reaction temperature over ZnO/cLDH

Table C13 The ethanol conversion and yield of products at 350°C

Time on stream (min)	60	120	180	240	300	360
Conversion (%)	36.8	35.2	36.6	34.8	34.1	32.7
Yield of products (%)						
Ethylene	4.2	3.9	4.2	3.9	3.7	3.5
Diethyl ether	2.8	2.7	2.5	2.5	2.5	2.5
Acetaldehyde	13.2	13.4	13.6	13.6	13.7	13.5
Butanal	2.9	3.0	3.1	3.0	2.8	2.5
Crotonaldehyde	0.6	0.6	0.7	0.6	0.6	0.6
Hexanal	0.4	0.3	0.3	0.2	0.2	0.2
C4 alcohols	10.8	9.8	10.6	9.5	9.1	8.4
C6 alcohols	1.4	1.2	1.2	1.1	1.1	1.1
C8 alcohols	0.3	0.2	0.2	0.2	0.2	0.2
2-Methylbenzaldehyde	0.1	0.1	0.1	0.1	0.1	0.1
2-Methylbenzyl alcohol	0.1	0.1	0.1	0.1	0.1	0.1

(Reaction condition; temperature: 350°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C14 The ethanol conversion and yield of products at 400°C

Time on stream (min)	60	120	180	240	300
Conversion (%)	61.8	60.6	60.3	60.9	60.8
Yield (%)					
Ethylene	15.8	15	15.6	14.9	15.3
Diethyl ether	1.5	1.2	0.9	1.0	0.9
Acetaldehyde	25	24.5	25.3	24.8	25.2
Butanal	7.0	6.7	6.8	6.7	6.8
Crotonaldehyde	2.4	2.4	2.6	2.7	2.7
Hexanal	0.8	1.1	1.1	1.1	0.7
C4 alcohols	6.5	6.4	5.5	5.8	5.7
C6 alcohols	1.3	1.5	1.3	1.7	1.5
C8 alcohols	0.4	0.5	0.2	0.5	0.4
2-Methylbenzaldehyde	0.7	0.8	0.5	0.9	0.8
2-Methylbenzyl alcohol	0.4	0.6	0.5	0.8	0.7

(Reaction condition; temperature: 400°C, pressure: 1 atm, contact time: 25 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

4.2 Effect of contact time over ZnO/LDH catalyst

Table C15 The ethanol conversion and yield of products at contact time of 15 g.h/mol

Time on stream (min)	60	120	180	240	300
Conversion (%)	27.4	27.4	25.8	24.5	22.4
Yield of products (%)					
Ethylene	3.1	3.0	2.8	2.5	2.1
Diethyl ether	1.7	1.6	1.5	1.4	1.4
Acetaldehyde	11.5	11.5	11.1	10.6	10.0
Butanal	1.8	1.8	1.7	1.5	1.3
Crotonaldehyde	0.5	0.5	0.5	0.4	0.4
Hexanal	0.2	0.2	0.1	0.1	0.1
C4 alcohols	7.2	7.7	7.1	6.8	6.2
C6 alcohols	1.0	0.8	0.7	0.7	0.7
C8 alcohols	0.2	0.2	0.1	0.1	0.1
2-Methylbenzaldehyde	0.1	0.1	0.1	0.1	0.1
2-Methylbenzyl alcohol	0.1	0.1	0.1	0.1	0.1

(Reaction condition; temperature: 350°C, pressure: 1 atm, contact time: 15 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

Table C16 The ethanol conversion and yield of products at contact time of 50 g.h/mol

Time on stream (min)	60	120	180	240	300
Conversion (%)	27.4	27.4	25.8	24.5	22.4
Yield of products (%)					
Ethylene	3.1	3.0	2.8	2.5	2.1
Diethyl ether	1.7	1.6	1.5	1.4	1.4
Acetaldehyde	11.5	11.5	11.1	10.6	10
Butanal	1.8	1.8	1.7	1.5	1.3
Crotonaldehyde	0.5	0.5	0.5	0.4	0.4
Hexanal	0.2	0.2	0.1	0.1	0.1
C4 alcohols	7.2	7.7	7.1	6.8	6.2
C6 alcohols	1.0	0.8	0.7	0.7	0.7
C8 alcohols	0.2	0.2	0.1	0.1	0.1
2-Methylbenzaldehyde	0.1	0.1	0.1	0.1	0.1
2-Methylbenzyl alcohol	0.1	0.1	0.1	0.1	0.1

(Reaction condition; temperature: 350°C, pressure: 1 atm, contact time: 50 g.h/mol, flow rate of N_2 carrier gas: 60 mL/min)

APPENDIX D

CATALYST CHARACTERIZATION

X-RAY DIFFRACTION PATTERN OF CATALYST

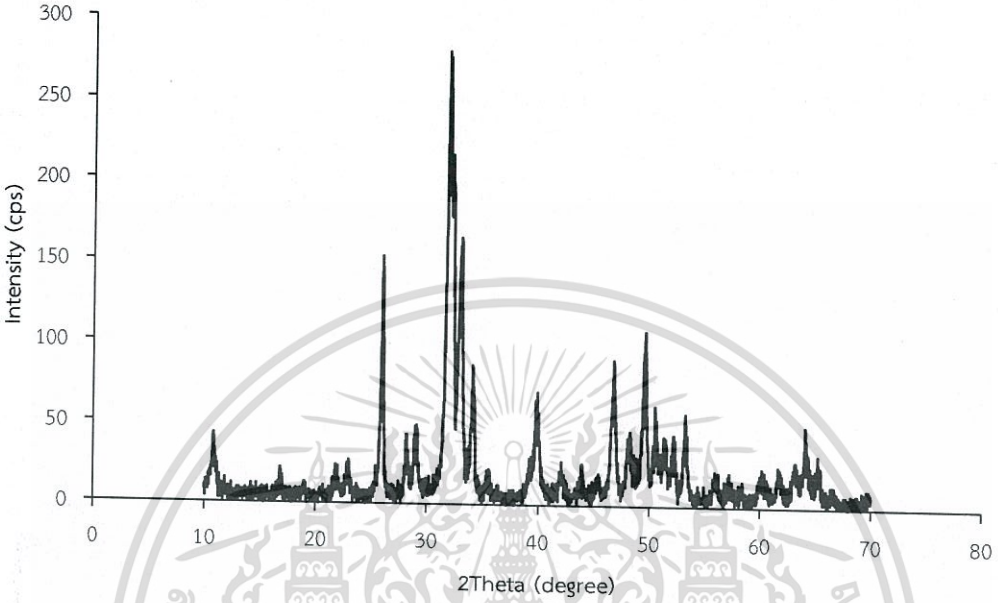

Figure D1 X-ray diffraction pattern of hydroxyapatite (HAp)

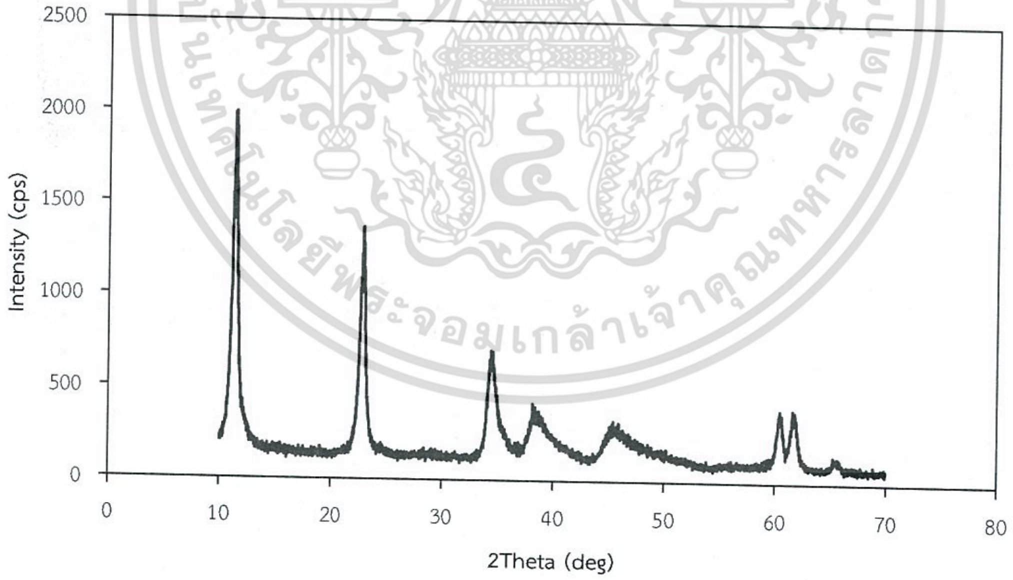

Figure D2 X-ray diffraction pattern of non-calcined LDH

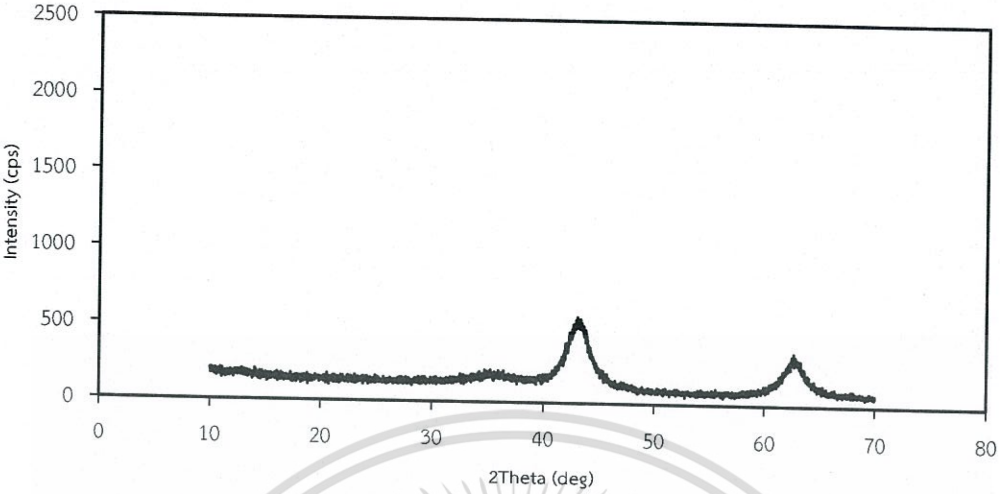

Figure D3 X-ray diffraction pattern of calcined LDH

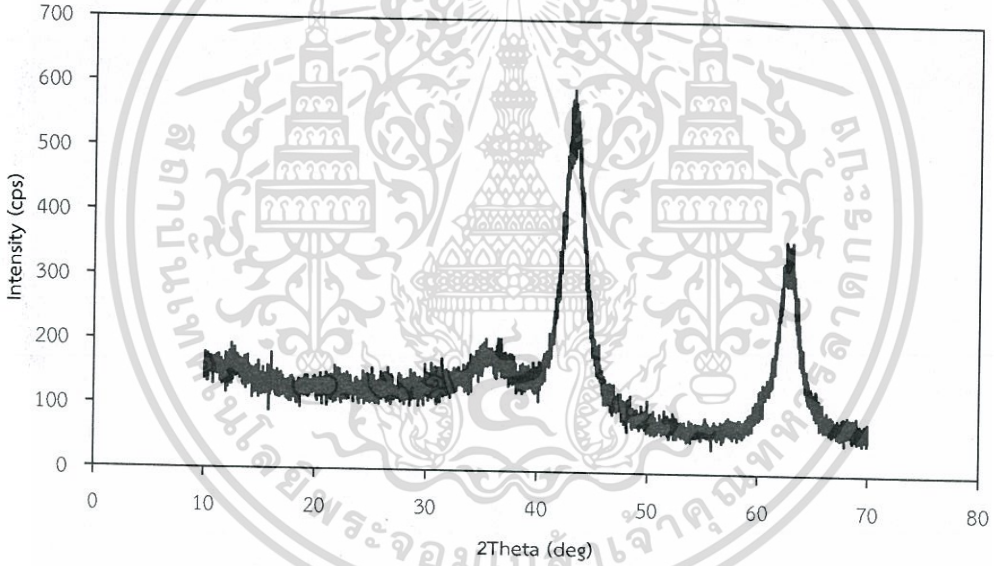

Figure D4 X-ray diffraction pattern of calcined K_2O/cLDH

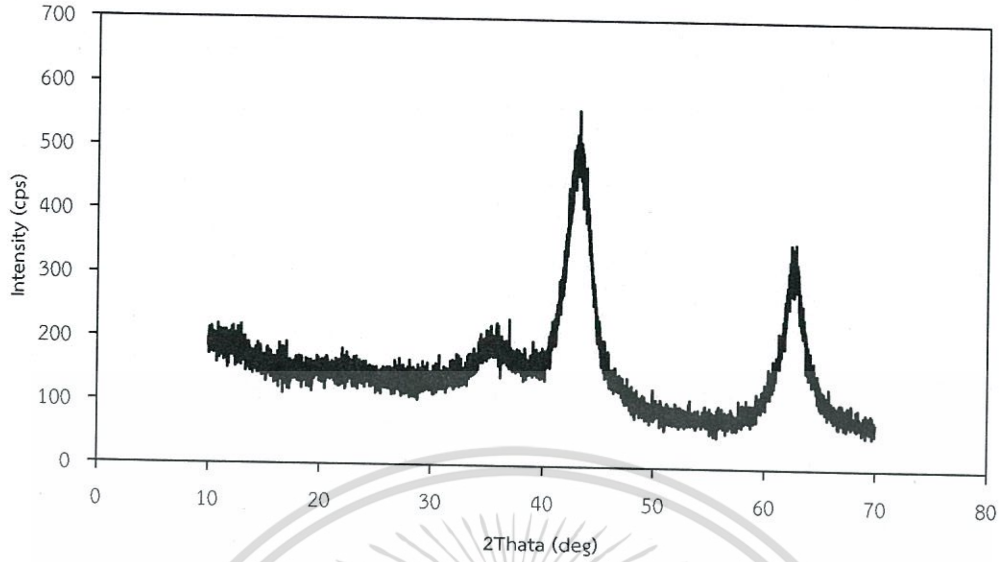

Figure D5 X-ray diffraction pattern of calcined ZnO/cLDH

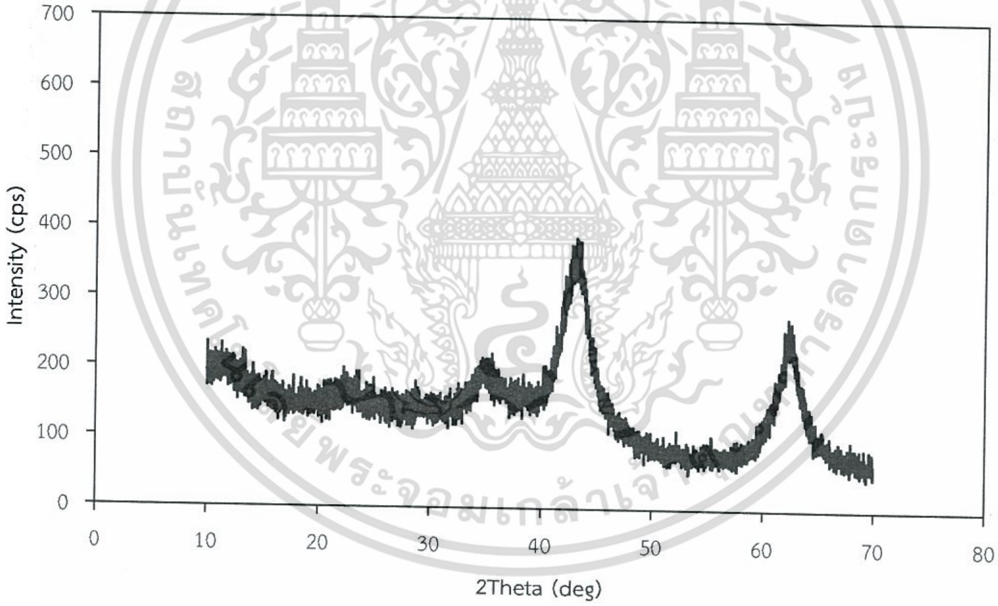

Figure D6 X-ray diffraction pattern of calcined Cs_2O/cLDH

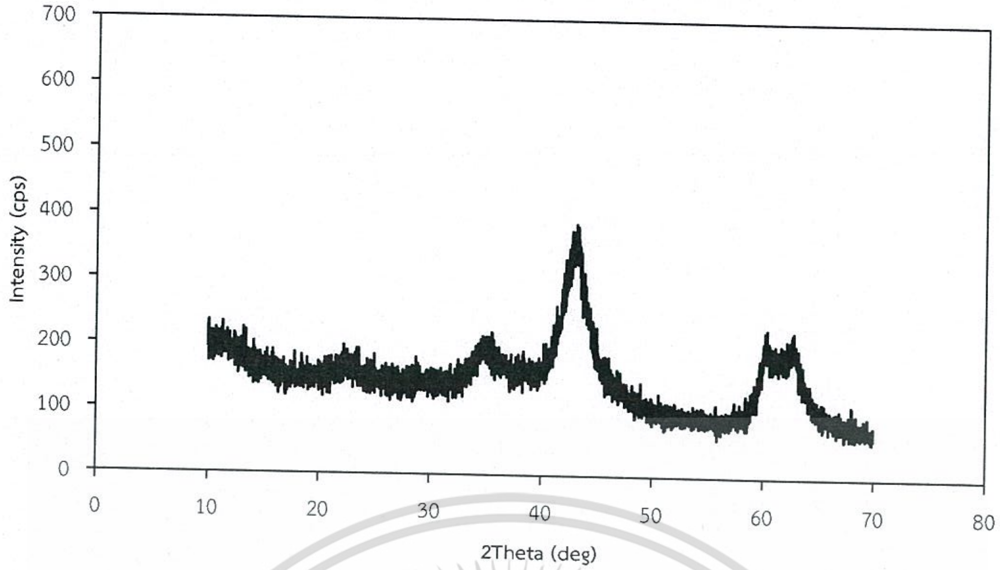

Figure D7 X-ray diffraction pattern of calcined La_2O_3/cLDH

ADSORPTION-DESORPTION ISOTHERM

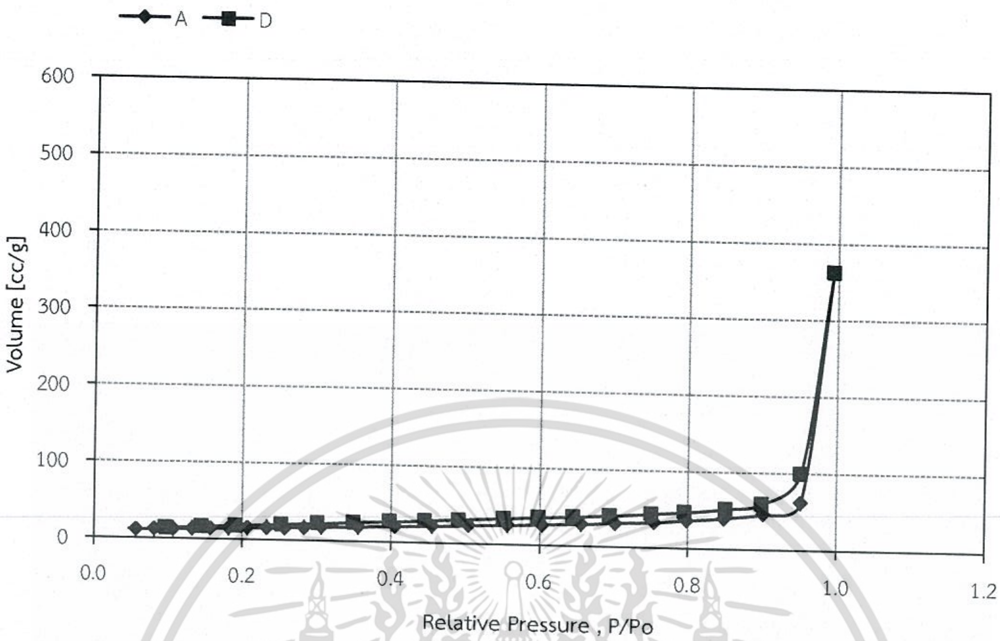

Figure D8 Adsorption-Desorption Isotherm of hydroxyapatite (HAp)

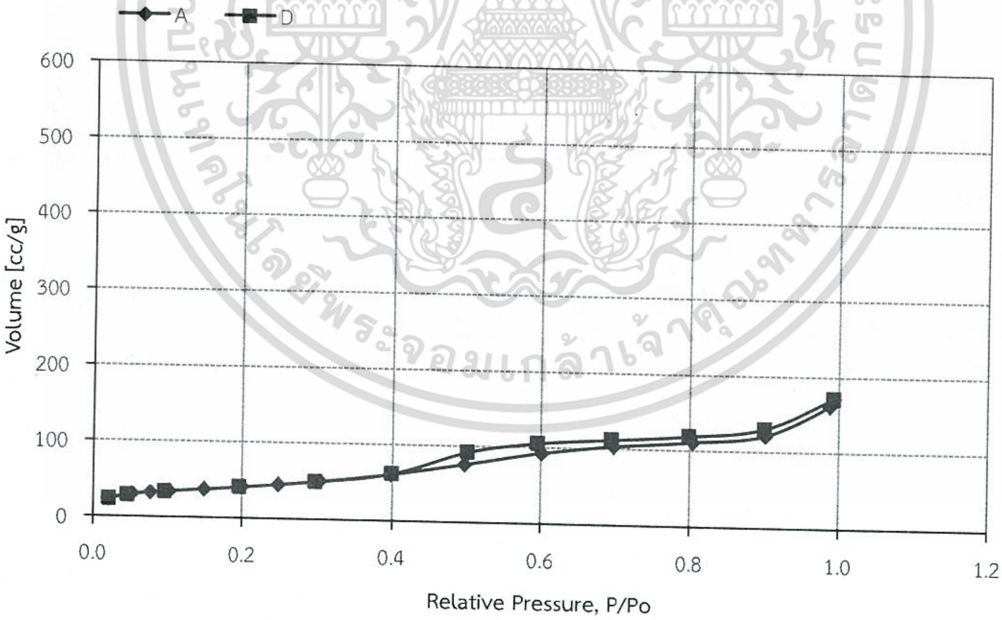

Figure D9 Adsorption-Desorption Isotherm of MgO

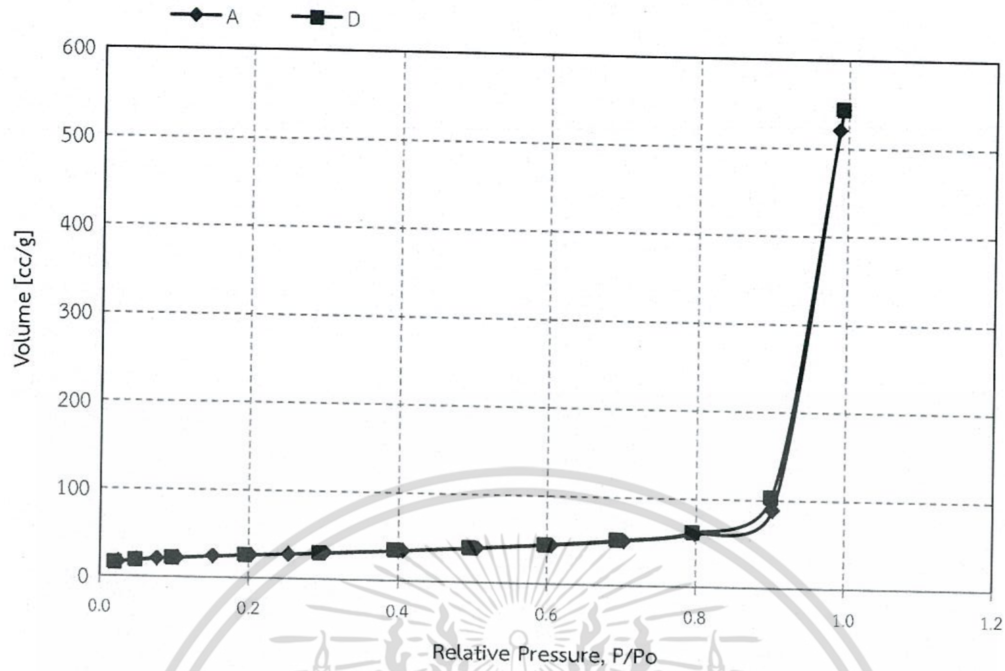

Figure D10 Adsorption-Desorption Isotherm of non-calcined LDH

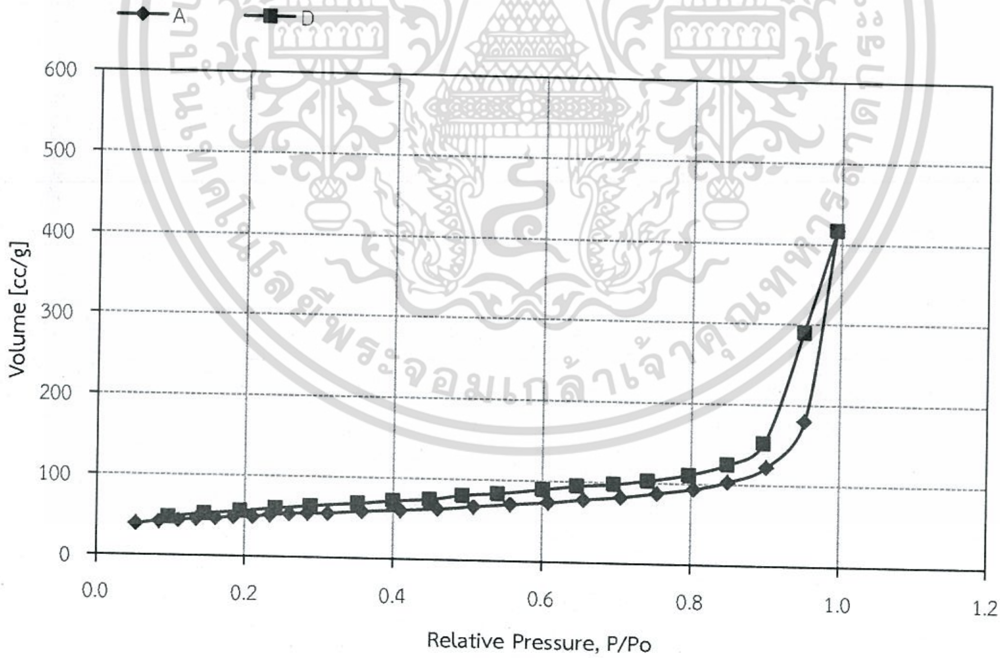

Figure D11 Adsorption-Desorption Isotherm of calcined LDH

TEMPERATURE PROGRAMED DESORPTION

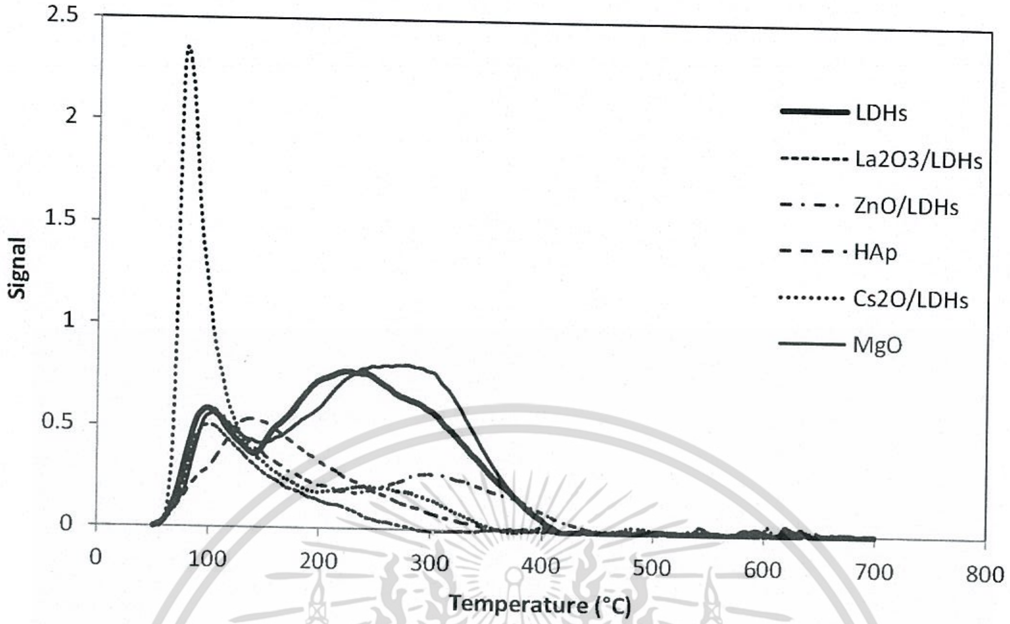

Figure D12 CO_2 TPD profile

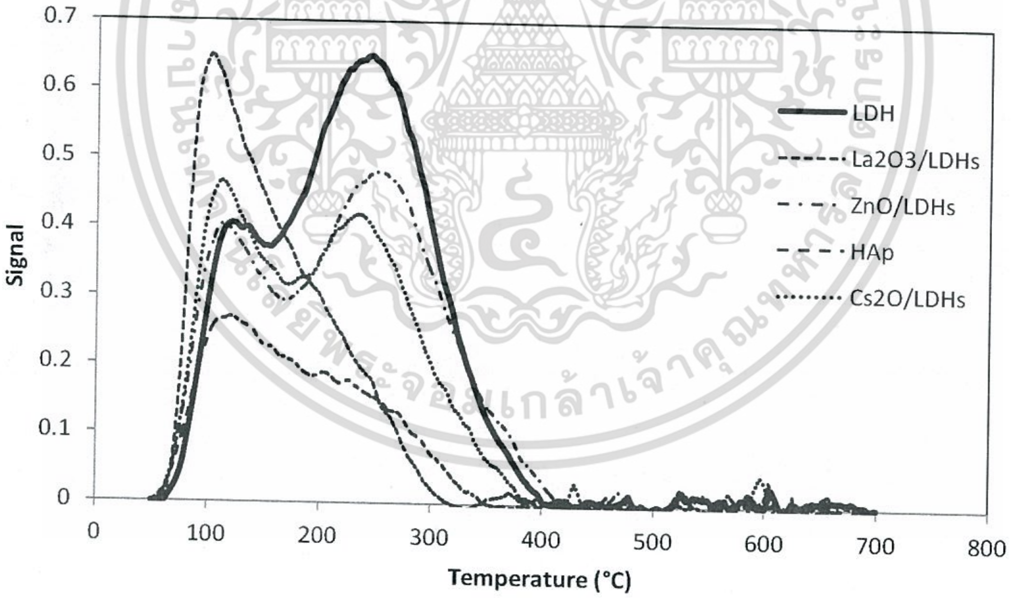

Figure D13 NH_3 TPD profile