การเปลี่ยนโพรพิโอนัลดีไฮด์เป็น 3-ไฮดรอกซี-2-เมทิลเพนทานาล
ด้วยปฏิกิริยา อัลดอล คอนเดนเซชั่น ในวัฏภาคของเหลว
LIQUID PHASE ALDOL CONDENSATION OF PROPIONALDEHYDE
TO 3-HYDROXY 2-METHYLPENTANAL

นางสาวมุทิตา พลอยพงศ์
นางสาวณัฐนิชา แสงวิเชียร
นางสาวพัชราพรรณ คัมราใบ

โครงงานพิเศษนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิทยาศาสตรบัณฑิต
สาขาวิชา เคมีอุตสาหกรรม
คณะวิทยาศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
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นางสาวณัฐนิชา แสงวิเชียร
นางสาวพัชราพรรณ อัมราใบ

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LIQUID PHASE ALDOL CONDENSATION OF PROPIONALDEHYDE TO 3-HYDROXY-2-METHYLPENTANAL

CHAPISA PHALHAPONG
NUTNICHA SANGVICHEAN
PUTCHARAPAN AMMARABAI

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Project Title	Liquid phase aldol condensation of propionaldehyde to 3-hydroxy-2-methylpentanal		
Student	Miss Chapisa	Phalhapong	53050201
	Miss Nutnicha	Sangvichean	53050220
	Miss Putcharapan	Ammarabai	53050293
Degree	Bachelor of Science		
Program	Industrial Chemistry		
Year	2013		
Advisor	Assoc. Prof. Dr. Tawan Sooknoi		
Co- advisor	Dr. Tosapol Maluangnont		

Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, has approved this special project submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in academic year 2013.

Committees	**Signatures**
Dr. Amnat Permsubscul	
Asst. Prof. Dr. Montree Thongkam	
Assoc. Prof. Dr. Tawan Sooknoi	
Dr. Tosapol Maluangnont	T. Maluangnont

Project Title	Liquid phase aldol condensation of propionaldehyde to 3-hydroxy-2-methylpentanal	
Student	Chapisa Phalhapong	53050201
	Nutnicha Sangvichean	53050220
	Putcharapan Ammarabai	53050293
Degree	Bachelor of Science	
Program	Chemistry	
Year	2013	
Project Advisor	Assoc. Prof. Dr. Tawan Sooknoi	

ABSTRACT

Synthesized hydrotalcites Mg/Al molar ratio 1.5, hydrotalcites Mg/Al molar ratio 2.5 form co-workers (HT 1.5, HT 2.5) and commercial layered double hydroxides (LDH) were investigated for aldol condensation of propionaldehyde using methanol as solvent at 50 - 70°C. Hydrotalcites converted to Mg-Al mixed oxide during calcination at 450°C. This is leads to increases in basicity and surface area of the catalysts. The surface area and basicity of HT-2.5 (153 m^2/g, 8.4 mmol/g) is lower than that of HT-1.5 (200 m^2/g, 8.8 mmol/g) and LDH (266 m^2/g, 11 mmol/g) respectively. The conversion of propionaldehyde increased with reaction time. HT-2.5 gives higher conversion of propionaldehyde and yield of 3-hydroxy-2-methylpentanal, as compared to those of HT-1.5 and LDH. Primary product, 3-hydroxy-2-methylpentanal can dehydrate to 2-methylpentenal that can be coupled with propionaldehyde to form 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane as by-product. The adsorption of products over the catalysts with high surface area were occurred. The calcined catalysts give conversion of propionaldehyde higher than that of the non-calcined catalysts. The reactions at 50°C, the higher selectivity of 3-hydroxy-2-methylpentanal is obtained but aldol product was found. At 70°C lower selectivity of 3-hydroxy-2-methylpentanal is observed. Appreciated condition for high selectivity of 3-hydroxy-2-methylpentanal is at 60°C.

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Chapisa Phalhapong
Nutnicha Sangvichean
Putcharapan Ammarabai

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CHAPTER 1

INTRODUCTION

1.1 Motivation

1, 3-Butanediol is commonly used as a solvent for food flavoring agents and co-monomer for certain polyurethane and polyester resins[1]. 1,3-Butanediol can be obtained from hydrogenation of 3-hydroxybutanal that is the product from self-aldol condensation of acetaldehyde. While, acetaldehyde is a biomass-derived aldehydes, prepared by the partial oxidation of ethanol [2] from cellulosic biomass such as corn leaves and stalks [3]. Therefore use of acetaldehyde as chemical feed stocks is of interest and eco-friendly.

3-Hydroxybutanal is generally observed as by-product since the aldol products can often undergo dehydration (loss of water) to give α,β-unsaturated aldehyde. In the mechanistic point of view, when the acid catalysts is used, the acid attacks on the hydroxyl group of aldol product. This usually dehydrates to give the unsaturated carbonyl compound [4]. In contrast, over base catalysts, dehydration is more difficult because the intermediate formed is a carbanion. Moreover, the hydroxyl group is not a good leaving group [5]. Accordingly, it is possible to obtain high selectivity of 3-hydroxybutanal using solid base catalyst.

Recently, hydrotalcites (HT) and alkali ion-exchanged zeolites have received much attention as solid base catalysts [6,8]. The results indicated that the selectivity of 3-hydroxybutanal over alkali ion-exchanged zeolites catalyst is less than that over hydrotalcites. The increase in the selectivity of 3-hydroxybutanal is due to the increased basicity of hydrotalcites that depending on Mg-content and hydroxyl groups. However, the reaction with solvent free at high temperature reaction (100 °C) gives lower selectivity of hydroxyl-aldehyde because dehydration occurs to give unsaturated-aldehyde [9]. Therefore, use of solvent at lower temperature will be studied in this work. Solid base catalyst such as commercial layered double hydroxides (LDH) were investigated as compare with the synthesized hydrotalcites. However, acetaldehyde is quickly evaporated and difficult to handle in liquid phase reaction at atmospheric pressure. Therefore, The catalysts were tested for aldol condensation of propionaldehyde to 3-hydroxy-2-methylpentanal as model compound for aldol condensation.

1.2 Objective

1.2.1 To obtain appropriate base catalyst and condition for aldol condensation of propionaldehyde to 3-hydroxy-2-methylpentanal.

1.2.2 To understand the effect of composition solid bases catalyst.

1.2.3 To understand the effect of temperature.

1.2.4 To understand the effect of time.

1.3 Scope of study

The scopes of study on self-aldol condensation of acetaldehyde in a bomb reactor over solid base catalysts are as follows:

1.3.1 Catalyst preparation by co-precipitation method at constant pH.

1.3.2 Characterization of solid base catalysts by Power X-ray Diffraction (P-XRD), Brunauer–Emmett–Teller (BET) and Thermogravimetric analysis (TGA).

1.3.3 Study effect of reaction temperature ranging from 50 to 70 °C

1.3.4 Study effect of reaction time ranging from 10 to 30 hours.

1.3.5 Analysis and quantification of products by Gas chromatography with flame ionization detector (GC-FID).

1.4 Expected results

It is expected that a new technology for production of 3-hydroxybutanal from acetaldehyde. 3-hydroxybutanal can be utilized in the production of 1,3butanediol in the industry.

CHAPTER 2

THEORY AND LITERATER REVIEWS

2.1 Aldol condensation

In an "aldol addition" reaction an enol or enolate of an aldehyde or ketone reacts with a second aldehyde or ketone forming a new carbon-carbon bond. This makes the aldol reaction an important reaction for organic synthesis. Originally, the aldol reaction used ethanal (see below) and therefore the product contained both an aldehyde and an alcohol functional group; thus it became known as the aldol reaction.

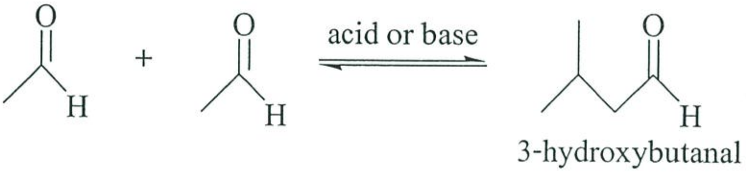


Fig. 2.1 Aldol reaction of ethanal.

The aldol addition demonstrates how carbonyl compounds can react as both an electophile and a nucleophile. The aldol reaction requires an aldehyde or ketone that contains at least one α-hydrogen (theα-hydrogen is on the carbon adjacent to the C=O group) since the α-hydrogen is required in order to form the enol or enolate.

In the base-catalysed aldol reaction, the relatively acidic hydrogen on the α-carbon (typical pKa 16-20) is deprotonated by a base to form the enolate. The enolate reacts as a carbon nucleophile that can then react with the electrophilic carbonyl carbon of another aldehyde or ketone molecule. Depending on the strength of the base used, the extent of deprotonation can be controlled. If a strong base is used (such as lithium diisopropylamide, LDA) then deprotonation is quantitative (100%). If weaker bases such as hydroxide or alkoxides are used, then there is equilibrium deprotonation (i.e. only a small amount of enolate is present at any one time).

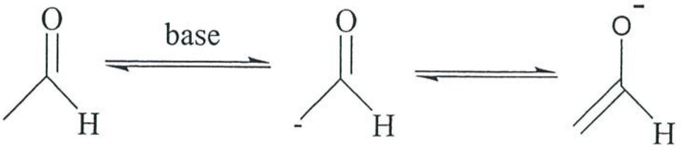


Fig. 2.2 Equilibrium for the aldol reaction

The equilibrium for the aldol reaction can lie in the direction of reactants or products, depending on their structure and the reaction conditions. The aldol product can often undergo elimination of water (i.e. dehydration) to give an α,β-unsaturated aldehyde or ketone, that contains a conjugated carbonyl group.The overall process is then referred to as an "aldol condensation".

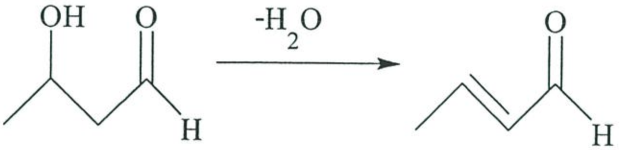


Fig. 2.3 Dehydration of 3-hydroxybutanal

The example using ethanal shown above only involves one starting material and is therefore referred to as a "self-aldol condensation". "Mixed" or "crossed" aldol condensations occur when two different molecules containing carbonyl groups are combined.

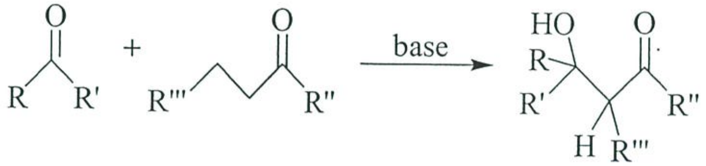


Fig. 2.4 Cross-aldol condensation of two different ketone

A generic mixed aldol reaction where two different carbonyl-containing molecules are mixed together. In terms of the scope of the reaction, the R-groups can be alkyl, aryl or H. This ability to join different aldehydes and ketones together with some degree of control is what gives this process its synthetic value. Typically, a mixed aldol condensation is only practical if one of the compounds has no α-hydrogens – thus only one enol or enolate is generated and so there is only a single nucleophile formed.

The mixed aldol reaction typically occurs between an aldehyde that has no α-hydrogens, and a ketone. Thus, the nucleophile is generated solely from the ketone. The aldehyde is usually more reactive towards nucleophiles than the ketone, further reducing the possibility of the ketone undergoing unwanted self-condensation. Minimizing any unwanted self-condensation of the ketone can also be achieved by taking care with the order in which the reagents are added. In the example below, the ketone would be added to a mixture containing the aldehyde and the base. This means that the ketone enolate forms in the presence of excess aldehyde.

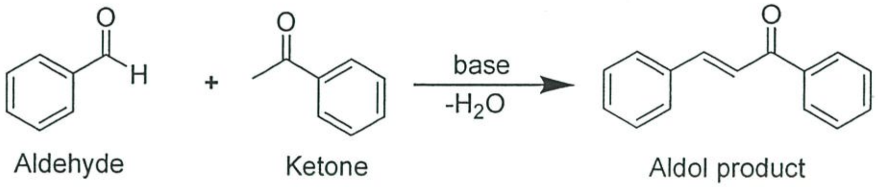


Fig. 2.5 Cross-aldol condensation of aldehyde and ketone

In contrast, prolonged contact between the ketone and base in the absence of the aldehyde can result in self-condensation of the ketone (in this case an unwanted side reaction).

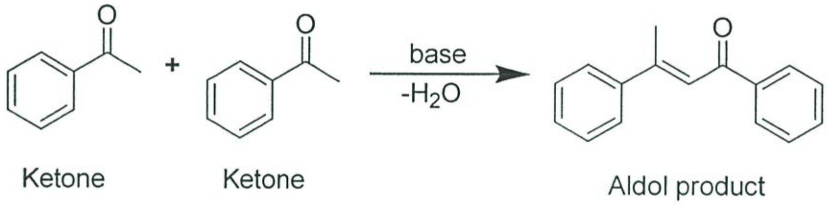


Fig. 2.6 Self-aldol condensation of ketone

In this experiment you will be reacting two equivalents of an aldehyde with a ketone (which is the limiting reagent), according to the following general scheme:

You will not be told the identity of either the aldehyde or ketone, but are expected to identify them once the product has been characterized. Melting point analysis of your products can be compared to the literature values provided, allowing you to deduce the identity of your starting aldehyde and ketone. The accuracy of your melting points is crucial to identifying your product, making this experiment a critical test of the practical skills that you have acquired in you chemistry career to date.

2.1.1 Self Aldol condensation

Aldol condensation reactions represent an important class of reactions for forming carbon-carbon bonds. In the aldol reaction, two carbonyl compounds are condensed to form a β-hydroxyaldehyde or β-hydroxyketonethe aldol product. The classic aldol reaction is a "self-condensation" of the reactant aldehyde or ketone where one molecule adds to another of the same type. An example of a self-condensation aldol reaction is shown in Fig. 2.7, using acetaldehyde as the sole reactant. Here, the aldol product, 3-hydroxybutanal, is the result of adding acetaldehyde to another acetaldehyde reactant molecule to form the aldol (aldehyde-alcohol) product.

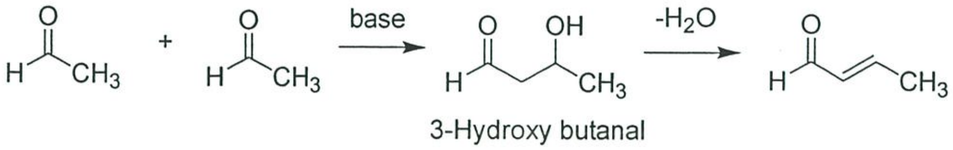


Fig. 2.7 Aldol self-condensation of acetaldehyde

Fig. 2.7 Aldol self-condensation of acetaldehyde. When carried out under base-catalyzed conditions, the aldol reaction proceeds via an enolate ion (**Fig. 2.8**). The resonance stabilized enolate then undergoes nucleophilic addition to the carbonyl carbon of another aldehyde or ketone molecule, forming a new C-C bond and an alkoxide ion (**Fig. 2.9**).

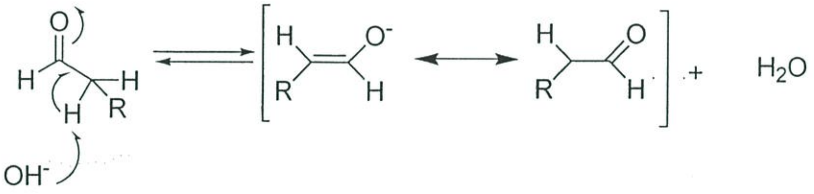


Fig. 2.8 Enolate ion was produced by base catalysts

Fig. 2.8 Step 1 – Base-catalyzed production of the enolate ion in the aldol self-condensation reaction (R = H, alkyl, phenyl)

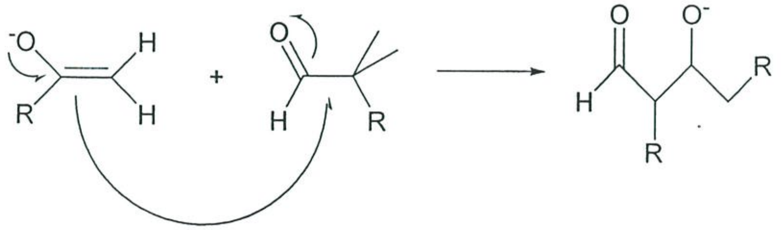


Fig. 2.9 Nucleophilic addition of enolate anion to the carbonyl group

Fig. 2.9 Step 2 – Nucleophilic addition of enolate anion to the carbonyl group (R = H, alkyl, phenyl)The β-hydroxy aldehyde or ketone is then formed in the next step by reaction with water, and the reaction is finalized by dehydration of the alcohol group in a strong base, resulting in the loss of water and the formation of an α,β-unstaturated product (**Fig. 2.10**).

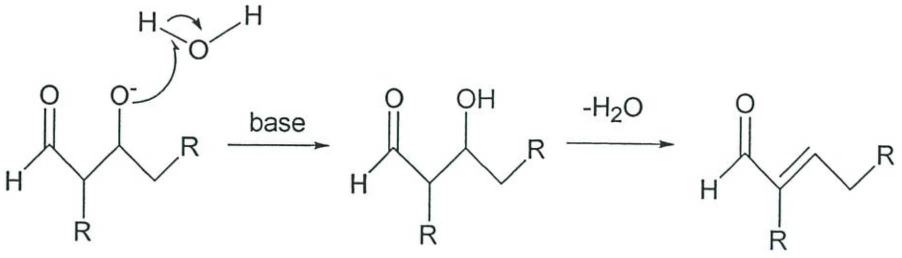


Fig. 2.10 Protonation and dehydration to an α,β-unsaturated carbonyl product

Fig. 2.10 Step 3 and 4 – Formation of the aldol product and dehydration to an α,β-unsaturated carbonyl product. Similar self-condensation reactions will occur for ketones, as well as derivatized aldehydes and ketones, so long as an enolizable proton at the α-carbon position exists

self-aldol condensation of acetaldehyde to 1,3-butanediol

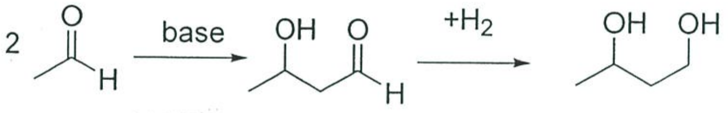


Fig. 2.11 Self-aldol condensation and reduction to 1,3-butanediol

From self-aldol condensation of acetaldehyde, hydroxides functions as a base and removes the acidic α-hydrogen giving the reactive enolate. The nucleophilicenolate attacks the aldehyde at the electrophilic carbonyl C in a nucleophilic addition type process giving an intermediate alkoxide. The alkoxide deprotonates a water molecule creating hydroxide and the β-hydroxyaldehydes.3-Hydroxybutanal is reduced to 1,3-butanediol with a Ni catalyst at 110 □C and 300 bar [10].

2.1.2 Cross Aldol condensation

Crossed aldol reactions between aldehydes and ketones result in the formation of mixed condensation products. Here, the enolate ion of one compound undergoes nucleophilic addition to the carbonyl carbon of a different compound. Crossed-condensation products are usually undesirable since they result in a mixture of products, and reduce the yield of a desired product.

Careful selection of starting materials where only one reactant has an enolizable α-hydrogen can minimize the formation of mixtures. This is illustrated in Fig. 2.12 and 2.13 where an aromatic aldehyde, benzaldehyde, is substituted for the alkylaldehyde as a reactant.

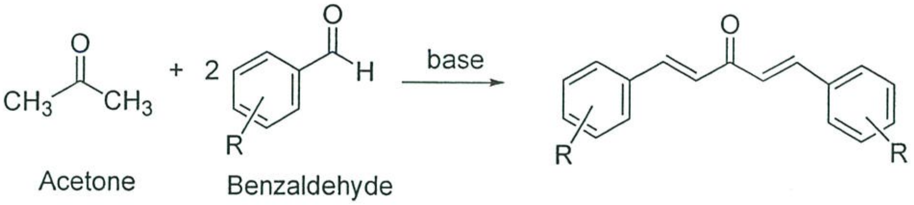


Fig. 2.12 Crossed aldol condensation reaction, producing the α,β-unsaturated ketone dibenzalacetone

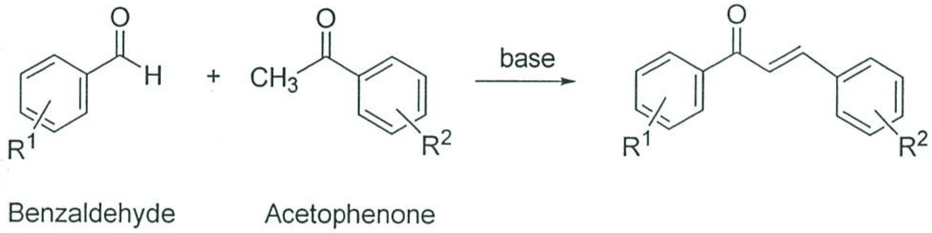


Fig. 2.13 Crossed aldol condensation reaction, producing the α,β-unsaturated ketone chalcone

Derivatives of the parent reactant molecules benzaldehyde and acetophenone can include a variety of R, R^1 and R^2 functional groups, such as methyl ($-CH_3$), methoxy ($-OCH_3$), chloro(-Cl), bromo (-Br), amino ($-NH_2$), hydroxy (-OH), nitrile (-CN), etc. and in various positions around the phenyl ring. Due to intermolecular hydrogen bonding, the hydroxyl group will show temperature, concentration and solvent polarity dependence, which complicates interpretation. Similarly, complications will arise in the spectrum of the amino group due to spin coupling of the proton with the ^{14}N nucleus. Halogen substitution does not introduce a new peak in a proton NMR spectrum but will affect peak positions and splitting patterns on the aromatic protons. Only the methyl and methoxy groups introduce new, non-overlapping resonance lines in the parent molecule spectrum, which affords straightforward interpretation[11].

2.2 Acid–Base catalysis

Acceleration of a chemical reaction by the addition of an acid or a base, the acid or base itself not being consumed in the reaction. The catalytic reaction may be acid-specific (acid catalysis),as in the case of decomposition of the sugar sucrose into glucose and fructose in sulfuric acid; or base-specific (base catalysis), as in the addition of hydrogen cyanide to aldehydes and ketones in the presence of sodium hydroxide. Many reactions are catalyzed by both acids and bases.

The mechanism of acid- and base-catalyzed reactions is explained in terms of the Brønsted–Lowry concept of acids and bases as one in which there is an initial transfer of protons from an acidic catalyst to the reactant or from the reactant to a basic catalyst. In terms of the Lewis theory of acids and bases, the reaction entails sharing of an electron pair donated by a base catalyst or accepted by an acid catalyst [12] The acid is often the proton and the base is often a hydroxide ion. Typical reactions catalyzed by proton transfer are esterification and aldol reactions. In these reactions the conjugate acid of the carbonyl group is a better electrophile than the neutral carbonyl group itself. Catalysis by either acid or base can occur in two different ways: specific catalysis and general catalysis.

- "Specific" acid-base catalysis involves H^+ or OH^- from the solvent that diffuses into the catalytic center
- "General" acid-base catalysis involves acids and bases other than H^+ and OH^- , which facilitate transfer of H^+ in the transition state[13]

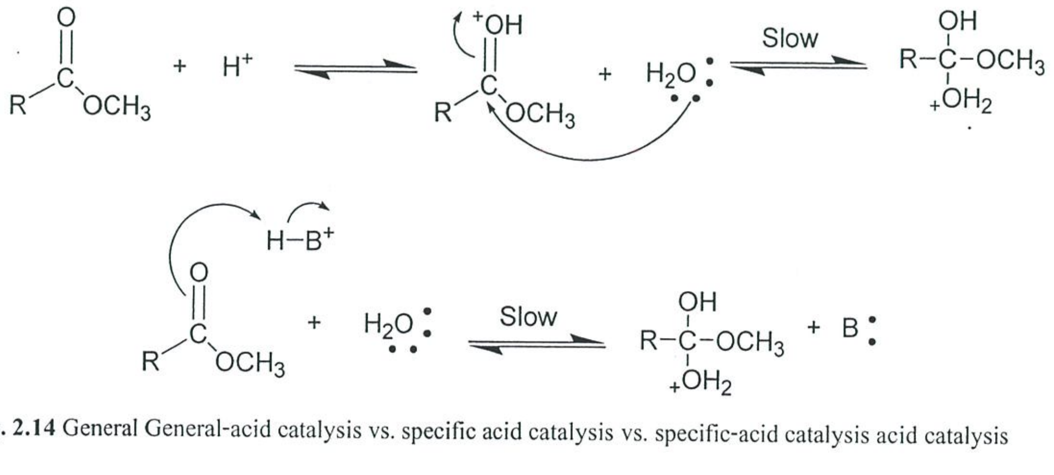
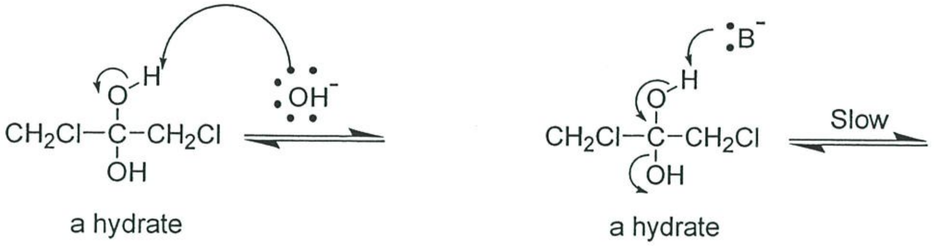


Fig. 2.14 General General-acid catalysis vs. specific acid catalysis vs. specific-acid catalysis acid catalysis



Specific base catalysis General-base catalysis

Fig. 2.15 General-base catalysis vs. specific base catalysis

2.2.1 Base catalysis

The primary commercial processes use homogeneous base catalysts which cause separation and wastewater discharge problems. Solid base catalysts can overcome these drawbacks. However, a solid base catalyst with high activity and stability. [14]An enormous number of studies have been devoted to heterogeneous acidic catalysts (solid acid catalysts). This is mainly because solid acids have been used as catalysts in many industrially important processes in petroleum refining and the production of petrochemicals. Such processes include naphtha cracking, xylene isomerization, alkylation of aromatics, etc. In contrast with extensive studies on solid acids, fewer efforts have been devoted to heterogeneous basic catalysts (solid base catalysts). The first study on the heterogeneous base catalyst was reported by Pines and Haag, who showed that the sodium metal dispersed on alumina was an effective catalyst for double-bond isomerization of alkenes.[15] In 1970, Tanabe published a book entitled Solid Acids and Bases.[16]This was an epoch-making book which made the term “solid base” more popular in the catalysis community. Most of the important works done in the 1950s and 1960s are cited in the book. Since then, studies of solid bases made extensive progress in terms of catalyst materials and catalytic reactions, although the development was slower compared with that of solid acids.[17]

Characterization of Solid Base Catalysts

In order to predict the capability of solid surface as base catalysts, the basic properties of the surfaces must be clarified. The basic character or basicity includes the following factors: a) the number of basic sites, b) the origin or location of basic sites, and c) the base strength of basic sites. These are not so easy to determine. Over the solid bases, there are often several kinds of basic sites. For example, on the surface of magnesium oxide, there are oxygen anions with different coordination numbers [15].Since the basic properties of the oxygen anions depend on the coordination number, the number and base strength of each species must be determined. In some cases, Brønsted and Lewis acid sites coexist on the surface. The heterogeneity of the surface basic sites is one of the complicating factors in determining the basic properties of solid surfaces.

2.2.1.1 Hydrotalcite

Hydrotalcite and related materials are very important catalysts and catalyst precursors. The synthesis, structure and catalytic application of hydrotalcite have been reviewed by several authors.[18-20]

Structure of Hydrotalcite

Hydrotalcite is a natural mineral with the approximate formula $Mg_6A_{l2}(OH)_{16}CO_3 \cdot$ 4H2O. The structure of hydrotalcite consists of positively charged, brucite-like hydroxide layers with negatively charged interlayers. In brucite, the magnesium cation is octahedrally surrounded by hydroxyl groups; the resulting octahedral share edges to form infinite sheets. In hydrotalcite, some of the magnesium ions in the brucite layer are isomorphously replaced by Al^{3+} ions. In natural hydrotalcite, CO_3^{2-} ions exist in the interlayers.

The composition of hydrotalcite can be modified in various ways.The composition of Mg/(Mg + Al) ratio, x, is changeable. Thus, the composition can be expressed as $[Mg_{1-x}Al_x(OH)_2]^{x+}[CO_3^{2-}]_{x/2} \cdot nH_2O$. The value of x can be varied from about 0.1 to 0.34.[21,22] The materials are often called layered double hydroxide. By synthesis, Mg can be isomorphously replaced by Zn, Fe, Co, Ni, Cu, while Al can be replaced by Cr, Fe, In.

The interlayer anion, CO_3^{2-}, can be replaced by a wide variety of anions, as described below.The layer spacings depend on the nature of the interlayer anions and the state of hydrostatic attraction between the layers and interlayer anions. The modifiedhydrotalcite materials are often called hydrotalcite-like materials.

A layered double hydroxide, $[Al_2Li(OH)_6]_2CO_3$ is also used as a source of Al_2O_3-Li_2O mixed oxide, which exhibits catalytic activities for various base- catalyzed reactions.[23,24]

As for the base catalysts, Mg, Al-containing hydrotalcite with CO_3^{2-} ions are most often used as starting materials. The description in this section deals with these materials unless otherwise noted.

Thermal Decomposition of Hydrotalcite

The thermal decomposition of hydrotalcite has been studied extensively. Below 473 K, only interstitial water is lost. Though XRD shows that the layer structure is retained by dehydration, ^{27}Al MAS NMR indicates that a certain amount of tetrahedrally coordinated Al appears at this temperature. Around 500 K, dehydroxylation of brucite layers starts. Between 523 K and 673 K, both carbon dioxide and more water by the dehydroxylation are lost. On calcination at 623 K to 973 K, the periclase (MgO) structure is formed, probably containing Al in solid solution[25](Fig. 2.16). On calcination at 1273 K, XRD shows the presence of $MgAl_2O_4$ together with periclase, and the $MgAl_2O_4$ structure cannot be reconstructed into hydrotalcite structure by rehydration.

SEM analysis of the periclase phase shows retention of the original morphology of hydrotalcite, indicating that during the thermal decomposition steam and carbon dioxide escape through holes in the surface.[26]

^{27}Al MAS NMR shows that as-synthesized hydrotalcite shows a single resonance (+10 ppm) due to octahedral aluminum. After the sample is heated to 723 K, a shoulder develops at +75 ppm due to tetrahedral aluminum, in addition to octahedrally coordinated aluminium in periclase.[27-29]

XPS shows that Mg/Al ratio at the surface of the calcined material is less than the bulk composition, indicating that the Al is not randomly distributed but concentrated near the surface.[30]These findings indicate that magnesium aluminate-type species are located at the outer surface of periclase-type MgO-Al_2O_3 solid solution. Therefore, the effect of the surface phase cannot be neglected in the surface properties of the calcinedhydrotalcite.

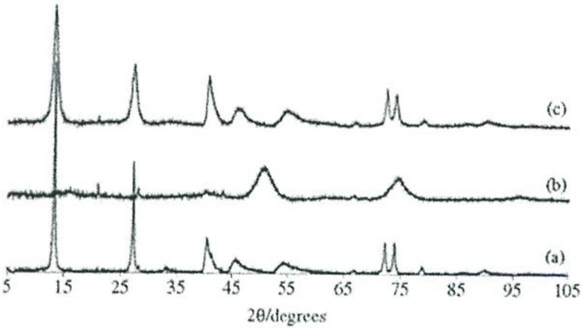


Fig. 2.16 XRD patterns of (a) as-synthesized hydrotalcite, (b) hydrotalcitecalcined at 723 K and (c) hydrotalcite rehydrated in water.

Introduction of Anions into Interlayers

Anions can be introduced into interlayers mainly by four methods: (a) synthesis, (b) anion exchange, (c) reconstruction (memory effect) and (d) chemical reaction.

(a) By synthesis Anions can be introduced into interlayers through the synthesis step by using com- pounds having the desired anions. The anions introduced by this method include CO_3^{2-}, Cl^-, NO^{3-}, ClO^{4-}, $-OCO(CH_2)_{12}COO-$, terephthalate, alkoxides. When hydrotalcite with anions other than CO_3^{2-} is prepared, exposure to air must be avoided and decarbonated water has to be used in all the synthetic procedures, since CO_2 is easily incorporated as carbonate from the atmosphere.

(b) By ion exchange Hydrotalcite or its analogues are anion exchangers. The order of stability for anions is approximately as follows.[31]

$$OH^- > F^- > Cl^- > Br^- > NO^{3-} > I^- \; CO_3^{2-} > SO_4^{2-}$$

Multiply charged anions are much more stable than monovalent anions. Complex anions such as $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Co(CN)_6^{3-}$, $NiCl_4^{2-}$, polyoxometalate ions and alkylbenzenesulfonate ions can also be introduced by the anion exchange method.

$^tBuO^-$ ions can be incorporated by exchanging NO^{3-} ions in the layers with 0.1 M solution of potassium t-butoxide in THF.[32,33]The material is a very active catalyst for base-catalyzed reactions, as described below.

(c) Under reconstruction conditions various anions can be incorporated in the interlayers of hydrotalcite structure by using the memory effect. The most important application with respect to base catalysis is the incorporation of OH^- ions from pure water. F^- ions can also be incorporated from an aqueous solution of KF.[34]The strongly basic ions, $^tBuO^-$ and isopropylamide ions, can also be introduced by the addition of calcinedhydrotalcite to a solution of KO^tBu and lithium diisoproylamide, respectively, in THF.[35,36] L-Proline anion can be incorporated into the interlayers by using the memory effect.[37,38]

(d) By chemical reactions Exchange of halide ions in the interlayers of hydrotalcite materials can be achieved by the reaction with alkyl halide. I^- (or Br^-) ions in $Zn_2CrOH)_6I$ ▪ $2H_2O$ (or $Zn_2Cr(OH)_6Br$ ▪ $2H_2O$) can be substituted with Br^- (or I^-) ions by the reaction with alkyl bromides (or iodide) in liquid phase (363 K) and in vapor phase (423 K).[39]

Fig. 2.17 shows the reaction of $Mg_6Al_2(OH)_{16}C_{12}$ and alkyl halides. The reaction was carried out using 1 g of hydrotalcite (Cl^- = 3.3 mmol) and 33 mmol of alkyl halide in toluene at 353 K. In the case of benzyl bromide, 92% of Cl^- ions was replaced by Br^- ions in 30 min. The rate of the substitution depends on the alkyl groups. The order is isobutyl < isopropyl < butyl ≈ propyl benzyl. The rate is also solvent dependent: DMSO > DMF > toluene. These orders are in general agreement with the reaction rates of alkyl halide in nucleophilic substitution reactions. Since benzyl bromide cannot penetrate into the interlayers, the reaction can occur only at the edges of the layers. The dependence of the rate on the alkyl groups shows that the rate-determining step is the chemical reaction at the edges, but not the diffusion of anions in the interlayers. Using these phenomena, hydrotalcite containing halide ions can be used as catalysts for halide substitution reactions.[40,41]

$$C_6H_5CH_2Cl + C_4H_9Br \quad C_4H_9Cl + C_6H_5CH_2Br$$

$$C_6H_5CH_2Cl + C_4H_9I \quad C_4H_9Cl + C_6H_5CH_2I$$

Substitution of CN^- ions in hydrotalcite with benzyl chloride proceeds to form benzyl cyanide.[42] Chloride ligands of $[NiCl_4]^{2-}$ in interlayers are also completely removed by the reaction with C_4H_9Br to form interstitial $[NiBr_4]^{2-}$ and C_4H_9Cl in DMF [43].

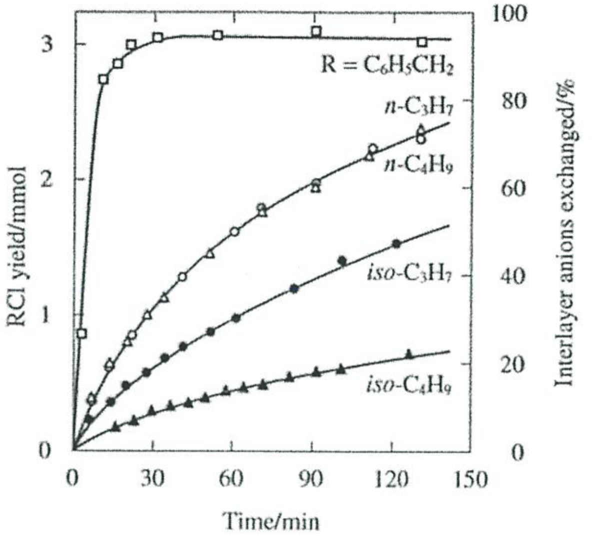


Fig. 2.17 Time course of the reaction of Cl– containing hydrotalcite with alkyl bromide. Conditions: hydrotalcites1 g (Cl– = 3.3 mol), alkyl bromide 33 mmol in toluene, 353 K

The catalytic activities of the mixed oxides prepared from a variety of hydrotalcite-like compounds have been tested. The activity is the highest for $MgO\text{-}Al_2O_3$ in most cases. The anions in the precursor hydrotalcite also influence the activity. For Oppenauer oxidation of cyclohexanol with benzophenone,[44]

Mg, Al > Co, Al > Fe, Ni >Mn, Al > Mg, Fe > Mg, Fe, Ni > Zn, Al

$CO_3^{2-} > Cl^- > SO_4^{2-} > NO^{3-}$

For vapor-phase aldol condensation of acetone and formaldehyde,[45].

Mg, Al > Li, Al > Zn, Cr > Ni, Al

$CO_3^{2-} > NO^{3-} > SO_4^{2-} > CrO_4^{2-}$

For reductive dehydration of propiophenone with 2-propanol,[46]

Mg, Al > Co, Al > Ni, Al > Cu, Al

$CO_3^{2-} > SO_4^{2-} > Cl^-$

For $MgO\text{-}Al_2O_3$, the basic character and catalytic activity depend on the Mg/ Al ratio. The number of basic sites as determined by a titration method has the maximum value at Mg/Al = 3 (x = 0.25). The basicity also depends on the calcination temperature and the maximum value was obtained at a calcination temperature of ca. 773 K. The catalytic activity of the methanolysis of soybean oil showed maximum value when hydrotalcite with Mg/Al = 3 was calcined at 773 K.[47] For alkylation of phenol with methanol, the highest activity was also observed at Mg/ Al =

3.6) In the isomerization of 1-pentene at 573 K, the sample with Mg/Al = 5 is more active than those with the ratio of 3 and 10.[48] For the transfer hydrogenation of phenylacetophenone with 2-propanol, the activity decreases in the order Mg/Al = 5 > 4 > 3.[49] The activities of the mixed oxides are higher than that of MgO.

The structure of hydrocalmite is very similar to that of hydrotalcite, except that Ca and Al octahedral are accommodated in an orderly manner in the layers. Calcination of synthetic hydrocalmite $[Ca_2Al(OH)_6]NO_3 \cdot mH_2O$ at 573, 773, and 873 K gives an amorphous pattern, CaO structure, and $Ca_{12}Al_{14}O_{33}$, respectively, their surface area being 116, 180 and 184 m^2g^{-1}, respectively. Temperature programmed desorption of CO_2 shows that strong basic sites develop by calcination at higher temperatures.

2.2.1.2 Layered double hydroxide

Layered double hydroxides (LDH) are a class of clays with brucite-like layers and intercalated anions which have attracted increasing interest in the field of catalysis. Benefiting from the atomic-scale uniform distribution of metal cations in the brucite-like layers and the ability to intercalate a diverse range of interlayer anions, LDH display great potential as precursors/supports to prepare catalysts, in that the catalytic sites can be preferentially orientated, highly dispersed, and firmly stabilized to afford excellent catalytic performance and recyclability. The approaches to prepare catalysts based on LDH materials include, but are not limited to, exfoliation of the brucite-like layers, lattice orientation/lattice confinement by the brucite-like

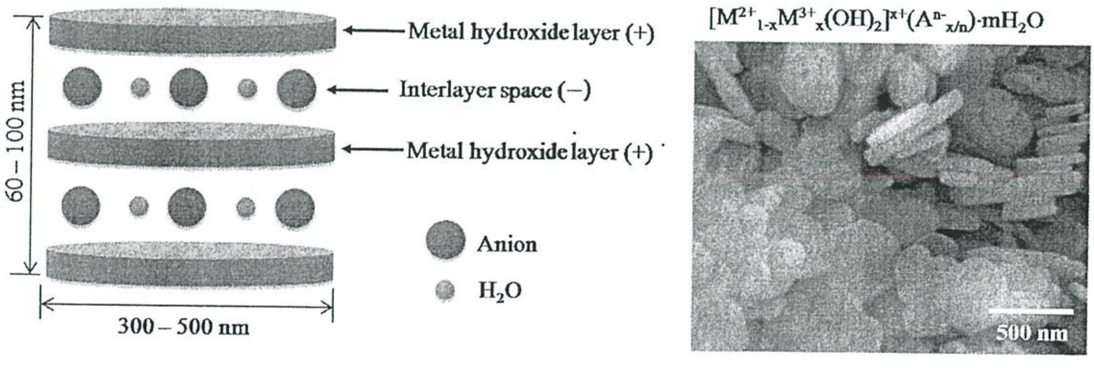


Fig. 2.18 Structure of Layered double hydroxides (LDH)

Layered double hydroxides (LDH), also known as anionic or hydrotalcite-like clay, are layered compounds that consist of positively charged metal hydroxides and interlayer anions along with water molecules to compensate the net positive charge. LDH have been known for over 150 years since the discovery of the mineral hydrotalcite, and a large class of minerals with colsely related structures are usually known to mineralogists as the als with closely sjogrenite-hydrotalcite group.

LDHs are one of the most useful classes of inorganic layered materials and have recently received attention in the field of optical filter, biological catalysts, and heterogeneous catalysts. we investigated the orientation and area coverage of LDH depending upon the applied substrates and solvents, the self-assembly of inorganic, polymeric and bio-materials on the charged LDH monolayers and new hybrid light sensitized for Dye-sensitized solar cell [50].

2.3 Co-precipitation

Precipitation is when an insoluble solid is separated from the solution due to a chemical change. There are three types of precipitation that can take place in the soil system. These are precipitation of an element due to supersaturation of that element in the soil solution, surface precipitation and co-precipitation of elements [51].The hydrotalcites as catalysts is used that were synthesized by co-precipitation method at constant pH

Co-precipitation is the method most frequently applied to prepare hydrotalcite. Co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed [52]. Precipitate can be obtained from the incorporation of trace element into structure during solid solution formation and recrystallization [51].

There are three main mechanisms of co-precipitation: inclusion, adsorption and occlusion [53]. An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.

Literature review

Aldol condensationreaction can catalytically undergo in the presence of a solid-base catalyst which havemixed oxides, alkali ion-exchanged zeolites and KOH impregnated on neutral alumina. Sumeet K. Sharmahave recently reported solvent free aldol condensation of propanal to 2-methylpentenal using solid base catalyst. The report studied alkali ion-exchanged zeolites, alumina, alkali treated alumina and hydrotalcite of varied Mg/Al molar ratio.The higher conversion of propanalwas observed using hydrotalciteasThe conversion and selectivity of 2-methylpentenal increased with increasing Mg/Al molar ratio of hydrotalcite. 97% conversion of propanal with 99% selectivity of 2-methylpentenalwas achieved using hydrotalcite ratio 3.5[9].

The vapor phase aldol condensation of the acetaldehyde was studied by Weijie, who reported acetaldehyde to produce crotonaldehyde with a good selectivity (ca. 90%) over silica supported low loading alkali metal. The optimized reaction temperature was around 625 K. The approximate order of the reactivity of these catalysts is $K/Si0_2$>$Na/Si0_2$>$Cs/ Si0_2$>$Li/Si0_2$. Surface silicate and carbonate are probably the active phases for the reaction[54].

The aldol condensation of acetaldehyde and heptanal has been carried out in the liquid phase between 353 and 413 K using different types of solid base catalysts: MgO with strong Lewis basic sites, Mg(Al)O mixed oxides with acid–base pairs of the Lewis type obtained from hydrotalcite precursor. The reaction of acetaldehyde and heptanal on catalysts elaborated from anhydrotalcite precursor (Mg/Al = 3) yields a wide variety of products. Most of them (usually more than 80%) originate from cross- and self-condensation of the aldehydes on basic and acid-pair sites. The most efficient material for the cross-condensation to 2-nonenal is Mg(Al)O calcined at 873 K. A maximum yield of 21% was reached at 393 K in ethanol as solvent and a moderate excess of acetaldehyde (acetaldehyde/heptanal, 2/1). This excess is necessary to achieve a good balance between both reactants in the adsorbed state and then to favor the cross-condensation[55]. This case of the hydrotalcite-type catalysts which have recently attracted much attention for various base-catalyzed reactions in fine chemistry[56].

Hydrotalcite is a type of layered double hydroxides or anionic clays, constitute a class of compounds with positively charged layers and exchangeable anions in the interlayer space [57-59].In the natural mineral hydrotalcite, whose name has been extended to this family of materials, some $Mg^{2+}$are isomorphously substituted for $Al^{3+}$and the formal positive charge thus appearing in the hydroxyl layers is usually compensated by carbonates linked by hydrogen bonds to water molecules[55].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 CHEMICAL REAGENTS

Chemical reagents	**Grade of purity**	**Manufactures**
1. Nitrogen gas	High purity	Praxair
2. Air zero	High purity	TIG
3. Magnesium Nitrate ($Mg(NO_3)_2 \cdot 6H_2O$)	99.0 %	UNILAP,AJEX CHEMICALS
4. aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$)	98.0 % AR	QReC
5. sodium carbonate	99.7 %	Carlo Erba
6. sodium hydroxide	98.0 %	SDFCL
7. Deionized water		
8. Acetaldehyde	99.0 %	FLUKA CHEMIKA
9. Methanol	99.9 % plus for HPLC	Carlo Erba
10. Heptane	99.87 %	Fisher Chemical
11. Toluene	Analytical	Fisher Chemical
12. Layered double hydroxides (LDH)	commercial	
13. Paraffin oil	commercial	

3.2 APPARATUS AND INSTRUMENTS

1. Bomb reactor (TAIATSU TECHNO® SUS316 200°C 100cc)
2. Beaker 600 ml.
3. Clamp

4. Stand
5. Magnetic stirrer hot plate with temperature controller system
6. Laboratory glassware
7. Laboratory plastic ware
8. Vacuum system
9. Oven
10. Tube furnace with a programmable temperature controller (Vesstar LABQUIP)
11. Centrifuge (Centution LABQUIP)
12. Gas chromatograph with flame ionization detector (5890 series II, Hewlett Packard)
13. X-ray powder diffractometer (Rigaku, DMAX 2200/ Ultima+, Faculty of science Chulalongkorn University)
14. BET surface area (Autosorb-1C, Quantachrome)
15. Gas Chromatograph/Mass spectrometer (Hewlett Packard, HP 6890 series GC system, Scientific Instrument Service Center, KMITL)
16. Thermogravimetric analysis (Perkin-Elmer, Scientific Instrument Service centre, KMITL)

3.3 PROCESS OF STUDY

A process of the study on preparation of the catalysts

3.3.1Synthesis and modification of catalysts

3.3.1.1 Synthesis of hydrotalcites with Mg/Al molar ratio of 1.5 by co-precipitation method at pH 12.5

3.3.1.2 Modification of the catalysts obtained by calcination at 450 °C

3.3.2 Characterization of catalysts

3.3.2.1 Investigate the catalysts structure by X-ray diffractometor(XRD)

3.3.2.2 Detremine the surface area by gas adsorption technique (Brunauer–Emmett–Teller ;BET)

3.3.2.3 Detremine the decomposition of the layered structure by Thermogravimetric analysis (TGA)

3.3.3Catalytic testing

3.3.3.1 Determination of product distribution

3.3.3.2 Testing of effect of type catalyst.

3.3.3.3 Testing of effect of reaction temperature.

3.3.3.4 Testing of effect of reaction time.

3.3.4 Analysis of products

3.3.4.1 Determine the amount of product by gas chromatograph equipped with a flame ionization (GC-FID)

3.3.4.2 Determine the qualitative of product by gas chromatograph-mass spectrometer (GC-MS)

3.4 Synthesis and modification of catalysts

3.4.1 Synthesis of Hydrotalcite with Mg/Al molar ratio of 1.5 by co-precipitation method at pH 12.5

The hydrotalcite samples with Mg/Al molar ratio of 1.5 were synthesized using co-precipitation method at pH 12.5.Typically, for hydrotalcite sample with Mg/Al molar ratio = 1.5, an aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ (0.0825mol) and $Al(NO_3)_3{\cdot}9H_2O$ (0.0550mol) in 125 ml. deionized water was prepared (first solution). The first solution was added dropwise into a second solution containing NaOH(0.45mol) and Na_2CO_3(0.13 mol) in 125 ml. deionized water, in around 4 h under stirring at room temperature. The content was transferred into the teflon coated stainless steel autoclave and aged at 70°C for 12 h under autogenous water vapor pressure. After 14 h, the precipitate formed was centrifuged for 5 minutes at 3000 rpm and washed thoroughly with hot distilled water until pH of the supernatant solution was 7. The washed precipitate was dried in an oven at 80°C for 14 h. The hydrotalcite samples of Mg/Al molar ratio 1.5 were calcined at 450°C for 4 h in a tube furnace. The solid material was then cooled and stored in desiccators prior to using those as catalysts for aldol condensation of propionaldehyde.

3.5 Characterization of catalysts

3.5.1 Powder X-ray diffraction

The catalysts structure were checked by X-ray diffraction (Rigaku, DMAX 2200/ Ultima+, Faculty of science, Chulalongkorn University) The sample was finely grinded to a permit packing of the sample into an XRD sample holder. The XRD pattern can be obtained by scanning over the angle range from 2θ=5 to 80°. The X-ray source is Cu-Kα generated at a voltage of 40 kV, 30 mA

3.5.2 Brunauer–Emmett–Teller

The specific surface areas of the catalysts were measured by gas adsorption technique (Brunauer–Emmett–Teller (Autosorb-1C, Quantachrome). The catalysts were activated at 110°C for 8 h under vacuum prior to N_2 adsorption measurements. The specific surface area of the samples was calculated from N_2 adsorption isotherms.

3.5.3 Thermogravimetric analysis

The decomposition of the layered structure were determined by Thermogravimetric analysis(Perkin-Elmer, Scientific Instrument Service centre, KMITL). The catalysts was carried out under flowing nitrogen (flow rate, 20 mL/min). The analyses were recorded by heating from 50°C to 700°C at heating rate 10°C/min.

3.5.4 Back titration

The basicity of the catalysts were determined by back titration method. First, 25 ml of acetic acid solution (0.1M) and 0.5 grams of the catalysts were mixed in Erlenmeyer flask. The mixed solution was stirred for 30 minutes. Then, the catalyst was removed by filtration and titrated with sodium hydroxide solution(0.1M). The result of basicity reported in millimoles of spent acetic acid solution per grams of the catalysts.

3.6 Catalytic Testing

Liquid phase catalytic conversion aldol condensation of propionaldehyde to 3-hydroxy-2-methylpentanal can be investigated in a batch process. The catalyst was added in bomb reactor and activated at 90°C before activity testing. The reactor was kept in a water bath equipped with temperature (90°C) and agitation speed controlling 250 rpm. The reactor was evacuated by suction pump for 10 minutes then N_2 was filled. The process was repeated for 5 times. Then, reactor was cooled at -11°C

propionaldehyde, ethyl alcohol (a solvent) and heptane(an internal standard) were prepared at volume ratio of 3:3:0.5, respectively. The mixture was cooled and used as feed for the reaction. In each run, feed mixture was injected in the reactor while it is cool. The reactor was then transferred in a water bath equipped with temperature controlled at 50 to 70°C and agitation speed of 150 rpm. The catalytic testing was continued for 10, 20 and 30 hrs. After the reaction, the reactor was cooled at -11°C.The products were mixed with cold toluene. The solution was withdrawn by syringe and filtered over nylon filter (0.2 micrometer) then kept at 5°C for analysis. Description of the reaction condition is summarized in Table 3.1

Table 3.1 Description of the reaction condition

Parameter	**Value**
Catalyst weight (g.)	0.5
Catalyst activation (before reaction)	Temperature : 90°C Agitation : 250 rpm
Amount of feed stock (ml.)	6
Reaction temperature (°C)	50 - 70
Reaction agitation (rpm)	150

3.7 Product Analysis

The product was kept in a vial at 5˚C. Product analysis was performed using an offline gas chromatograph. Product sample was injected (0.1microliter) in to GC column (HP-5 capillary column) connected to flame ionized detectors. The component was separated as they pass through the column with inert carrier gas (N_2) and was recorded as a chromatogram. The peak area from the chromatogram was integration and calculated peak area percentage by internal standardization method. Then the unknown peak was identified by gas chromatograph-mass spectrometer (GC-MS) technique.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst characterization

The XRD patterns of hydrotalcites (Mg/Al molar ratio 1.5) [HT 1.5] and layered double hydroxide [LDH] were presented in Fig. 4.1A and Fig. 4.1B. This pattern corresponds to a typical layered structure of clay minerals showing sharp-symmetric peaks at (003), (006), (110), and (113) planes and broad-asymmetric peak at (009), (015) and (016) planes [60]. Calcination at 450°C decomposed the hydrotalcites structure [HT 1.5-cal] and layered double hydroxide [LDH] to Mg-Al mixed oxide as shown by XRD-pattern in Fig. 4.1C and Fig. 4.1D [61].

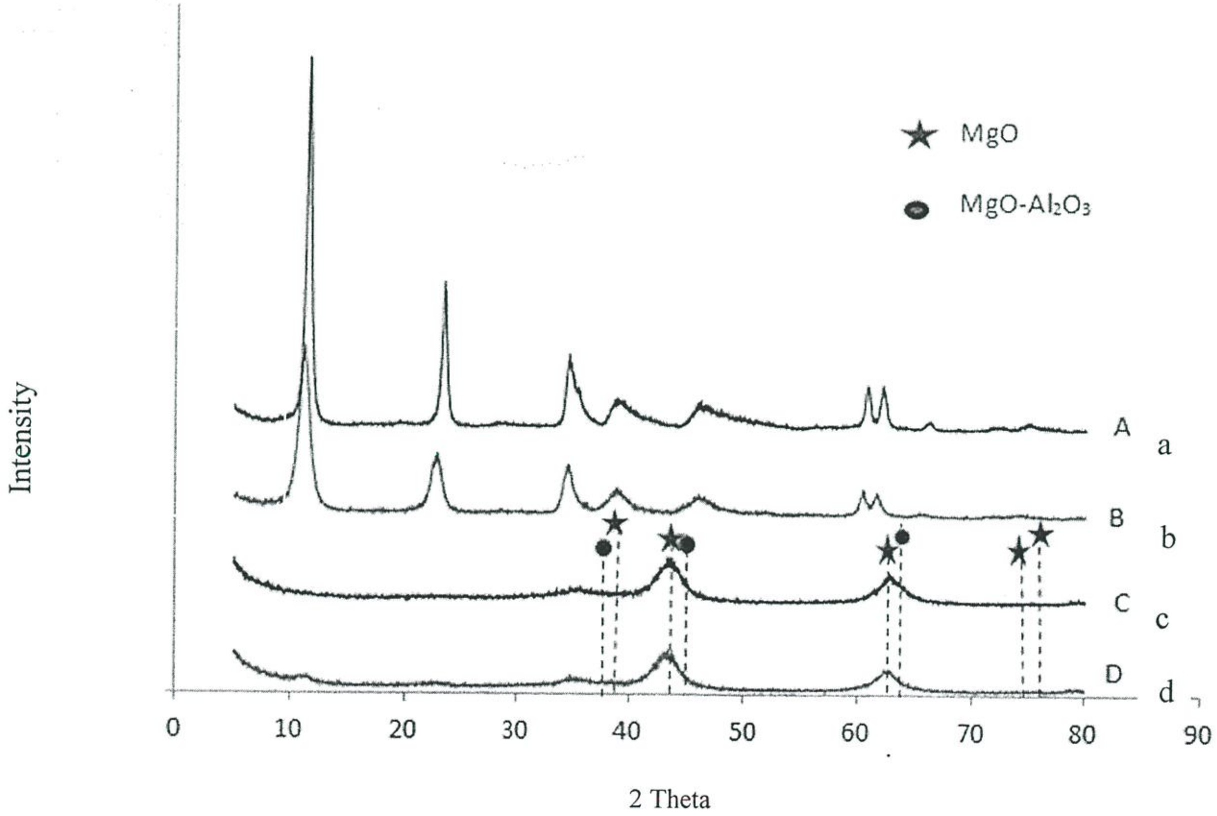


Fig. 4.1 XRD patterns of (a) Non-calcined hydrotalcites Mg/Al molar ratio 1.5, (b) Non-calcined LDH, (c) Calcined hydrotalcites Mg/Al molar ratio 1.5 at 450°C, (d) Calcined LDH at 450°C

The decomposition of the layered structure is confirmed by Thermogravimetric Analysis of HT 1.5 as shown in Fig. 4.2. It is clear that the initial weight loss (2.7%) between 60 °C - 80 °C is due to the loss of surface water. The second weight loss (17.1%) of interlayered water is detected between 150 °C - 200 °C. The higher temperature loss at 300 °C - 400 °C is attributed to the decomposition of interlayered carbonate and hydroxyls. Above 400 °C, water is released from dehydroxylation of the mixed oxides [62].

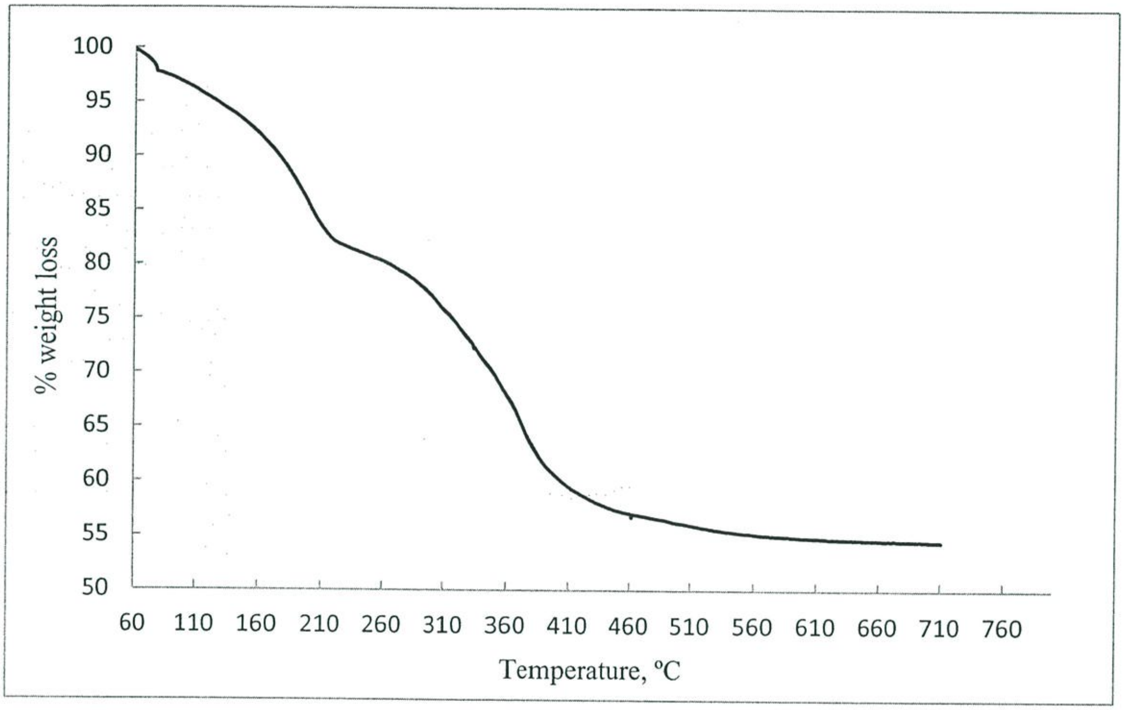


Fig. 4.2 Thermogravimetric analysis of hydrotalcites Mg/Al molar ratio 1.5

Table 4.1 shows basicity and surface area of the catalysts. The calcined catalysts possess surface area higher than that of non-calcined catalysts. This is because the layered structure of the catalyst is exfoliated during calcination forming Mg-Al mixed oxides as discussed. In addition, basicity of the calcined catalysts is increased, as compared with that of the non-calcined. This can be attributed to the exposed oxygen ions (O^{2-}) on the surface catalysts which is formed after calcination.

Table 4.1 Basicity and surface area of the catalyst

Catalysts	Basicity [mmol/g.]	Surface area [m^2/g.]
HT 1.5 (non-calcined)	4.2	130
HT 1.5 (calcined)	8.8	200
HT 2.5 (calcined)	8.4	153
LDH (non-calcined)	7.9	100
LDH (calcined)	11.0	266

** Catalysts calcined at 450°C

4.2 Catalytic testing

The conversion of propionaldehyde and yield of products over varied catalysts is shown in Fig. 4.3. For all catalyst, the conversion of propionaldehyde is proportionally increased with the reaction time. It appears that aldol condensation to 3-hydroxy-2-methylpentanal is initially promoted for all catalysts. As the reaction time increases, 3-hydroxy-2-methylpentanal undergo dehydration to 2-methylpentenal.

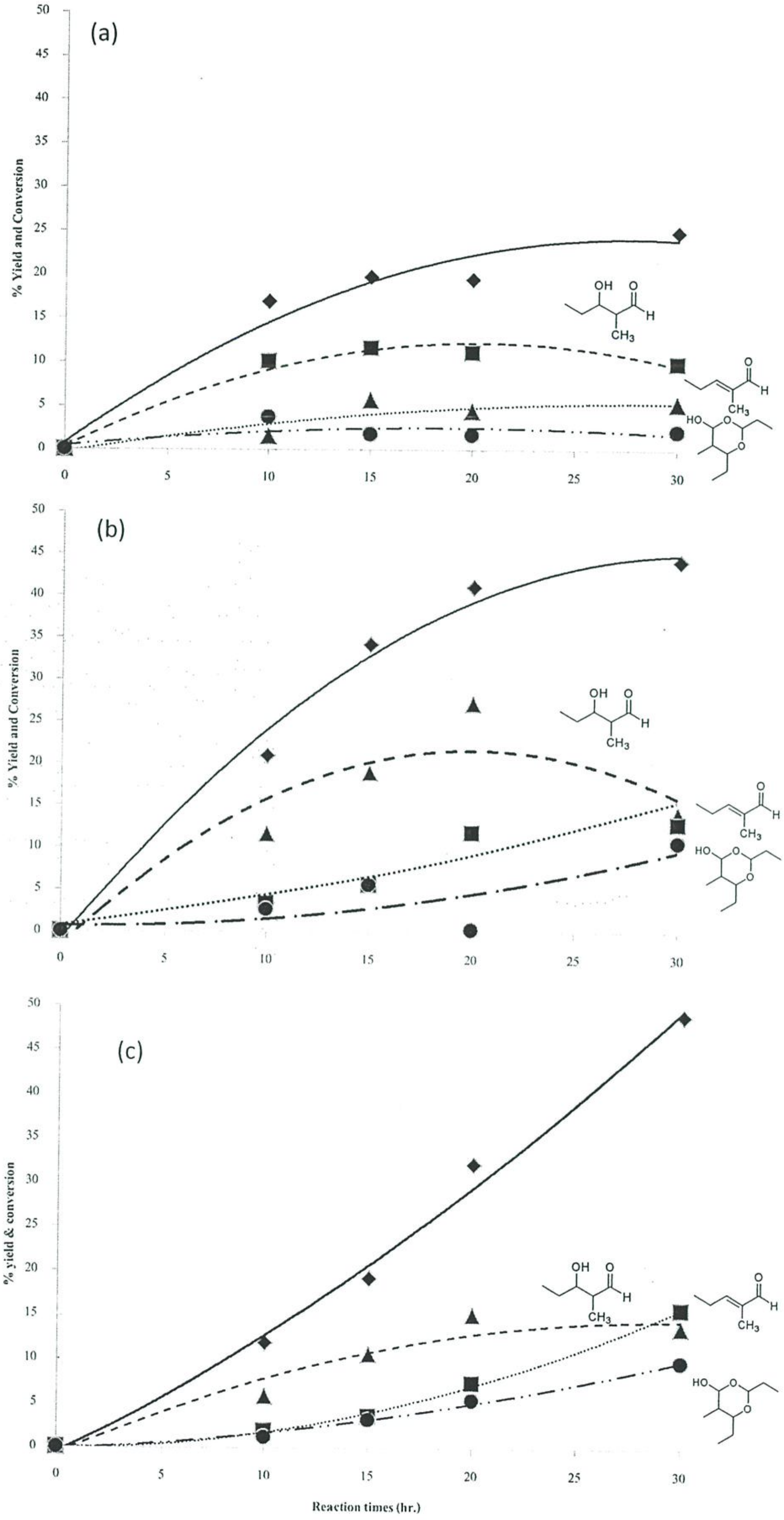


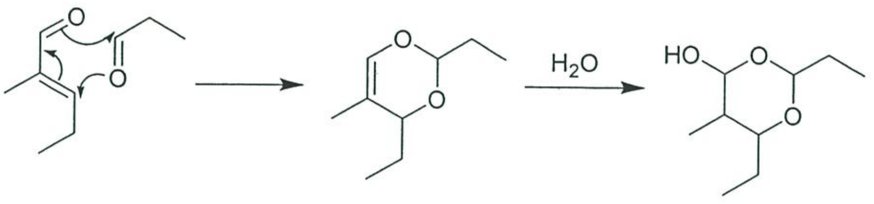
Fig. 4.3 Aldol condensation of propionaldehyde over (a) non-calcined LDH, (b) HT 1.5, (c) HT 2.5

**Reaction conditions; Catalyst 0.5 g., Temperature: 60°C.

◆Conversion ▲Yield of 3-hydroxy-2-methylpentanal ■ Yield of 2-methylpentenal

● 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane

In addition, 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane was found as by-product. It is believed that 2-methylpentenal can be coupled with propionaldehyde to form 2,4-diethyl-5-methyl-1,3-diox-5-ene that can be re-hydrated to 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane as observed.



2,4-Diethyl-5-methyl-1,3-diox-5-ene   2,4-Diethyl-6-hydroxy-5-methyl-1,3-dioxane

Accordingly, the yield of 3-hydroxy-2-methylpentanal was decreased while 2-methylpentenal and 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane was increased with reaction time. The general reaction pathway can be propose as shown in Fig. 4.4

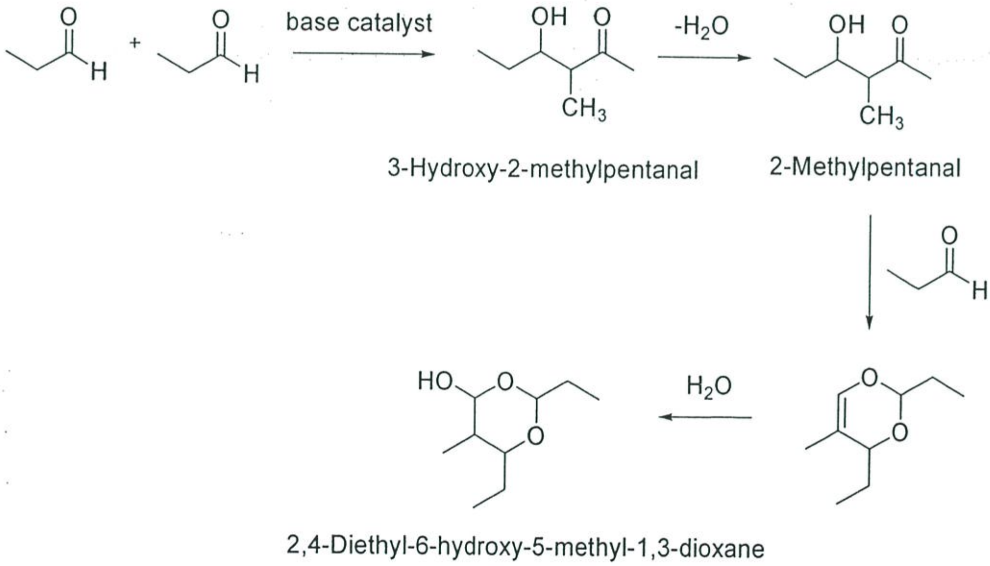


Fig. 4.4 Reaction pathway using solid base catalysts

It can also be seen from Fig. 4.3 that the conversion of propionaldehyde and the yield of 3-hydroxy-2-methylpentanal over HT 2.5 is higher than over HT 1.5 and LDH, despite HT 2.5 possess a lower surface area. This is because the saturation of feed as enolate anion on the surface takes place over the catalyst with high surface area as shown in Fig. 4.5. The feed was fully adsorb on the catalyst surface. Thus, aldol condensation with the non-activated feed is limited.

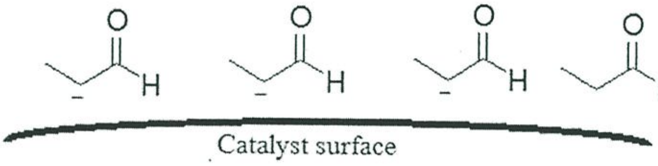


Fig. 4.5 The saturation of feed as enolate anion on catalyst high surface

Moreover, catalyst with high surface area can adsorb the products as evidenced by chloroform extract from the spent HT 1.5. The chromatogram of chloroform extract is shown in Fig. 4.6b. It can be seen that large amount of aldol product is extracted from the spent HT 1.5, indicating that adsorbed propionaldehyde transforms into aldol product that retained on the HT surface..

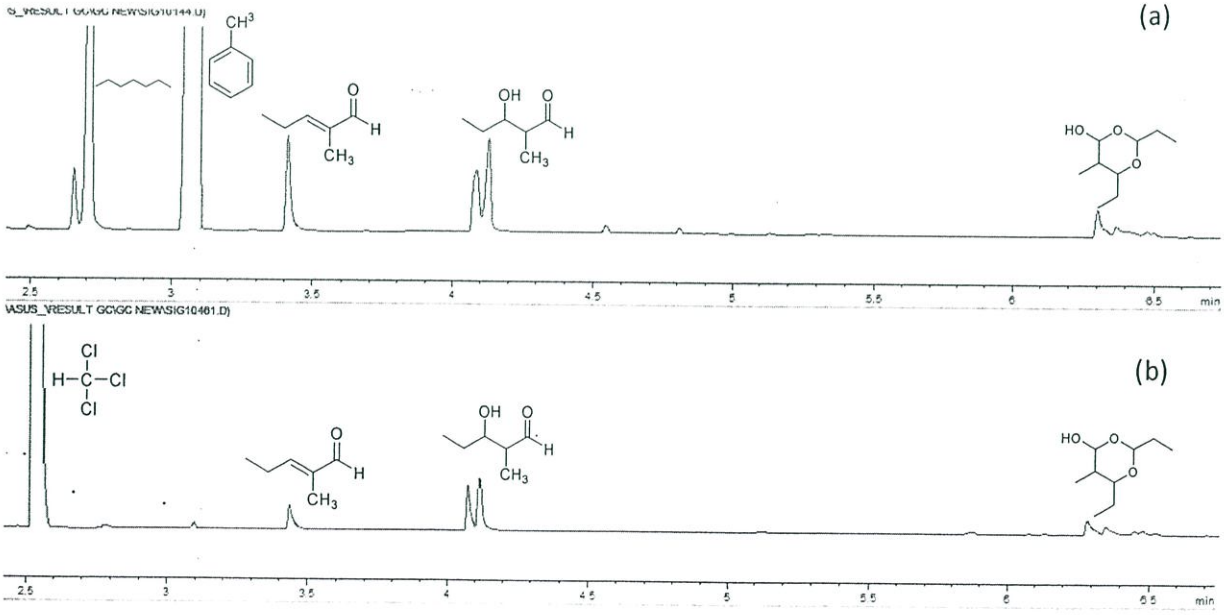


Fig. 4.6 (a) Chromatogram of reaction mixture over HT 1.5 at 60 °C, 15 hrs.

(b) Chromatogram of chloroform extract from spent HT 1.5 at room temperature, 1 hr.

In addition, Table. 4.2 indicates that the calcined catalysts give higher conversion of propionaldehyde, as compared that from the non-calcined catalysts.

Table 4.2 The effect of catalysts type on conversion and yield

Catalyst	Time (hrs.)	% Conversion	%Yield	
			3-hydroxy-2-methylpentanal	2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane
HT 2.5 (Calcined)	15	34	19	6
HT 1.5 (Calcined)	15	19	11	3
HT 1.5 (non-Calcined)	15	13	7	1
LDH (Calcined)	15	26	12	5
LDH (non-Calcined)	15	20	11	2

**Calcined at 450°C

This is because the calcined catalysts become Mg-Al mixed oxides that expose oxygen ions (O^{2-}) as active sites. This site is strongly basic site, as reported by St. Malinowski [63]. However, the yield of 3-hydroxy-2-methyl pentanal from calcined LDH is the same as the non-calcined LDH. While yield of by-product, 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane were higher, presumably due to the higher exposed surface that strongly adsorb both propionaldehyde and 2-methyl pentenal. Therefore, the non-calcined LDH seems to be more selective for 3-hydroxy-2-methylpentanal, as compared with calcined catalyst as shown in Table 4.3. However, the absorb higher selectivity may be influence for the difference conversion.

Table 4.3 The effect of catalysts type on conversion and selectivity

Catalyst	Time (hrs.)	% Conversion	Selectivity			
			3-hydroxy-2-methylpentanal	2 methyl pentenal	2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane	Other Product
HT 2.5 (Calcined)	15	34	56	16	18	10
HT 1.5 (Calcined)	15	19	58	19	16	7
HT 1.5 (non-Calcined)	15	13	54	21	8	17
LDH (Calcined)	15	26	46	15	21	18
LDH (non-Calcined)	15	20	59	29	9	3

In orders to compare the selectivity of 3-hydroxy-2-methylpentanal, the reactions at the same level of conversion of propionaldehyde were considered as shown in Table 4.4.

Table 4.4 The conversion and selectivity over all catalysts

Catalyst	Time (hrs.)	% Conversion	Selectivity			
			3-hydroxy-2 methylpentanal	2- methyl pentenal	2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane	Other product
LDH (non-calcined)	15	20	57	29	9	5
HT 1.5 (Calcined)	15	19	55	19	17	9
HT 2.5 (calcined)	10	21	56	16	13	15

*Reaction condition; Catalyst 0.5 g., Temperature 60°C

It can be seen that the selectivity of 3-hydroxy-2-methylpentanal for HT 1.5, HT 2.5 and LDH are similar indicating that all catalyst possess the same type of active site. However, less selectivity of 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane was observed in case of LDH. In order to modify the product selectivity, the reactions with different temperature were compared as shown in Fig. 4.7.

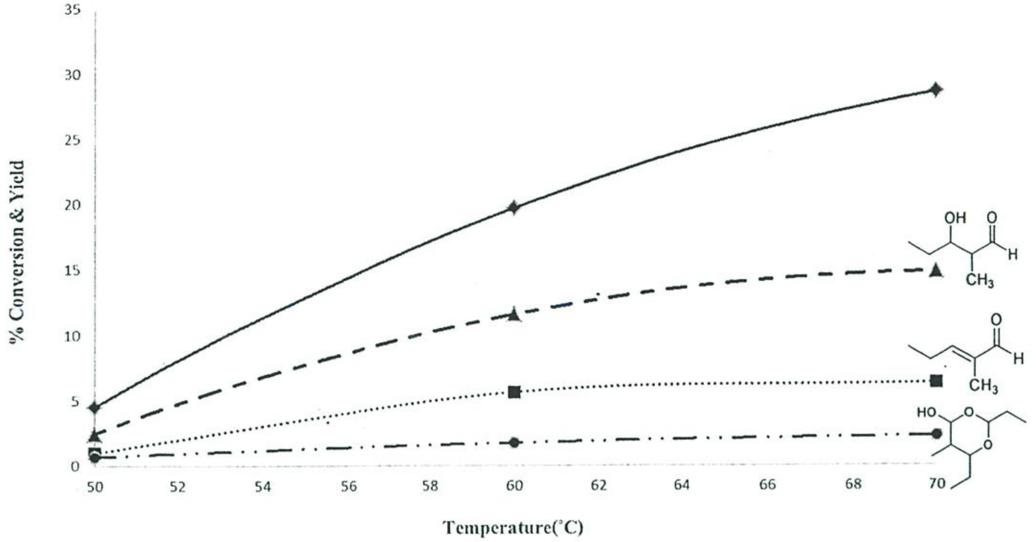


Fig. 4.7 Aldol condensation of propionaldehyde over LDH at 15 hrs., Catalyst 0.5 g.

It is clear that conversion of propionaldehyde and yield of 3-hydroxy-2-methylpentanal increase when the temperature is increased due to the higher reaction rate. Considering at a similar conversion of propionaldehyde as demonstrated in Table 4.5, the lower selectivity of 3-hydroxy-2-methylpentanal was observed at 70°C because at high temperature, 3-hydroxy-2-methylpentanal can easily be dehydrated to 2 methylpentenal. Furthermore, 2 methylpentenal will be coupled with propionaldehyde to form the 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane as by-product. The reaction temperature at 50°C presents a high selectivity of 3-hydroxy-2-methylpentanal but the reaction take noticeably longer, as compared to that at 60°C. It is suggested that, the optimized temperature for high selectivity of 3-hydroxy-2-methylpentanal is 60°C

Table 4.5 The conversion and selectivity of temperature over LDH at the same level of conversion

Temperature (°C)	Time (hrs.)	% Conversion	Selectivity			
			3-Hydroxy-2-methylpentanal	2 methylpentenal	2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane	Other product
50	75	24	52	21	10	17
60	15	20	59	29	9	3
70	10	19	49	31	14	6

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

Propionaldehyde was tested by synthesized hydrotalcite Mg/Al ratio 1.5 [HT 1.5], hydrotalcite Mg/Al ratio 2.5 [HT 2.5] from co-workers and commercial layered double hydroxides [LDH] via the aldol condensation using methanol as solvent at 60 °C to produce 3-hydroxy-2-methylpentenal. Calcination at 450°C decomposed the hydrotalcite structure to Mg-Al mixed oxide that increased surface area of calcined catalyst. For the calcined catalyst, the surface area and basicity of LDH is higher than HT 1.5 and HT 2.5. The Mg-Al mixed oxide possess the exposed oxygen ions (O^{2-}) on the catalyst surface. Thus, the basicity of the calcined catalysts is increased. For all catalysts, the conversion of propionaldehyde increase with reaction time. The first product is 3-hydroxy- 2-methylpentanal that undergo dehydration to 2-methylpentenal. Moreover, 2-methylpentenal can be coupled with propionaldehyde to 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane as by product. The conversion of propionaldehyde and the yield of 3-hydroxy-2-methylpentanal over HT 1.5 and LDH are lower while those over HT 2.5 is relatively higher. This is because HT 1.5 and LDH possess surface area higher than HT 2.5. The catalyst with high surface area would promoted saturation of feed as enolate anion on the surface. This consequently limited aldol condensation. Furthermore, high surface area catalyst can adsorb the products. The yield of 3-hydroxy-2-methylpentanal and 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane over calcined catalysts are higher than the non-calcined catalysts because the basicity of calcined catalysts is higher than non-calcined catalysts. The selectivity of 3-hydroxy-2-methylpentanal at the same level of conversion of propionaldehyde are similar for HT 1.5, HT 2.5 and LDH. This point out that HT 1.5, HT 2.5 and LDH possess the same type of active site. At the low reaction temperature, the selectivity of 3-hydroxy-2-methylpentanal is higher than the high reaction temperature but the reaction take long time particularly at 50 °C. At high reaction temperature, 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane was found because 3-hydroxy-2-

methylpentanal can be dehydrated to 2-methylpentenal, that can be coupled with propionaldehyde to 2,4-diethyl-6-hydroxy-5-methyl-1,3-dioxane, as observed. At reaction temperature 60 °C gives high selectivity of 3-hydroxy-2-methylpentanal and less by product was less found.

5.2 Suggestion for Future Studies

5.2.1) Due to the limit of the pressure in reactor, the complete acetaldehyde conversion can not be achieved. For further study, reaction under controlled pressure can be investigated to reduce evaporation of acetaldehyde.

5.2.2) Synthesis of hydrotalcites with larger crystal size by increasing temperature during the co-precipitation, could lead to a decrease in the surface area of the catalyst. This may avoid saturated of the feed and strong adsorption of the product on the surface which leads to the catalysts deactivation.

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APPENDIXES

APPENDIX A

CHARACTERIZATION OF CATALYSTS

Reference X-ray diffraction patterns

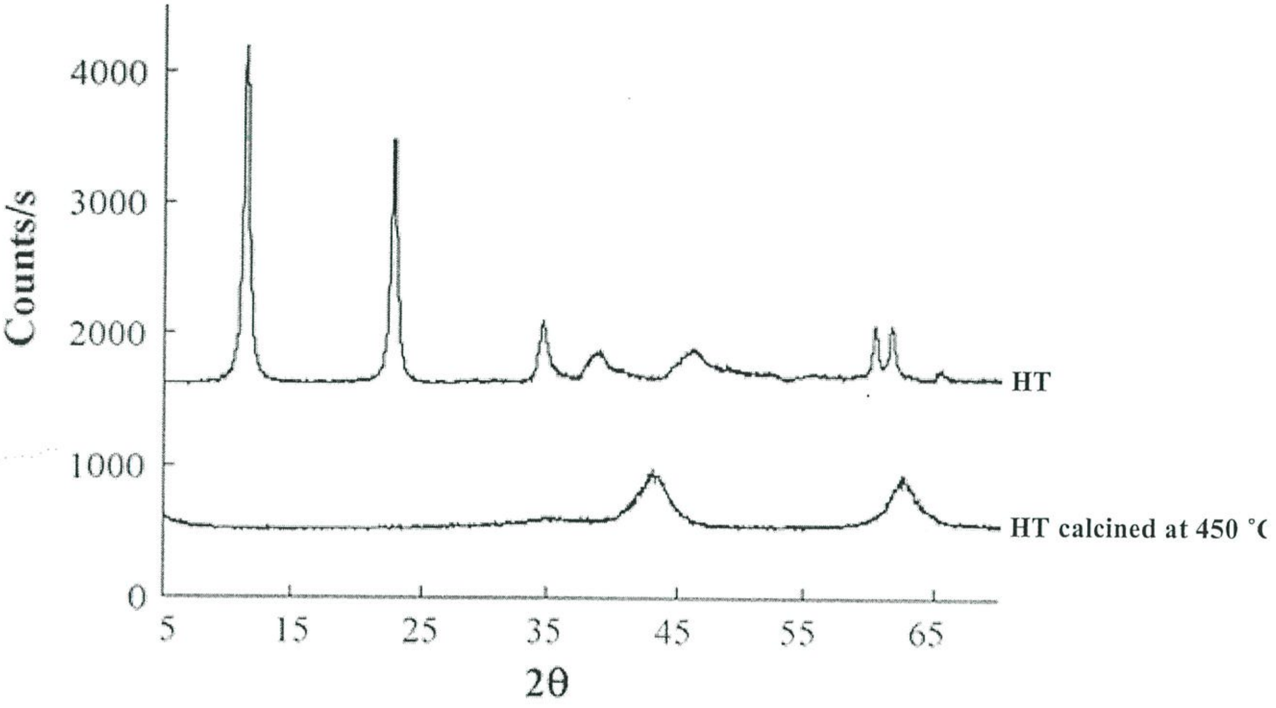

Fig. A.1 Reference X-ray pattern of hydrotalcite

Thermogravimetic Analysis of catalyst

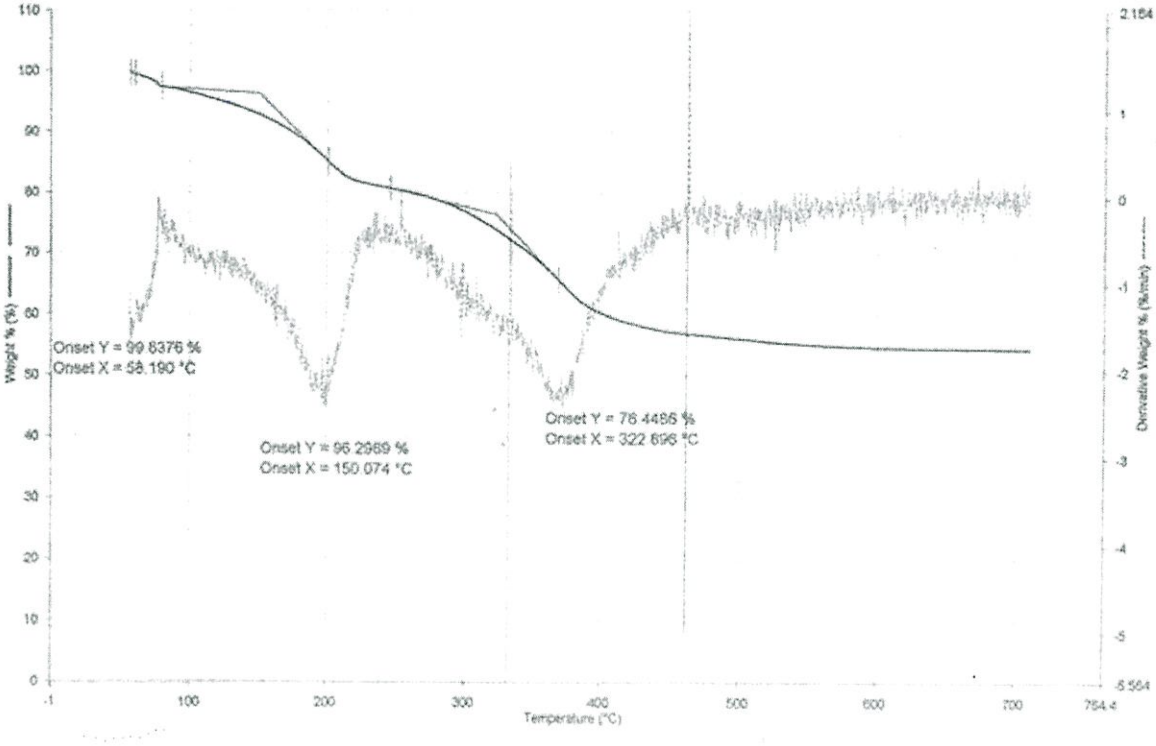

Fig. A.2 TGA of used hydrotalcites Mg/Al molar ratio 1.5

Gas Sorption (BET)

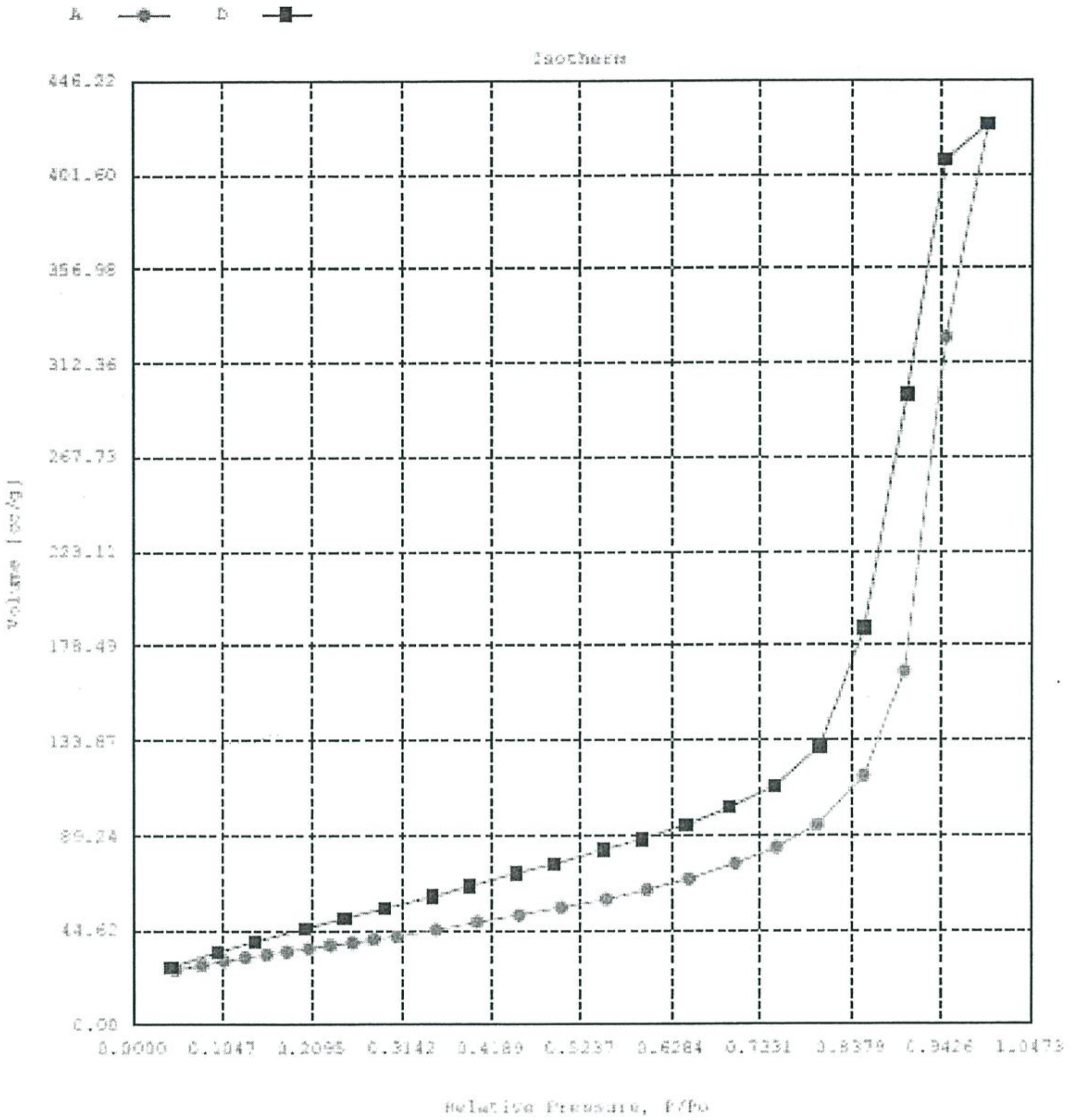

Fig. A.3 Hydrotalcites Mg/Al molar ratio 1.5

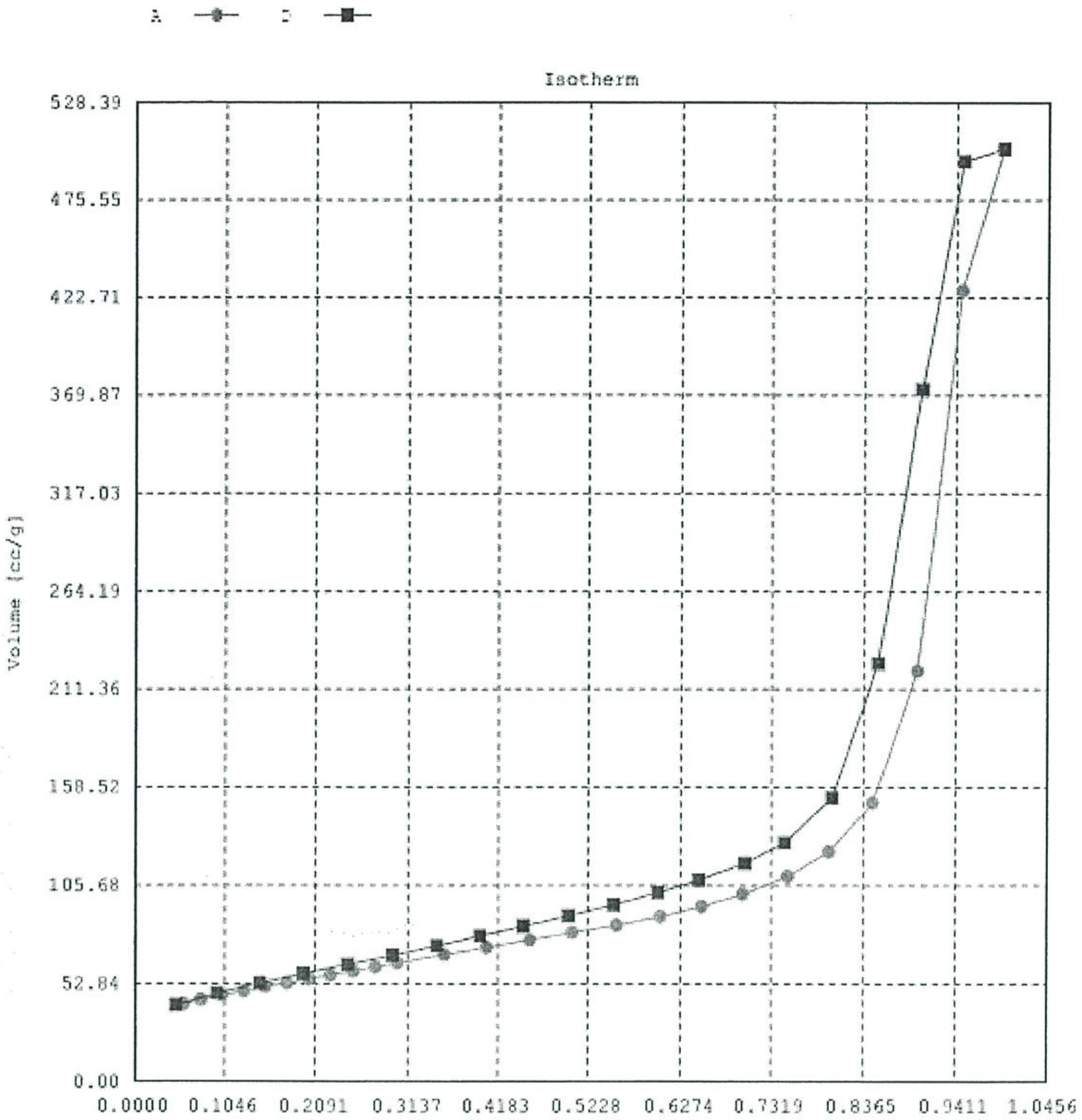

Fig. A.4 Hydrotalcites Mg/Al molar ratio 1.5 calcined at 450 °C

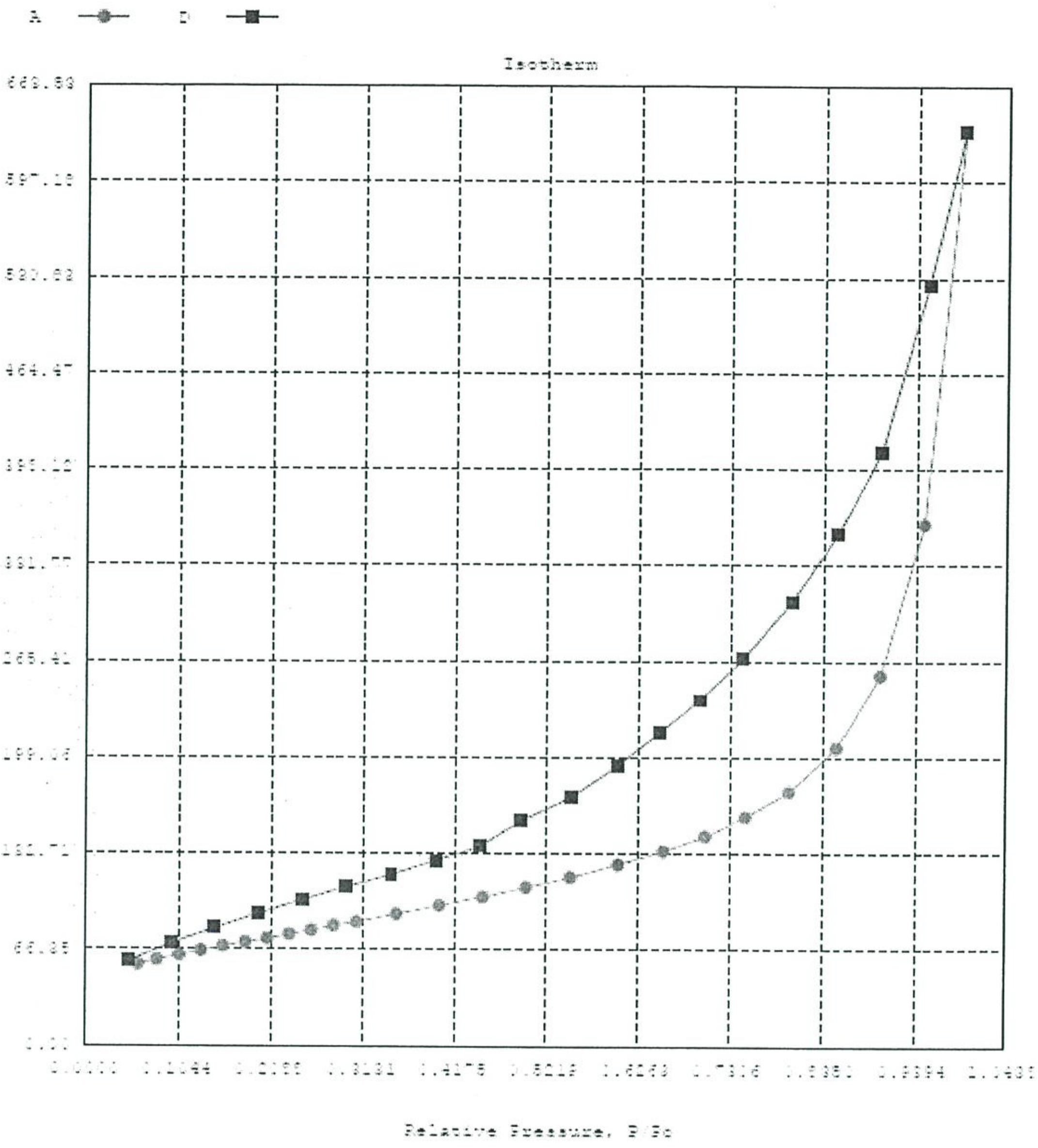

Fig. A.5 Layer double hydroxides calcined at 450 °C

APPENDIX B

PRODUCT ANALYSIS

Prior analysis, the structure of products in sample is identified the by GC-MS (gas chromatography with mass spectrometer detector). Then, the quantitative analysis of products was carried by GC-FID (gas chromatography with flam ionization detector) with the condition expressed in Table B1. An example of chromatogram from aldol condensation of propionaldehyde is present in figure B1. The retention time of chromatogram in figure B.1 is shown in Table B.2.

Table B.1 The GC condition for quantitative analysis

Column	HP 5 , 30 m x 0.32 mm x 0.25 μm
Temperature program	70°C (1 min hold) to 160°C (7 min hold) at 20°C/min
Carrier gas	Nitrogen at 30 ml/min
Injection	200 °C , 0.1 μl
Detector	FID at 200 °C

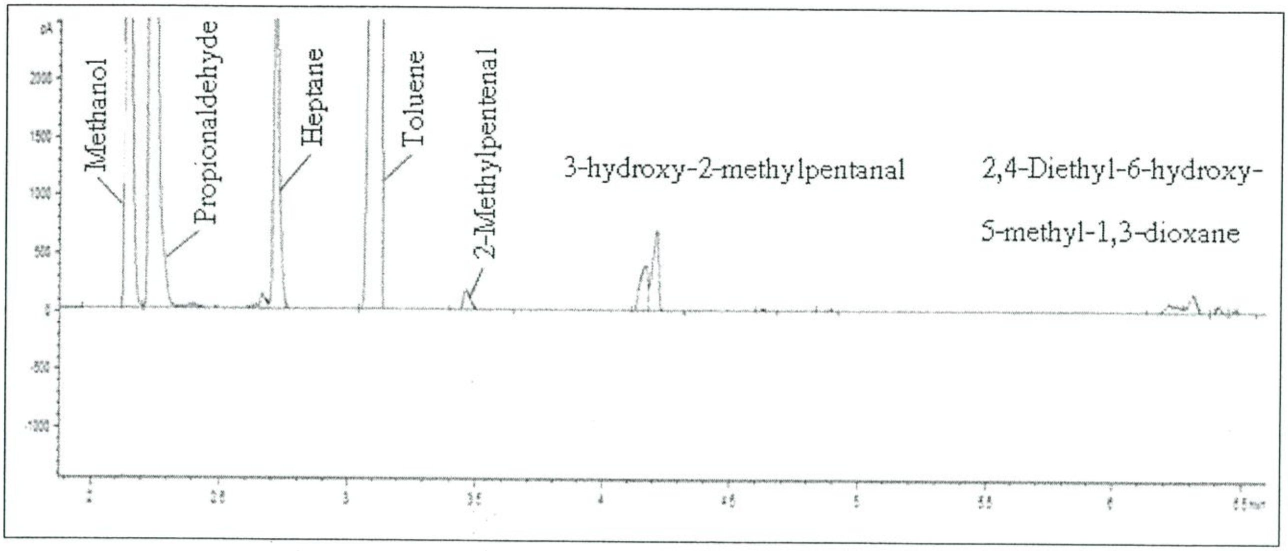

Fig. B.1 The GC chromatogram of aldol condensation of propionaldehyde

** Reaction condition : catalyst : LDHs, temperature : 60 °C, time : 10 hrs*

Table B.2 The retention time from chromatogram in Fig. B.1

Products or feed	Retention time
Methanol	2.13
Propionaldehyde	2.23
Heptane	2.71
Toluene	3.12
2-Methylpentenal	3.46
3-hydroxy-2-Methylpentanal	4.16
3-hydroxy-2-Methylpentanal	4.21
2,4-Diethyl-6-hydroxy-5-methyl-1,3-dioxane	6.21
2,4-Diethyl-6-hydroxy-5-methyl-1,3-dioxane	6.31
2,4-Diethyl-6-hydroxy-5-methyl-1,3-dioxane	6.41
2,4-Diethyl-6-hydroxy-5-methyl-1,3-dioxane	6.47

*Reaction condition ; Aldol condensation over LDH at 60C, 10hrs.

Reference GC-MS patterns

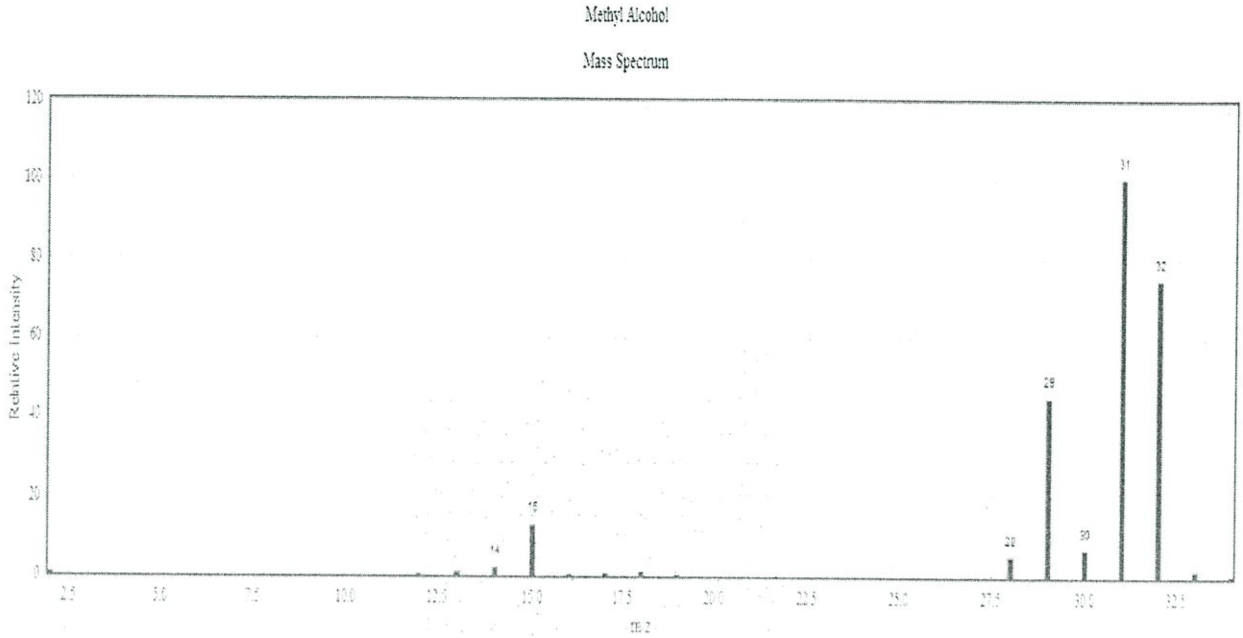

Fig. B.2 Methanol

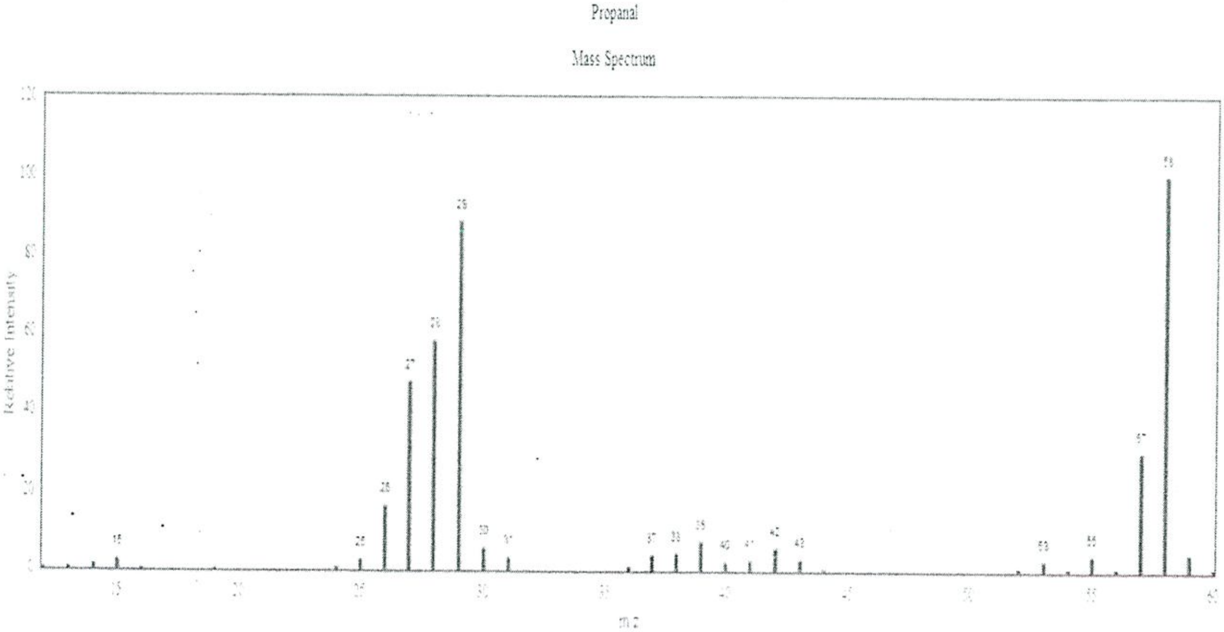

Fig. B.3 Propionaldehyde

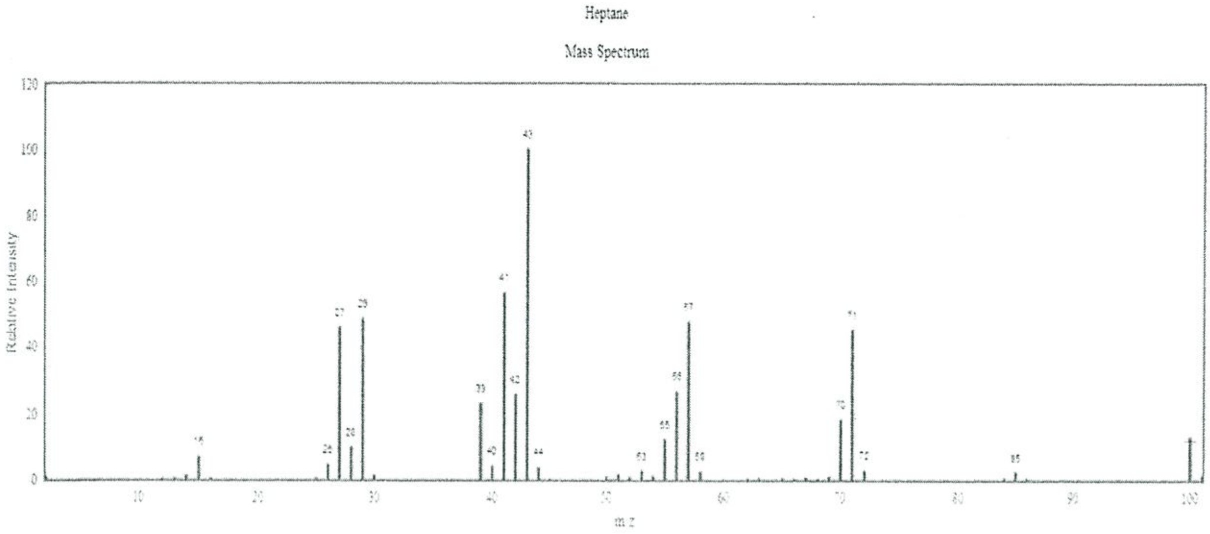

Fig. B.4 Heptane

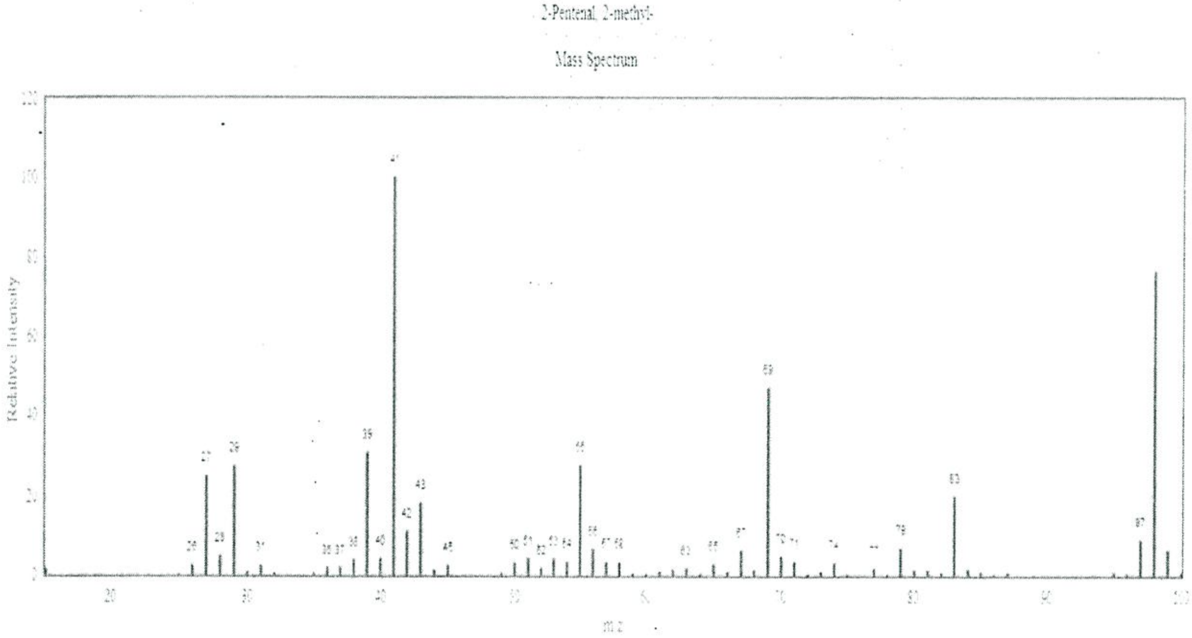

Fig. B.5 2-Methyl-2-pentenal

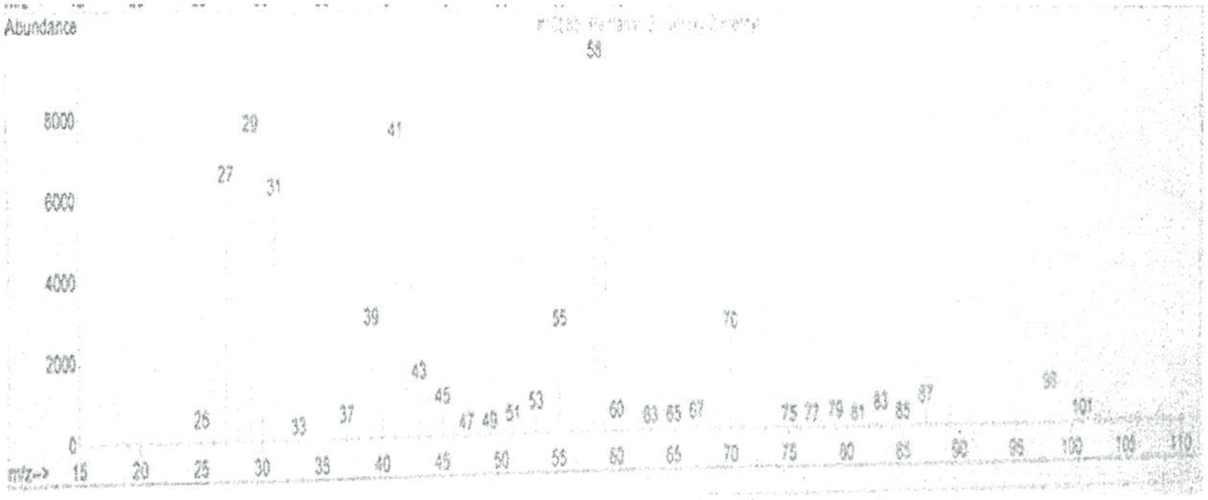

Fig. B.6 3-Hydroxy-2-Methylpentanal

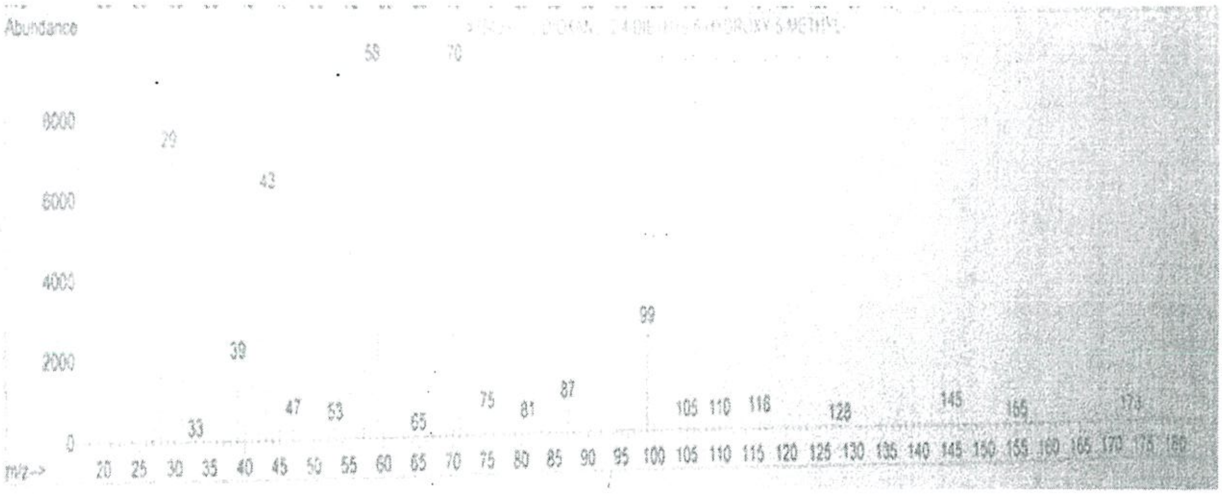

Fig. B.7 2,4-Diethyl-6-hydroxy-5-methyl-1,3-dioxane

APPENDIX C

CALCULATION

Calculation of % Conversion and Yield from gas chromatography (FID)

Table C1.The peak area from chromatogram in Fig. B.1 and calculation for obtaining the conversion

and yield.

Product	Peak area	$\frac{\text{Peak area of product}}{\text{Peak area of internal standard}}$	%Yield
Propionaldehyde	16451	3.2461	-
Heptane	5068	-	-
2 methylpentanal	303.9	0.0600	1.5370
3 hydroxy 2 methyl pentanal (isomer)	874.4	0.1725	4.4196
3 hydroxy 2 methyl pentanal (isomer)	1109.7	0.2190	5.6099
2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane (isomer)	267	0.0527	1.3500
2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane (isomer)	337.6	0.0666	1.7060
2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane (isomer)	80.9	0.0160	0.4099
2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane (isomer)	43.7	0.0086	0.2203

*Reaction condition ; Aldol condensation over LDH at 60°C, 10hrs.

In this study, the internal standard (heptane) is used for quantitative analysis. Firstly, the peak area of product must be corrected by the peak area of internal standard to eliminate the effect of volume injection.

$$\text{Corrected area of product} = \frac{\text{Peak area of product}}{\text{Peak area of internal standard}}$$

For example; in case of 2 methylpentanal

$$\text{Corrected area of 2 methylpentanal} = \frac{303.9}{5068} = 0.0600$$

After that, the yield of product can be calculate from corrected area of product and correct area of feed

$$\text{Yield} = \frac{\text{Corrected area of product} \quad \text{x } 100}{\text{Corrected area of feed introduce}}$$

For example; in case of 2 methylpentanal (corrected area of feed introduce = 3.9038)

$$\text{Yield of 2 methylpentanal} = \frac{0.0600 \text{ x } 100}{3.9038} = 1.5370\%$$

The remaining feed can be evaluated the conversion by the following equation.

$$\%\text{Conversion} = \frac{(\text{Corrected area of feed introduce - Corrected area of feed remaining}) \text{ x } 100}{\text{Corrected area of feed introduce}}$$

For example;

$$\%\text{Conversion} = \frac{(3.9038\text{-}3.2461) \text{ x } 100}{3.9038} = 16.8477\%$$

Finally, the selectivity of product can be derived from yield and conversion as seen below

$$\%\ \text{Selectivity of product} = \frac{\%\ \text{yield of product}}{\%\ \text{conversion}}$$

For example; Selectivity of 3-hydroxy-2-methyl pentanal

$$\text{Selectivity of 3-hydroxy-2-methyl pentanal} = \frac{10.0295 \quad \text{x } 100}{16.8477}$$

$$= 59.5304$$

Calculation Basicity of catalysts

Concentration of KHP	=	0.1000 M
Concentration of NaOH	=	0.0893 M
Concentration of CH_3COOH	=	0.0944 M
Volume of CH_3COOH initial (blank)	=	10.75 ml.
Grams of catalyst (HT-1.5)	=	0.0511 g.

Basicity of catalyst can be calculated from these formulas;

- V_{CH_3COOH} (were used in interact) $= V_{CH_3COOH\text{- initial}}$ (blank) $- V_{CH_3COOH}$ (remaining)
- $C_1V_1 = C_2V_2$; $(C_{CH_3COOH})(V_{CH_3COOH\text{ - remaining}}) = (C_{NaOH})(V_{NaOH})$
- Basicity of catalyst $= \dfrac{V_{CH_3COOH}\text{(were used in interact) x } C_{CH_3COOH}}{\text{Grams of catalyst}}$

For example; Hydrotalcite ratio 1.5

First, volume of CH_3COOH remaining can be calculated from this equation

$$(C_{CH_3COOH})(V_{CH_3COOH\text{ - remaining}}) = (C_{NaOH})(V_{NaOH})$$

$$(0.0944\text{ mol/L})(V_{CH_3COOH\text{ - remaining}}) = (0.0893\text{ mol/L})(6.30\text{ mL.})$$

$$(V_{CH_3COOH\text{ - remaining}}) = 5.9596\text{ mL.}$$

Therefore; volume of CH_3COOH were used in interact = 10.75 - 5.9596 = 4.7904 mL.

*Volume of CH_3COOH initial (blank) = 10.75

Finally, basicity of catalyst can be derived from this formula

$$\text{Basicity of catalyst} = \frac{V_{CH_3COOH}\text{ (were used in interact) x }C_{CH_3COOH}}{\text{Grams of catalyst}}$$

$$= \frac{4.7904\text{ mL x }0.0944\text{ mol/L}}{0.0511\text{ g.}}$$

$$= 8.8495\text{ mmol/g.}$$

APPENDIX D

Reaction Data

1. Aldol condensation of propionaldehyde to reaction times

Table D.1 The conversion and yield of propionaldehyde to reaction times over non-calcined LDH

Time (hrs.)	%Conversion	% Yield		
		2-methylpentenal	3-Hydroxy-2-methylpentanal	2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane
10	16.8	1.5	10.0	3.7
15	19.7	5.6	11.6	1.7
20	19.4	4.4	11.1	1.7
30	24.9	5.3	9.9	2.2

*Reaction conditions: Feed stock (Propionaldehyde, Methanol (solvent) and heptane (internal standard) were prepared at a volume ratio of 3:3:0.5) = 6 ml, temperature=60°C, Catalyst 0.5 g

Table D.2 The conversion and yield of propionaldehyde to reaction times over calcined HT 2.5.

Time (hrs.)	%Conversion	% Yield		
		2-methylpentenal	3-Hydroxy-2-methylpentanal	2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane
10	20.9	3.4	11.7	2.7
15	34.1	5.6	18.9	5.5
20	41.0	11.8	27.2	0.3
30	44.1	12.8	14.1	10.6

*Reaction conditions: Feed stock (Propionaldehyde, Methanol (solvent) and heptane (internal standard) were prepared at a volume ratio of 3:3:0.5) = 6 ml, temperature=60°C, Catalyst 0.5 g

Table D.3 The conversion and yield of propionaldehyde to reaction times over calcined HT 1.5

Time (hrs.)	%Conversion	% Yield		
		2-methylpentenal	3-Hydroxy-2-methylpentanal	2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane
10	11.8	1.9	5.8	1.2
15	19.1	3.6	10.6	3.2
20	32.1	7.3	15.1	5.4
30	48.8	15.7	13.6	9.6

*Reaction conditions: Feed stock (Propionaldehyde, Methanol (solvent) and heptane (internal standard) were prepared at a volume ratio of 3:3:0.5) = 6 ml, temperature=60°C, Catalyst 0.5 g

2. Effect of calcination

Table D.4 The conversion and yield of calcination over HT 1.5 and LDH

60°C at 15 hrs.		%Conversion	% Yield		
			2methyl pentenal	3-Hydroxy-2-methylpentanal	2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane
LDH	calcined	26.5	3.9	11.9	5.4
	non-calcined	19.7	5.6	11.6	1.7
HT 1.5	calcined	19.1	3.6	10.6	3.2
	non-calcined	12.8	2.7	7.4	1.1

3. Aldol condensation of propionaldehyde to reaction temperature on LDH

Table D5. The conversion and yield of propionaldehyde to reaction temperature over LDH

Temperature (°C)	% Conversion	% Yield		
		2-methylpentenal	3-Hydroxy-2-methylpentanal	2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane
50	4.5	1.0	2.5	0.7
60	19.7	5.6	11.6	1.7
70	28.6	6.3	14.8	2.2

*Reaction conditions: Feed stock (Propionaldehyde, Methanol (solvent) and heptane (internal standard) were prepared at a volume ratio of 3:3:0.5) = 6 ml, time = 15 hrs. , Catalyst 0.5 g

Table D.6 The conversion and yield of temperature over LDH at the same level of conversion

Temperature (°C)	Time (hrs.)	% Conversion	Selectivity	% Yield		
				2 methyl-pentenal	3-Hydroxy-2-methylpentanal	2,4-Dimethyl-6-hydroxy-5-methyl-1,3-dioxane
50	75	4.5	52	1.0	2.5	0.7
60	15	19.7	59	5.6	11.6	1.7
70	10	28.6	49	6.3	14.8	2.2

*Reaction conditions: Feed stock (Propionaldehyde, Methanol (solvent) and heptane (internal standard) were prepared at a volume ratio of 3:3:0.5) = 6 ml, Catalyst 0.5 g